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STEPS TOWARDS DEFOSSILIZATION: RETHINKING PETROCHEMICAL PRODUCTION

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RETHINKING PETROCHEMICAL PRODUCTION

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ABSTRACT

Fossil fuel production and usage is the single greatest contributor to anthropogenic climate change. To stop the world-altering impacts of global warming, CO_2 emissions must be cut in half by 2050 and eliminated by 2100. The U.S. processes 19% of global oil and natural gas, the largest capacity in the world; it also has vast resources to defossilize this industry.

While there are known renewable energy replacements for fuels, essential petrochemical products such as plastics and fertilizers will require different alternative production methods. This study sought to characterize both current fuels and petrochemical production totals and primary intermediate chemicals by creating a Sankey flow diagram. Over 95% of all petrochemical products are derived from methanol, ethylene, propylene, ammonia, and BTX aromatics intermediates. An analysis of potential alternative production methods was then completed by identifying numerous routes, which depend entirely on waste products (biomass, biogas, CO_2) and renewables (energy, H_2) for feedstocks.

Large scale production of fossil-free petrochemicals is already occurring in some instances and should continue to focus on upstream chemicals. Further expansions will be dictated by the availability of renewable energy, policy, funding, and technological advancement.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

INTRODUCTION

To avoid a global temperature rise of less than 2°C global emissions must be reduced from 37 gigatons CO_2e to 20 gigatons CO_2e by 2050.[2,3] By 2100, the goal is to reach net zero emissions. The production and combustion of fossil fuels is the largest contributor to CO_2 emissions, and while ceasing fossil fuel usage entirely seems like an obvious solution, it overlooks the world's vast dependence on them. Crude oil, natural gas, and coal are not only used for heating and transportation, but for petrochemical production as well. Almost everything in our everyday lives, from the fertilizers used to grow our food to the plastic fibers in our clothes, is in some way derived from petrochemicals.

The U.S. has the largest refinery oil capacity in the world, with the ability to refine 19.5 million barrels per day (19% of the global total).[4] A significant amount of refinery products are then used as petrochemical feedstocks; combined these industries are huge contributor to global emissions.

Renewable energy alternatives have already been proposed for heating and transport fuels, but green alternatives for petrochemical production are less quantified. Therefore, understanding the scale of U.S. petrochemical production and possible green alternatives to current processes will be essential to defossilizing this industry. This paper seeks to explore these areas by mapping the current output of the crude oil, natural gas, and coal industries and then assessing alternate methods to supplement targeted sections of those industries for CO_2 avoidance.

BACKGROUND

Refineries and coal gasification plants use carbon-rich feedstocks (crude oil, natural gas, and coal) to produce useful products; 836 Mt, 28.4 Mt, and 10 Mt of crude oil, natural gas, and coal were used in the U.S. in 2019, respectively. Some of coal gasification and refinery products, such as finished motor gasoline, are ready for immediate use while others, such as refinery olefins and naphtha, are processed further in downstream chemical processes.

Refinery petrochemical feedstocks include still gas, liquefied refinery gases, naphtha, natural gas liquids, and olefins. These feedstocks provide the foundation for petrochemical products such as, thermoplastics, thermosets, fibers, additives, solvents, and explosives. Ammonia and methanol, the primary products of coal gasification, are also used in the petrochemical industry for fertilizers and solvents/additives, respectively.

METHODS

To map current U.S. fossil fuel usage and the end products of refineries and petrochemical plants, a Sankey diagram was generated. There were essentially three research steps involved in creating the Sankey diagram: production research, reaction research, and distribution (branching) research. The process for the production research involved finding the total mass of each chemical in the Sankey diagram. Depending on the chemical, this process varied slightly. For most of the downstream chemical production, the process was as simple as assessing database information.

The reaction research presented a unique challenge in that the industry knowledge for petrochemical reaction chemistry is not standardized. In some instances, it was difficult to determine which reaction pathways were used and with what efficacy (yield). In this regard, the study relied on industry-accepted reactions and yields wherever possible. Secondary reactants and products were also a challenge in determining the proper reaction mass balance. For downstream chemical reactions, the mass of the reactants and products associated with a given primary product production were determined. For the initial coal gasification and refinery reactions, the process was more difficult since it was hard to assess the reaction data needed to calculate the secondary reactants. As a result, emission data from various refineries and coal gasification plants was assumed to be a representative sample for secondary reactants. The emission samples for the refinery and coal gasification plants were then scaled to satisfy the mass balances around the respective plants.

The distribution research was the foundation to the branching effect in the Sankey diagram. The distribution used the information from the first two research steps to determine how much of one product flowed to the next. This process was facilitated by a comparison between the total production amounts for each product, and the reaction information where, in theory, the database-cited production should equal the production obtained from the reaction chemistry. In the event of a discrepancy between the two, balancing methods were applied to maintain consistency.

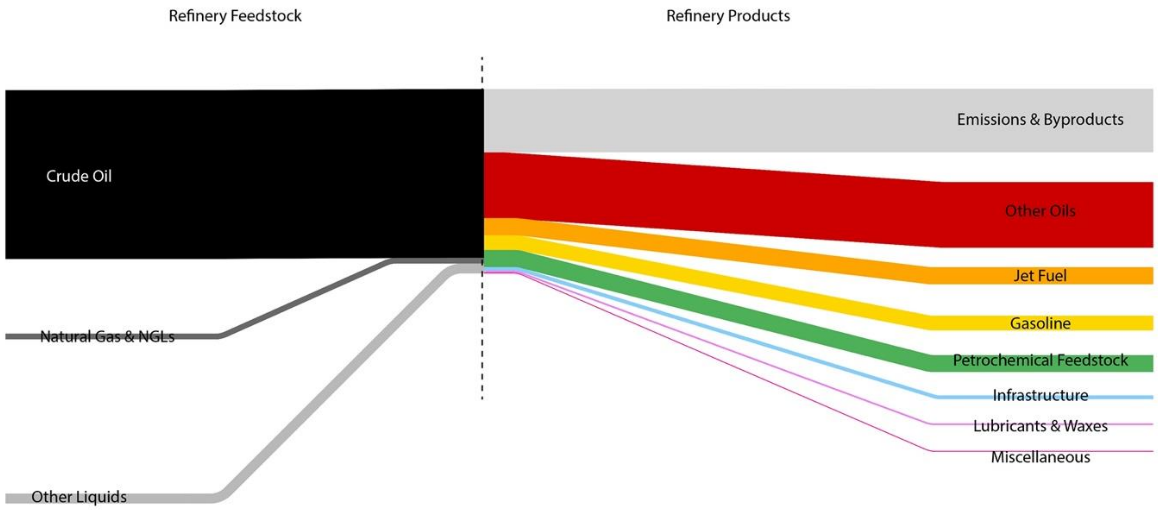


Figure 1: U.S. refinery feedstocks and products from 2019. The refinery feedstocks are comprised of fossil fuels such as crude oil and natural gas. The products contain mostly oils as well as fuels and petrochemical feedstocks.

FINDINGS

WHERE DO FOSSIL FUELS GO?

Crude oil, coal and natural gas are initially processed through two types of facilities: refineries and coal gasification plants. The U.S. has largely moved away from coal; in 2019 only four coal gasification plants were in operation which consumed 10.22 Mt of coal and lignite. There were also 132 refineries operating in the U.S. in 2019 which combined processed 836.2 Mt of crude oil, the equivalent of 6.045 billion barrels or 385,000 Olympic swimming pools. They also processed 16.95 Mt/y of natural gas and 49.1 Mt/y of other liquids. Not all the crude oil and natural gas processed by a refinery is transformed into product—refineries alone emitted 205.7 Mt/y of CO_2e in 2018, around 25% of their total input.

Coal gasification plants primarily produce syngas, a mixture of H_2 and CO, as a feedstock for ammonia fertilizer and methanol synthesis. Refineries produce an array of products, some of which are used as is, and others are further transformed into useable products at petrochemical plants. Liquid fuels, natural gas liquids (NGLs), and oils comprise 71% of the total mass of products produced by refineries and are the primary source of global CO_2 emissions because they are burned for energy almost immediately after they are refined. Refineries also produce lubricants, waxes, petroleum coke, and asphalt/road oil, which may require some further processing but are basically in their final form as they exit the refinery.

Petrochemical feedstocks are made up of NGLs (ethane, propane, n-butane, isobutane), olefins (ethylene, propylene, n-butylene, isobutylene), naphtha, still gas, and BTX (benzene, toluene, xylene) aromatics. In some instances, depending on the proximity of the refinery to the petrochemical plant, these compounds may be further broken down into a desired feedstock before leaving the refinery.

MAJOR PETROCHEMICAL PRODUCTS

Primary Intermediates

The primary intermediates for the petrochemical industry include ethylene, propylene, BTX aromatics, ammonia, and methanol. These chemicals are considered primary intermediates because of their size of production: 32.3 Mt yr^{-1}, 15.2 Mt yr^{-1}, 21.1 Mt yr^{-1}, 16.4 Mt yr^{-1}, and 9.6 Mt yr^{-1}, respectively. Furthermore, >95% of all petrochemical products are derived from a combination of these chemicals.

Thermoplastics and Thermosets

Unsurprisingly, the major product from U.S. petrochemical plants is plastics, where ethylene, propylene, and BTX aromatics serve as initial feedstocks. This study estimated that 46.9 Mt of thermoplastics were produced in 2019, while the EPA reported 35.7 Mt. This discrepancy is likely due to assumptions made in the calculations procedure of the study, but both show the huge scale of the thermoplastics industry. Additionally, 7.0 Mt of thermoset material was produced.

Solvents and Additives

Solvents and additives production totaled 11.1 Mt yr^{-1} and was supported by a myriad of intermediate chemicals including acetic acid, methyl-tert-butyl ether, 2-ethylhexyl alcohol, and the C_4 stream. Note that while these were the primary contributors, there are other chemicals that are used for solvent and additive applications.

Fertilizers

Fertilizers are the second-largest petrochemical product as 21.6 Mt yr^{-1} are produced in the U.S. Urea is the largest contributor to the fertilizer industry, with all the contributors being ammonia derivatives. As such, ammonia is an exceedingly important chemical in the petrochemical industry.

ALTERNATIVE PROCESSES

Almost all petrochemical end-products are synthesized from five intermediates: methanol, propylene, ethylene, ammonia, and BTX aromatics. Replacing the processes responsible for producing each of these intermediates with renewables-based technologies is the simplest way to reduce the fossil-fuel dependence and emissions intensity of the petrochemical industry. This also avoids the replacement of equipment for many existing secondary processes (for example propylene to polypropylene reactors), reducing the capital needed to accomplish this feat. The following is a summary of existing a new production processes for these intermediates.

Syngas

Syngas is an extremely reactive mixture of CO and H_2 used in many reactions. It is typically produced from coal, through **coal gasification**, or through **steam reforming** of natural gas or light naphtha. When additional hydrogen is desired, the water gas shift reaction may be used to convert CO to H_2.

Coal Gasification:

$$3C + O_2 + H_2O \rightarrow H_2 + 3CO$$

Steam Reforming:

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m}{2} + n\right)H_2$$

Water Gas Shift Reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Syngas may also be produced through **biomass gasification**, where biomass is dried and pyrolyzed (heated to high temperatures) to produce pyrolysis gas, a mixture of CO, H_2, CO_2, and light hydrocarbons. Pyrolysis gas is then reacted with residual carbon, called char, to form the final syngas mixture. Biogas is a mixture of methane and CO_2 and can sourced from anaerobic digesters which treat municipal and industrial wastewater, or landfills. Through **biogas dry reforming**, it can be converted to syngas for petrochemical production. Both processes present an opportunity to use waste materials to make value added chemicals.

Dry Reforming of Biogas:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

It is also possible to produce sustainable hydrogen separately through **electrolysis of water**. Renewable electricity is used to split water into H_2 and O_2 molecules via an anode and cathode in an electrolyzer reactor.

Electrolysis of Water:

$$2H_2O \rightarrow 2H_2 + O_2$$

A similar process for the **electrochemical reduction of CO_2** to CO has also been envisioned but has not been demonstrated on a reasonable scale due to side reactions and limitations in catalyst and reactor design.

Fischer Tropsch Synthesis (FTS)

Fischer Tropsch Synthesis (FTS) was one of the first synthetic fuels and chemicals processes to reach industrial scale. Syngas is catalytically reacted to form CH_2 monomers which combine to form a mixture of various hydrocarbon molecules, called syncrude. Depending on the choice of catalyst and reaction conditions, the syncrude composition can favor gasoline, diesel, middle distillates, or waxes. FTS also has the potential to generate petrochemical feedstocks such as olefins and aromatics. There are at least six industrial FTS plants operating world-wide.

Monomer Formation:

$$CO + 2H_2 \rightarrow (CH_2) + H_2O$$

Direct CO_2 FTS has been proposed to use captured CO_2 and renewable H_2 as feedstocks. This reaction proceeds through a pseudo-syngas route where CO_2 and H_2 are first converted to CO and H_2O and the second step is the monomer formation. Difficulties in improving kinetics and selectivity are the result of the stability of CO_2, and thus current research is mostly focused on catalyst improvement.

Methanol

Most methanol is synthesized through the low-pressure Synetix process, which uses syngas produced from coal or natural gas feedstocks and copper catalysts. This two-step process (syngas production followed by conversion to methanol) is extremely energy intensive, so naturally other processes have been pursued.

Methanol Synthesis:

$$CO + 2H_2 \rightarrow CH_3OH$$

Researchers have proposed a **Direct Methane to Methanol (DMTM)** route which avoids the initial syngas production stage, using methane as a feedstock. But this process is thermodynamically difficult in practice because of the instability of methanol. Instead, more stable species such as formaldehyde, CO, CO_2, and H_2O are favored. Efforts towards identifying suitable catalysts and reaction conditions are still being made, but DMTM is currently not available on a large scale. The same is true for **methanotrophy**, a process that utilizes methanotrophic bacteria to convert methane to methanol. A **methyl formate** route also exists, where methanol is reacted with CO to form methyl formate as an intermediate, then further reacted to produce twice the original amount of methanol. This process has a lower energy requirement than traditional methanol synthesis but is not widely used byproduct formation.

CO_2 hydrogenation to methanol is a process that has been demonstrated using renewable H_2, captured CO_2 and traditional methanol synthesis catalysts. Several large-scale pilot plants are currently in operation, including the George Olah Plant in Iceland and the pan-European MefCO_2 project in Germany. Both ventures are great examples of the potential of defossilized petrochemical production.

CO_2 Hydrogenation:

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

Methanol is a feedstock for the production of formaldehyde, methyl tert-butyl ether (MTBE), acetic acid, methylamines, methyl methacrylate, fuel additives, and other chemicals. Through the **Methanol to Olefins (MTO)** and **Methanol to Gasoline (MTG)** processes, it can also be converted to ethylene, propylene, and fuels.

Ethylene & Propylene

Ethylene ($C_2^=$) and propylene ($C_3^=$) are homologues of one another and are both largely produced through **steam cracking** of other petroleum feeds such as ethane or naphtha. Refinery off gases from **fluid-catalytic cracking** units also contain ethylene and propylene which is recovered. Propylene production may be supplemented by **propane dehydrogenation** or **olefin metathesis**, where ethylene and butene are converted to propylene.

Propane Dehydrogenation:

$$C_3H_8 \leftrightarrow C_3H_6 + H_2$$

Olefin Metathesis:

$$CH_2{=}CHCH_2CH_3 + \ CH_2{=}CH_2 \rightarrow 2CH_2{=}CHCH_3$$

Oxidative Coupling of Methane (OCM) to ethylene is another well studied reaction but is limited by stable reaction conditions and catalyst activity. Ethylene may also be produced by cell factories of **cyanobacteria**, which enzymatically convert CO_2, solar energy, and water to hydrocarbon products. Currently, cyanobacteria technologies are only at the proof-of concept stage and the costs associated with them are prohibitive. However, biological catalysis processes are promising given their ability to utilize CO_2 without the need for complex process design. Additionally, advances in the MTO process have be made wherein CO_2 is hydrogenated to methanol, then converted to olefins within the same reactor.

Ammonia

Ammonia is produced through the extremely energy intensive **Haber-Bosch process**, where fossil-fuel derived H_2 is combined with atmospheric N_2 at high pressure and temperature. Ammonia production accounts for around 2% of global energy usage and 1.44% of CO_2 emissions, thus finding renewables-based alternatives is very advantageous to climate goals.[5,6]

Ammonia Synthesis:

$$N_2 + 3H_2 \rightarrow NH_3$$

One alternative is to replace fossil based H_2 with **green H_2** from water electrolysis. Several large projects are underway in Australia, New Zealand, Spain, and the U.S. to integrate green H_2 production into new and existing ammonia plants.

Ideally, the process energy needed for NH_3 synthesis could also be sourced from renewable electricity. **Electrochemical NH_3 synthesis** reduces the process energy required by operating at atmospheric pressure and lower temperatures than the Haber-Bosch process. This technology is very similar to water electrolysis, where an electric current is applied via an anode and cathode to ionize and recombine H_2 and N_2. Reaction selectivity and kinetics are limited due to nitrogen's extreme stability; there is much progress to be made in improving catalyst design and lowering energy requirements before this process can reach industrial scalability.

BTX Aromatics

BTX aromatics (which includes benzene, toluene, and xylenes) are produced directly from crude oil in hydrotreating and catalytically reforming naphtha. Alternative routes seek to use captured CO_2, renewable H_2 and electricity, or biomass to synthesize these compounds.

Direct CO_2 to BTX synthesis is essentially a modified Fischer-Tropsch process where different catalysts which are more selective towards aromatic compounds are used to increase yields. This typically includes a bifunctional catalyst to convert CO_2 to olefins and a zeolite catalyst to convert olefins to aromatics. This process has not yet been demonstrated on a large scale, but because FTS is a mature technology this process looks promising.

Another route is **thermochemical production from biomass**, where fast pyrolysis is used to convert biomass to bio-oil; catalytic cracking then converts the bio-oil into a mixture of aromatic compounds. Biomass feedstocks can come from a variety of sources including agricultural, industrial, and household waste or dedicated crops. Land usage for chemical production crops is a controversial topic which will likely limit the scale of this alternative, but it presents an excellent opportunity to repurpose waste biomass. A final option is **biological production from biomass**, where biomass is first converted to isobutyraldehyde through microbes, then into aromatics with zeolite catalysts. This process remains at the proof-of-concept stage, whereas thermochemical routes have already reached pilot scale production.

CURRENT CHALLENGES

The analysis presented in this paper shows that there is always a route to utilize waste resources (CO_2, biogas, biomass) and renewables (energy, H_2) to synthesize valuable and essential chemicals. However, there are several things that will determine the feasibility of implementing these processes: their technological readiness, ability to reduce emissions, the status of renewable energy and carbon capture, economics, and policy.

Each major intermediate has some form of a green alternative being implemented on a pilot scale somewhere in the world. While these processes may not be entirely fossil-fuel independent, they demonstrate that progress can be made. Many electrochemical processes utilizing capture CO_2 and renewable H_2 are on the brink of success and represent the future of a potentially carbon-negative petrochemical industry.

Many of these alternative production processes only reduce CO_2 emissions when renewable electricity is used for both feedstock production and process energy. A study by Kätelhön et al. estimated that while 3.5 Gt CO_2e could be avoided by switching the global petrochemical industry over to these alternative processes, it would require 55% of the projected global electricity production in 2030.[7] Therefore defossilization must be accompanied by a massive expansion in renewable energy production. This is currently limited by energy storage capacity, governmental policies, and funding. In 2017, $23 billion were allocated to the expansion of renewables in the U.S. alone, but a more dedicated focus will be needed to completely convert the energy sector. CO_2 capture projects, either from industrial sources or direct air capture, will also need to be implemented to provide carbon feedstocks. As governments increasingly prioritize climate change mitigation, renewable energy and carbon capture projects will likely expand to meet demands.

OUTLOOK AND RECOMMENDATIONS

As is the case with many alternative processes, there are challenges associated with scaling up many of the processes discussed in the paper. Many of the alternative technologies exist only at a proof-of-concept level, and thus are not viable to offset the impact of petrochemical products. Processes which have progressed further into pilot plant levels of operation should continue to scale up if they want to be competitive with the current infrastructure. In future studies, greater emphasis should be placed on the largest markets, including oils and fuels. Since the oil and fuel sectors are so large, it makes sense to analyze how carbon capture initiatives could be implemented to offset the current crude oil and natural gas usage. The transition away from petroleum-based chemicals would be aided by government policies and subsidies. Government policies and subsidiaries could help lower cost of renewable options. The analysis of this project could be improved by looking into current government efforts and policies that improve the progress of alternative pathways.

To aid future projects of this nature, it would be helpful if production data were more accessible. Particularly for the fertilizer portion of the Sankey diagram, data was often difficult to find as there is no standardized procedure for reporting what goes in and out of a coal gasification plant. While refinery data was more accessible, additional transparency would be helpful. It was also difficult to assess the emission profiles for the different processes in the study. As with the production values, it seemed as though emission tracking is unstandardized such that each refinery/coal gasification plant reported different types of data if they posted any data at all. While a policy change would be needed to influence this change, it is worth noting since greater transparency in the space would facilitate a better framework for alternative method intervention.

NOMENCLATURE

AEM	Anion Exchange Membrane
BASF	Badische-Anilin & Soda-Fabrik
BTX	Benzene, Toluene, Xylene
C_4	Crude 4
CCUS	Carbon Capture, Utilization, and Storage
CH_4	Methane
CO	Carbon Monoxide
CO_2e	Carbon Dioxide Equivalence
CPOX	Catalytic Partial Oxidation
CRI	Carbon Recycling International
CTL	Coal to Liquid Fuels
DAC	Direct Air Capture
DME	Dimethyl Ether
DMTM	Direct Methane to Methanol
EIA	Energy Information Administration
EIP	Environmental Integrity Project
EPA	Environmental Protection Agency
FCC	Fluid Catalytic Cracking
FCDH	Fluidized Catalytic Dehydrogenation
FTS	Fisher Tropsch Synthesis
GDE	Gas Diffusion Electrodes
GHG	Greenhouse Gasses
GTL	Gas to Liquids
HAPS	Hazardous Air Pollutants
HTFT	High-Temperature Fischer Tropsch
IBA	Isobutyraldehyde
ICCP	Integrated Cascading Catalytic Pyrolysis
ICI	Imperial Chemical Industries
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
KBR	Kellogg Brown Root
LCA	Life Cycle Analysis
LPG	Liquid Petroleum Gas
LTFT	Low-temperature Fischer Tropsch
MeOH	Methanol
MMA	Methyl Methacrylate
MTBE	Methyl Tert-butyl Ether
MTG	Methanol to Gasoline
MTO	Methanol to Olefins
$Mt\ yr^{-1}$	Million Tons per Year
NH_3	Ammonia
NGL	Natural Gas Liquids
NO_X	Nitrogen Oxides as an Atmospheric Pollutant
OCT	Olefins Conversion Technology
PCFC	Protonic Ceramic Fuel Cell
PCMR	Protonic Ceramic Membrane Reactor
PEM	Polymer Electrolyte Membrane
PM	Particulate Matter
RWGS	Reverse Water Gas Shift
SMR	Steam Methane Reforming
SO_2	Sulfur Dioxide
TKIS	ThyssenKrupp Industrial Solutions
TPOX	Thermal Partial Oxidation
$t\ y^{-1}$	Tons per Year
VOCs	Volatile Organic Compounds

INTRODUCTION

Global atmospheric carbon dioxide (CO_2) concentrations have drastically increased since the discovery of fossil fuels in the late 1880s. This has induced anthropogenic global warming and climate change, effects of which are already observable. Rising sea levels, devasting floods and droughts, heat waves, wildfires, and extreme weather patterns will impact every aspect of society. The U.N. estimates that climate change will displace 25 million to 1 billion people by 2050 and cause billions of dollars in damages.[8]

Scientists predict that the effects of climate change may be subdued by immediate emissions reductions. To avoid a global temperature rise of 2°C, the IEA and IPCC have advised that global emissions must drop from 37 gigatons CO_2e to 20 gigatons CO_2e by 2050.[2,3] By 2100, the goal is to reach net zero emissions.

The easiest solution seems to be to stop the use of oil, natural gas, and coal altogether. While this may be achieved by using renewable energy for fuels and heating, there are thousands of other products made from fossil fuels that are not so easily replaced. The compounds derived from fossil fuels are feedstocks for the petrochemical industry, which produces everything from the fertilizers used to grow food to the plastics in your home and synthetic fibers in your clothes. So much of the world is reliant on these products we cannot stop making these products altogether. While this problem is complex, there are ways to defossilize the petrochemical industry by implementing new processes which rely on renewable feedstocks and green energy.

The U.S. is one of the largest producers and consumers of fossil fuels and petrochemicals, and a country with enormous resources to work towards emissions reduction. This report serves to characterize current fossil fuel consumption and petrochemical production in the U.S., identify alternative processes to synthesize major petrochemical feedstocks, and analyze the feasibility of defossilizing the industry.

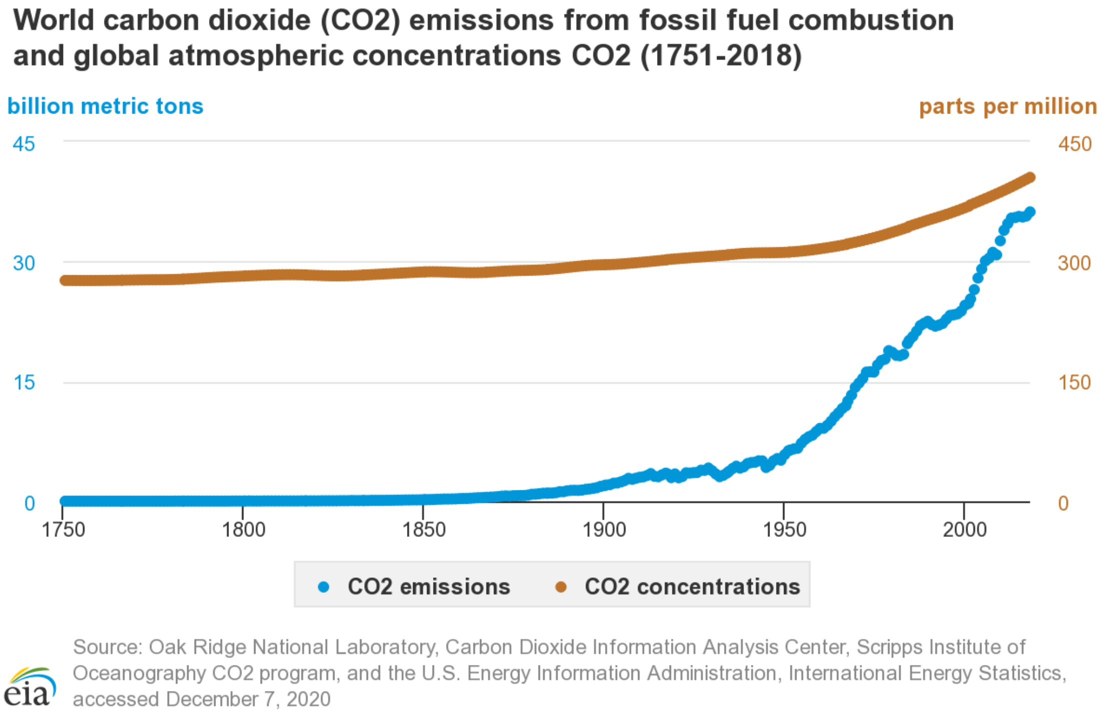


Figure 2: *CO_2 concentration in the past 267 years. Carbon dioxide levels in the atmosphere fluctuate naturally but after the industrial era, there was a sharp increase in CO_2 levels which have resulted in global warming.* [9]

BACKGROUND

WHY CO_2?

There are four primary greenhouse gases (GHGs): carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and fluorinated gases. So why is so much emphasis put on CO_2 when we talk about global warming? The answer lies in the individual lifetimes of the gases in the atmosphere, their 100-year global warming potential (GWP), and how much is produced annually. GWP is a measure of how much warming 1 kg of a given compound will cause in comparison to 1 kg of CO_2 (EPA, 2020b). To measure the amount of GHG's that are emitting from a refinery or petrochemical plant, a CO_2 equivalent (CO_2e) is used. The CO_2e shows the amount of CO_2 which would have the same global warming impact.[10] CO_2 has an atmospheric lifetime of 300-1,000 years, meaning that changes in atmospheric CO_2 concentrations accumulate and persist for lifetimes. Eliminating CO_2 emissions and removing the CO_2 currently stored in the atmosphere is the single largest step we can take towards slowing climate change.

CO_2 AND CLIMATE CHANGE: WHERE DOES IT COME FROM?

Since the industrial revolution, the world relied on fossil fuels as a cheap and easily obtainable way to generate energy and chemical products. Fossil fuels are made up of carbon containing compounds called hydrocarbons; when combusted they release CO_2 as well as other greenhouse gasses (GHG). While the earth's natural carbon cycle can store some of this CO_2, much of it remains in the atmosphere. In 2019, the average atmospheric CO_2 concentration was 409.8 parts per million, the highest it has ever been in the past 800,000 years, as shown in Figure 2.[11]

The International Energy Agency (IEA) and the Intergovernmental Panel on Climate Change (IPCC) have advised that global warming should not exceed 2˚C of warming above pre-industrial levels. Most predictions to stay below this level contain an overshoot period where warming will be above the goal.[12,13] Currently global temperatures have increased by 1˚C since 1880.[12] To limit warming to no more than 2˚C, CO_2 emissions need to be limited to 20 Gt_{co2} per year by 2050; in 2018 the global emissions were 36.58 Gt_{co2} per year.[2,3] By 2100, emissions should be net zero or net negative to reduce the impacts of climate change such as flooding or droughts, ocean acidification, rising sea levels and extreme temperatures.[14]

A 2010 IPCC study stated 60% of CO_2 emissions are from burning fossil fuels or industrial processes.[9] In 2017, fossil fuels make up around 79.7% of the energy consumed globally. In the US, renewable energy is projected to provide 24% of energy consumed by 2030, but this still leaves a large dependence on fossil fuels.[15] To help mitigate the carbon emissions produced by fossil fuel industries, carbon capture utilization and storage (CCUS) technology is an attractive solution to reduce atmospheric CO_2 emissions, and presents an opportunity to generate negative CO_2 emissions through permanent storage.[2] When carbon capture is used at the exhaust of an industrial source, carbon dioxide emissions can be reduced by 80-90%.[16]

One opportunity to reduce emissions from fuel and petrochemical production is through on-site CCUS. Refineries account for 4% of the global CO_2 emissions at around 1 billion tons emitted each year from the combustion of fuel on site or fugitive emissions from daily operations.[2,17] Refineries emit GHG from a variety of sources, so carbon capture must be focused on the largest exhausts such as the combined stack which accounts for about 40% of the total emissions.[17] .

A more ideal, long term option would be to replace fossil fuel feedstocks altogether. To understand where alternative production methods are necessary, one must first understand how refineries and petrochemical plants work and what they produce. The next sections will explain this.

REFINERIES

WHAT ARE REFINERIES?

Crude oil contains thousands of different compounds with varying physical and chemical properties. Depending on the location of the oil well, the composition of the crude oil also varies, with some crudes containing heavier or lighter compounds.[18] Refineries are used to separate these crude oil sources into desired, uniform products for use as transportation fuels or feedstocks for petrochemical production. Refining methods have been fine-tuned over decades to increase yields of desirable products, resulting in a complex series of innovative unit operations.

WHAT ARE REFINERY FEEDSTOCKS?

Refinery feedstocks are crude oil and natural gas, which are extracted together at drilling sites. Natural gas is primarily made up of methane, but contains other heavier compounds called natural gas liquids, which are separated in a natural gas plant on site at the refinery.[18]

Crude oil is a varying mixture of thousands of hydrocarbon compounds of different molecular weights, structures, and chemical properties. Because of their varying heats of vaporization, these compounds can be separated through distillation. [18] Table 1 lists compound categories that result from these separations.

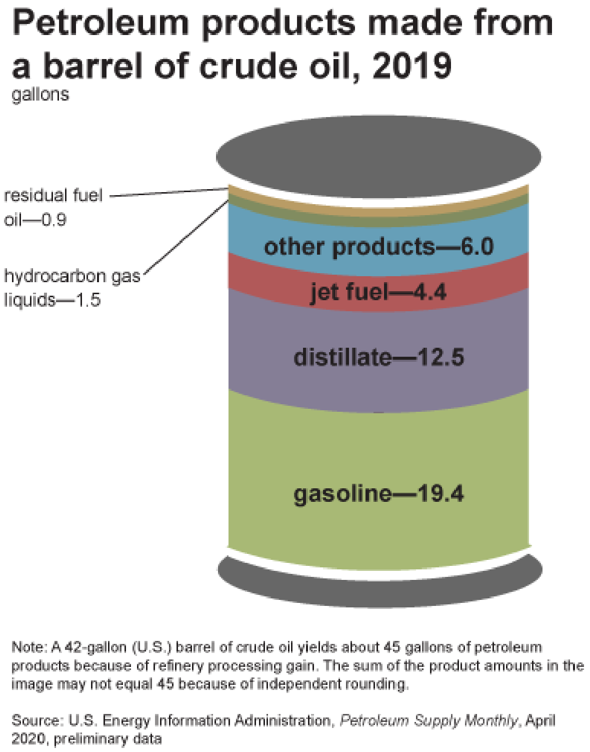
Table 1: *Compound categories resulting from the separation of natural gas and crude oil.*

Common Name	Compound Characteristics
Methane	C_1
Ethane	C_2
Propane	C_3
n-Butane	nC_4
Isobutane	iC_4
Gasoline	C_4—C_{12}
Naphtha	Mid-Range
Kerosene	C_6—C_{20}
Diesel	C_{10}—C_{15}
Fuel Oil	Low Viscosity Residue
Asphalt	High Viscosity Residue
Coke	C, Free Carbon Deposits
Hydrogen Sulfide	H_2S
Aromatics	Contain Ring Structures
Paraffin	Saturated Hydrocarbon
Olefin	Unsaturated Hydrocarbon

How do refineries work?

Due to varying demands for products in different regions, and different characteristics of each crude oil feed, the layout and operation of refining processes is specific to each refinery. However, there are several general unit operations under the categories of separators, converters, and treatment steps used in every plant, which will be discussed further.

The first step in all refineries is to separate any light gases from the crude oil stream, which are sent to a refinery gas plant.[18] The crude oil feed is then sent to an atmospheric distillation column, where compounds are separated into different classes based on their boiling points. Lighter fractions of the crude oil rise to the top of the column and the heavier fractions fall to the bottom.[18]



Petroleum products made from a barrel of crude oil, 2019

gallons

Note: A 42-gallon (U.S.) barrel of crude oil yields about 45 gallons of petroleum products because of refinery processing gain. The sum of the product amounts in the image may not equal 45 because of independent rounding.

Source: U.S. Energy Information Administration, *Petroleum Supply Monthly*, April 2020, preliminary data

Figure 3: *A representative depiction of the products from crude oil refining in 2019.[19]*

The product from the top of the column (lowest boiling point) is a mixture of butane and lighter components. This is sent to the gas processing plant with the rest of the light gases that were initially separated. Next are the compounds known as straight run gasoline, or light naphtha, which are used in motor gasoline blending after further processing. The middle of the column produces heavy naphtha which is sent to hydrotreating and catalytic reforming processes to be later used in gasoline blending. Kerosene and light gas oil (diesel), are also separated in the middle of the column and sent for further processing.[18]

The bottom of the column produces two streams: heavy gas oil and residue. Residue is further separated in a vacuum distillation column to produce streams of gas oil, residue, and asphalt feedstock. There may also be other conversion steps to transform heavier compounds into lighter compounds or vice versa.[20]

Refinery Gas Plants

Refinery gas plants process lighter hydrocarbon vapors (butanes, propane, ethane, and methane) in a series of separation steps. First, the feed stream for the gas plant is compressed and expanded to allow for some phase separation between lighter and heavier hydrocarbons. The heavier cut includes propane and butanes and is sent to a process downstream known as a debutanizer. The lighter cut, which includes ethane, methane and some butane and propane, is separated with an absorber.[18]

WHAT DO REFINERIES PRODUCE?

With only a few different types of unit operations, refineries can transform crude oil into a set of intermediate product streams that have a wide range of applications. A refinery gas plant produces methane, ethane, propane, n-butane, and isobutane. Methane is typically retained within the refinery and used as fuel gas; it can also be used in select petrochemical processes. Ethane is a feedstock to ethylene plants, which produce polyethylene plastics. Propane in the primary component of liquified petroleum gas (LPG) which is the "natural gas" supply for homes and businesses around the country. N-butane is also a component in LPG and is used in gasoline blending; it also serves as a feedstock to some petrochemical processes. Isomerization plants convert n-butane to additional isobutane when the demand is present. Isobutane is a feedstock for petrochemical processes and alkylation plants, which convert lighter compounds into heavier compounds suitable for gasoline blending.[18] Aromatics, including benzene, toluene, and xylene (BTX) are also separated from naphtha as it is reformed. These three compounds are the building blocks for thousands of petrochemical intermediates and products.[21]

Gasoline, kerosene, and diesel are important transportation fuels, used in everything from consumer automobiles and long-distance trucking to airplanes. Fuel oil produced from the distillation residue of a refinery is one of the least valuable products of a refinery, and typically sells below the price of crude oil. It is used as fuel for marine vessel engines, power plants, and industrial facilities as well as for heating commercial buildings. It can also be blended with other compounds to produce lubricants, motor oils, and industrial greases.[21] After being treated, petroleum coke has a variety of applications, including electrode and charcoal production and smelting. High viscosity asphalt residue is the base for asphalt roads and roofing materials.[21]

***Table 2:** A summative table on commonly referred to chemicals.*

Common Name	Compound	Use
Methane	C_1	Fuel Gas for Refinery Petrochemical Feedstock
Ethane	C_2	Ethylene Plant Feedstock
Propane	C_3	Liquified Petroleum Gas (LPG)
n-Butane	nC_4	Gasoline Blending Isomerization Plant Feedstock Petrochemical Feedstock LPG
Isobutane	iC_4	Alkylation Process Feedstock Petrochemical Feedstock
Gasoline	C_4—C_{12}	Gasoline Blending
Kerosene	C_6—C_{20}	Jet Fuel Kerosene
Diesel	C_{10}—C_{15}	Diesel Fuel
Fuel Oil	Low Viscosity Residue	Heating Oil Engine Oil Maritime Fuel Oil
Asphalt	High Viscosity Residue	Asphalt Roads Pitch
Coke	C	Electrodes Smelting Industry
Aromatics	Benzene, Toluene, Xylene	Petrochemical Feedstocks
Hydrogen Sulfide	H_2S	Petrochemical Feedstock

HOW MUCH IS PRODUCED GLOBALLY?

The largest refinery in the world is the Jamnagar refinery complex, which is in India. This singular plant processes 1.2 million barrels (50.4 million gallons) of crude oil per day, but this only makes up 1.6% of global refinery capacity. At the Jamnagar refinery complex they produce gasoline, diesel and propylene, which is used to make other product like plastics, fibers and films.[22] In September of 2020, the EIA estimated 95.3 million barrels are consumed globally per day. Oil consumption is not equal across the world however—the U.S. consumes about 20% of the world's oil but is home to only 4.25% of the world's population.[4] Global energy consumption is set to increase as the global population grows and countries continue to industrialize, which will increase the demand for products and fuels derived from crude oil.

REFINERIES IN THE U.S.

The U.S. has the largest refinery oil capacity in the world, with the ability to refine 19.5 million barrels per day (19% of the global total).[4] Figure 4 shows the distribution of U.S. refineries and their relative capacities.

The Gulf Coast region alone is home to 58 refineries that contribute about 50% of the U.S. oil refining capacity. Crude oil is transported to this region from the Midwest and Canada. In 2015, this region had the capacity to refine 9.7 million barrels per day, a 1.9 million barrel per day increase since 2010.[23] Currently, the Port Author refinery in Texas is the largest in the country, producing 607,000 barrels per day.[23] The Port Arthur refinery produces conventional gasoline commercial aviation fuel, and different variations of diesel, which is made for the trucking industry and heavy machinery.[24]

A 2017 study on CO_2 emissions from refinery products concluded that petroleum coke is the most CO_2 emission intensive refinery product based on upstream, refining, distribution, and combustion processes. Heavy fuel oil, gasoline, diesel, and jet fuel are also very emissions intensive.[4] When looking at resin products, polyvinyl chloride (PVC) produced 14.7 million t_{CO2} in 2015 when accounting emissions in the whole process. High density polyethylene and propylene produced 12.9 and 11.6 million t_{CO2} respectively.[25] On average, one ton of plastic resin emits 1.89 t_{CO2} in production. Regional refinery trends evolve to accommodate increased domestic crude oil production.

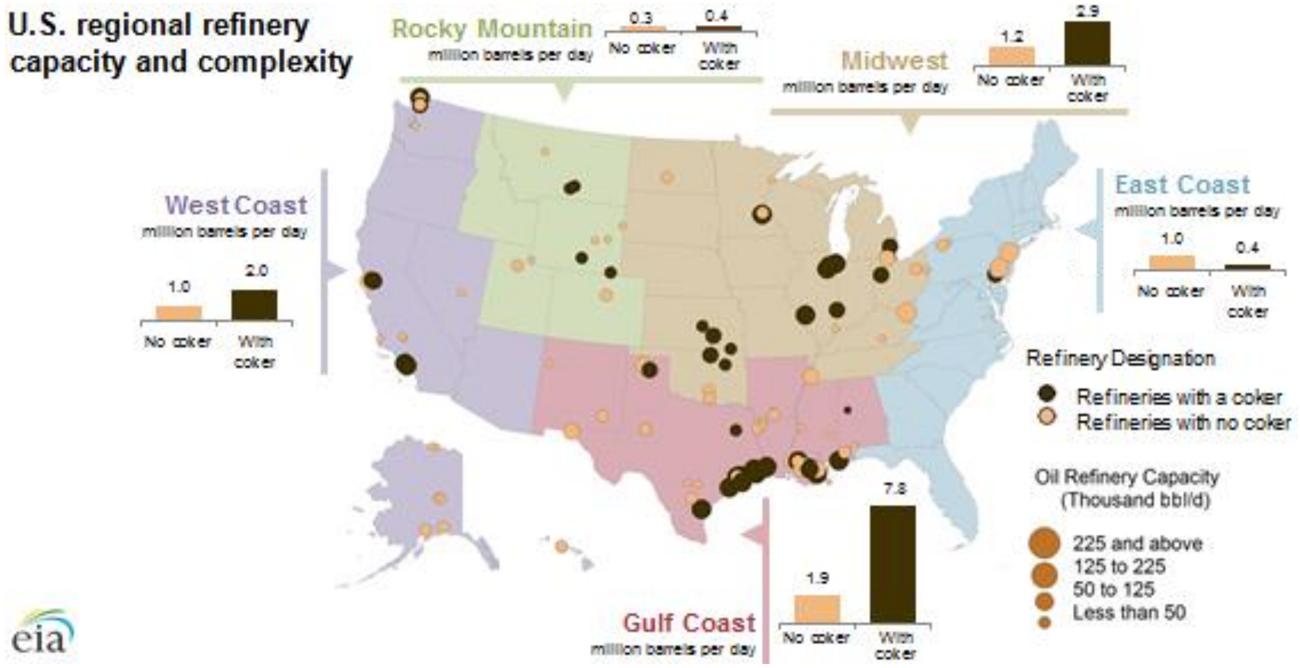


Figure 4: All of the refineries in the U.S. listed till 2015. The size of the dots conveys the oil refinery capacity. The brown dots are refineries with a coker, while the yellow dots are refineries without a coker. The diagram shows that the gulf coast has the most refineries in the U.S. [23]

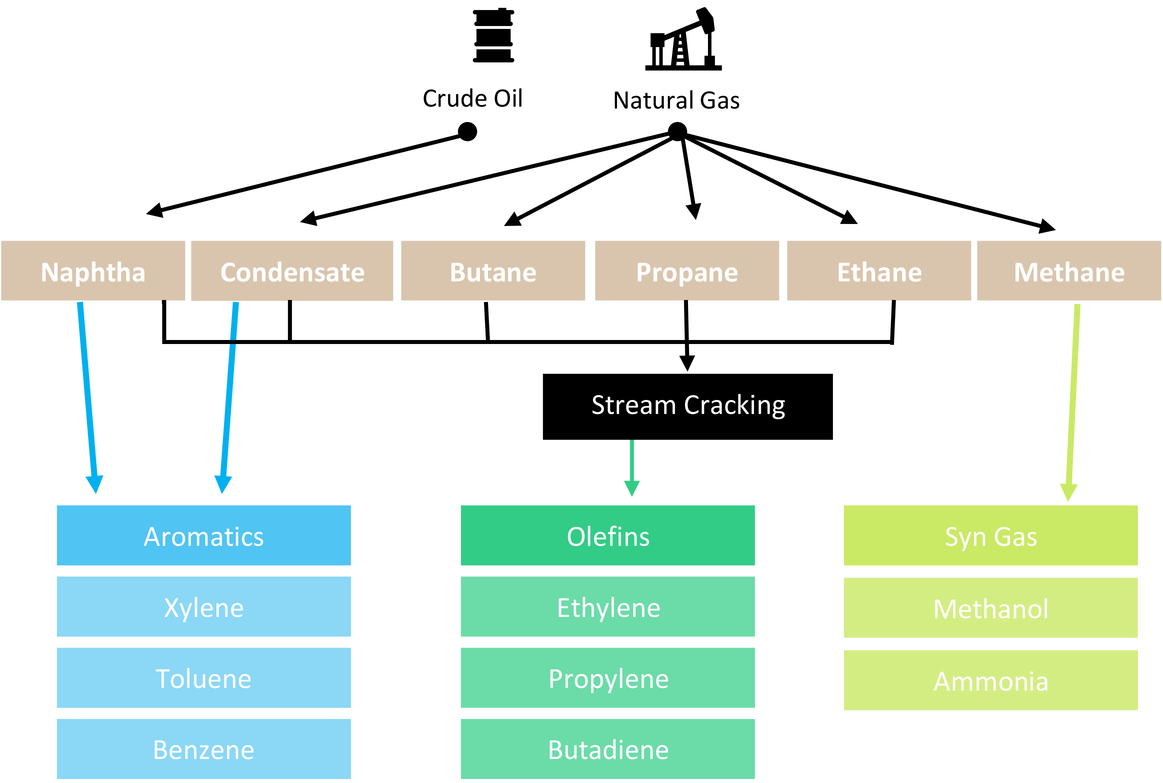
Petrochemical Production

The growth of petrochemicals industry began in the 1950's as the petroleum industry boomed following the end of World War II. Prior to World War II, petrochemicals were a small segment of the chemical industry limited primarily to a small set of companies that derived chemicals from oil and gas. However, during the war the demand for synthetic rubber increased and by the late 1940's the U.S. had produced 2 million tons of synthetic rubber – consuming half of the country's total petrochemical output in the process.[26] With that, the foundation for a petrochemical boom was well established.

Petrochemicals are derived from the refining and processing of petroleum or natural gas. As discussed above, the refining process creates a myriad of outputs that vary based on the specific input to the process – light crude, heavy crude, etc. Of interest are the three primary petrochemical outputs shown in Figure 5. While there are numerous ways to categorize petrochemicals, a popular method is to conceptualize petrochemicals by their placement in the progression from feedstock to market products. For instance, the petrochemicals that are derived directly from feedstocks are often referred to as primary petrochemicals. Naturally, primary petrochemicals are further derived into various stages of intermediate petrochemicals that eventually yield end-use products. Differentiating between primary and intermediate petrochemicals is important since the latter often presents numerous, intricate, steps that vary based on the desired inputs and outputs.[27]

Note that Figure 5 is a simplification of the primary petrochemical generation. That is, it does not include important considerations such as mass flow and yield for the different streams. Even so, the tree contextualizes the relationship between crude oil/natural gas and petrochemicals. Aromatic petrochemicals are the starting material for a wider range of consumer products and come almost exclusively from crude oil – and by extension naphtha. Olefins – compounds that contain one or more alkenes, but no other functional group – are derived from cracking feedstocks from raw materials. Lower olefins are of interest because of their use in plastic products, though higher olefins with chains up to twenty or more carbon atoms do exist.[28] Synthesis gas (syngas) is a valuable byproduct from refineries in that they can be used to create methanol and ammonia.

Figure 5: *A sample petrochemical tree from feedstock to primary petrochemical output. Petrochemicals are divided into one of three categories left to right – aromatics (red), olefins (blue), or synthetic gas (green). These three categories are often referred to as the primary petrochemicals. The subsequent intermediate petrochemicals, that will eventually form end products, are derived from the primary petrochemicals*



Petrochemicals are well-contextualized by the markets and industries that they enter after intermediate processing. Petrochemicals are special, in part, because they can be used to make a seemingly endless selection of products (Table 3). The economy is largely dependent on the petrochemical industry since so many products are made from petrochemicals. On a global scale, more than half of ammonia is converted to urea, which is primarily used as a fertilizer for elevated crop production.[29] Unlocking the potential behind the petrochemical industry will be key to maximizing the energy industry and minimizing CO_2 emissions.

Table 3: *Petrochemical products across an assortment of industries. The selection below represents a sample of petrochemical products. Petrochemicals manifest themselves in several industries and products. Note that raw petrochemicals often undergo a rigorous transformation process to achieve final market products.*

Products	Primary Constituents	Notes
Thermoplastics	• Polyethylene • Polypropylene • Polyvinyl Chloride	Plastics that can be remolded when heated. As such, thermoplastics are recyclable.
Thermosets	• Polyethylene Terephthalate • Propylene Oxide	Plastics that cannot be remolded after they are cooled. Thermosets are non-recyclable.
Solvents	• Acetic Acid • 2-Ethylhexyl Alcohol • Methyl-tert-butyl Ether	Solvents are used in a myriad of applications to dissolve other substances.
Additives	• Sulphites • Nitrites • Benzoates	Additives are used to preserve other substances.
Fertilizers	• Urea • Ammonium Sulfate • Nitric Acid	Fertilizers are used to enhance soil nutrients.

SANKEY METHODOLOGY

Our methods were adapted from the paper, *Mapping Global Flows of Chemicals: From Fossil Fuel Feedstocks to Chemical Products,* by Levi and Cullen published in 2018 by the Environmental Science and Technology journal. Their methodology from the Supporting Information document for the global chemical flow was applied to the U.S. petrochemical industry.

COAL GASIFICATION

To calculate the input of coal in the Sankey diagram, the Coal to Liquids/Chemicals Project Database from March 2019 was used as well as the respective patent and GHG emission documents from the four operating coal gasification plants in the U.S.[30–34] They are located in West Virginia, Utah and North Dakota. The four plants consume 10.2 Mt yr^{-1} of coal and lignite. Depending on the plant, the products include gasoline, fertilizer such as urea and ammonia, liquified petroleum gas, naphtha, diesel, jet fuel, reformate, and flaked residue. To obtain the total GHG emissions from each plant, the construction patents were used, and the maximum emissions were collected. This accounted for NO_x, SO_2, CO, VOCs, PM, and HAPs as seen in Table 4 that the Environmental Protection Agency (EPA) requires to be reported. For coal gasification reactions, air and steam are needed as inputs but those values were excluded from the Sankey diagram. This was due to the assumption that the outputs of air and water vapor would be the same as the inputs but the companies are not required to provide exhaust flowrates so we could not get the exact mass amounts.

AMMONIA AND METHANOL CALCULATIONS

Ammonia and methanol, or methyl alcohol, are made from feedstocks consisting of natural gas, coal, and crude oil products such as naphtha and fuel oil. The amount of ammonia and methanol produced from each of these feedstocks in the U.S. was not obtainable from existing databases, so global estimates were used instead.[27] In 2013 globally, the feedstock for ammonia was comprised of 71% natural gas, 8.5% oil, and 20.5% coal and the feedstock for methanol was 80% natural gas, 3% oil, and 17% coal. Realistically, in the U.S., more natural gas and oil would be used to create ammonia than the global estimate since coal gasification plants are becoming scarce as the country moves away from coal.

To produce both ammonia and methanol, each feedstock is used to produce syngas first. Then to produce ammonia, nitrogen is added following the Haber-Bosch process. For methanol, either CO or CO_2 is added for the synthesis reaction with the syngas. When completing the mass balance, overall process yields, production efficiencies, the stoichiometric relationships, and the feedstock compositions were accounted for. For a further methodology of the global mass balance for the ammonia and methanol production see the paper by Levi *et. al*.[27]

In 2018, 16.4 Mt yr^{-1} of ammonia were produced in the U.S.[35] The total methanol production was projected to be 9.4 Mt yr^{-1} in 2019.[36] The previously mentioned global feedstock composition break down was used to determine the amount of natural gas, oil, and coal that would produce a portion of the product. The percentage of ammonia produced from syngas was determined from the global break down, as well as the amount of CH_n used to produce the syngas. CH_n represents the feedstocks stoichiometric characterization. The last ratio used was the composition of each feed for the CH_n and non-C/H split. This resulted in the total amount of feedstocks needed for the chemical synthesis of both ammonia and methanol. Ratios were used again to relate the total input and outputs from the natural gas, oil, and coal using the Non-C/H & CH_n and the product amounts. These were used to calculate the secondary products. All total values can be seen in the Table 5 below.

Table 4: *Inputs and outputs of coal gasification plants in the U.S. from 2019. The outputs are the GHG required to be recorded by the EPA for each plant. The inputs are the water and oxygen needed for the reaction of coal gasification. These values are used in the Sankey diagram for the secondary reactants and products, primarily made up of carbon dioxide.*

Inputs/Outputs ($Mt\ y^{-1}$)	**Plant**				**Total**
	Direct Liquefaction Coal to Liquids Facility	New Coal to Liquids Facility	Adams Fork Energy - TransGas WV CTL	Great Plains Urea Project/ Synfuels Plant	
Inputs	.583	.583	.444	7.86	9.853
Water	.3	.333	5.624	8.82	18.74
Oxygen	.284	.11	2.234	1.03	15076.7
Outputs	3.68 x 10^{-4}	.295	3.86 x 10^{-4}	2.9	3.66
NO_x	8.2 x 10^{-5}	2.3 x 10^{-5}	4.9 x 10^{-5}	3.83 x 10^{-4}	3.199
SO_2	2.7 x 10^{-5}	2.0 x 10^{-6}	9.2 x 10^{-5}	1.34 x 10^{-4}	5.37 x 10^{-4}
CO	7.1 x 10^{-5}	8.4 x 10^{-5}	6.7 x 10^{-5}	8.13 x 10^{-4}	2.54 x 10^{-4}
VOCs	8.6 x 10^{-5}	9.0 x 10^{-5}	4.2 x 10^{-5}	2.84 x 10^{-4}	.001
PM	8.4 x 10^{-5}	5.8 x 10^{-5}	1.32 x 10^{-4}	6.94 x 10^{-4}	4.22 x 10^{-4}
HAPs	1.7*10^{-5}	6.0 x 10^{-5}	4.0 x 10^{-6}	8.3 x 10^{-5}	9.69 x 10^{-4}
CO_2	-	.295	-	2.9	1.11 x 10^{-4}

Table 5: *Inputs and outputs of ammonia and methyl alcohol plants in the U.S. from 2019. The inputs represent the chemicals needed in the reactions to create ammonia or methanol excluding the main carbon feed stock depending on the fossil fuels such as natural gas, oil, and coal. The outputs are the secondary products from the reaction that includes the GHG, carbon dioxide. The loss values correspond to the efficiency of the process since more inputs are needed compared to the outputs produced. These values are used in the Sankey diagram for the secondary reactants and products.*

Inputs/Outputs ($Mt\ y^{-1}$)	**Ammonia**				**Methyl Alcohol**			
	Natural Gas	**Oil**	**Coal**	**Total**	**Natural Gas**	**Oil**	**Coal**	**Total**
Inputs	*30.71*	*4.5*	*16.35*	*51.6*	*13.1*	*.766*	*7.94*	*21.8*
Non-C/H & CH_n	6.85	.981	4.02	*11.85*	4.63	.21	2.002	*6.85*
H_2O	14.07	1.24	5.04	*20.34*	4.77	.089	1.49	*6.34*
O_2	-	1.11	4.46	*5.57*	-	.466	4.46	*4.92*
CO_2	-	-	-	-	3.7	-	-	*3.692*
N_2	9.8	1.17	2.83	*13.8*	-	-	-	-
Outputs	*30.66*	*4.49*	*16.33*	*51.48*	*13.08*	*.757*	*7.93*	*21.77*
NH_3	1.17	1.395	3.36	*16.41*	-	-	-	-
CH_4O	-	-	-	-	7.52	.282	1.598	*9.4*
H_2O	-	-	-	-	1.03	-	-	*1.03*
CO_2	11.7	2.86	10.83	*25.34*	-	.208	3.196	*3.403*
Loss	7.36	.24	2.14	*9.74*	4.53	.267	3.14	*7.93*

REFINERY

The feedstock into a refinery includes crude oil, natural gas liquids (NGL) and other liquids. Natural gas liquids include n-butane, isobutane, natural gasoline, pentanes plus, and liquified petroleum gas. Other liquids include hydrogen renewable fuels, fuel ethanol, renewable diesel fuel, other hydrocarbons, unfinished oils, naphtha's and lighter fuel, kerosene and light gas oils, heavy gas oils, residuum and aviation gasoline blending components. To find the total production from a refinery, all the feedstocks were added together to get a total of 902 Mt yr^{-1}. These values were all found from the 2019 EIA manufacturing energy consumption survey.

Several assumptions were made to find the refinery secondary reactants and products since there are hundreds of refineries in the U.S., emission values from the Environmental Integrity Project (EIP) database were used to find an "average" emissions value for all the reported refineries. This ratio was found based off 6 refineries that listed their barrels per year, seen in Table 6. The ratio was calculated by dividing the total emissions by the total production made at the refinery. The total production value was found by adding up the total production made from each refinery. This ratio was then multiplied by the refinery total production in the U.S. to get the total theoretical emissions, which is included in the emissions and byproducts section of Figure 7.

PETROCHEMICAL

Similar to refineries, all the petrochemical total feedstock values were found first through the EIA database of refinery products. Next, the total production values for each chemical used throughout the petrochemical section were found. Most of these values were obtained from the *Guide to the Business of Chemistry 2020* but some were harder to find, therefore the sources used were inconsistent. A list of all these products can be found in the appendix, Table 14, along with the intermediates.

After finding the total amount of each chemical produced in the U.S., the amount of each intermediate used to produce the chemicals were found. These reaction input relationships were collected from the paper by Levi *et. al.*[27] These input numbers were directly quoted from this paper and represent the tons of primary reactant required per ton of primary product taking into account production efficiencies and yields. These values were then multiplied by the total production amount of the respective product to find the amount of reactant needed. These can be seen in the appendix, Table 15.

In addition to the main flows, there were also secondary reactants that need to be accounted for such as CO_2, O_2, and H_2. This was done through looking at the reaction equations for each chemical and using the molar mass and stoichiometry to find the amount of secondary reactant and products used. These values can be seen in the appendix, Table 17.

Although most of these products had a simple reaction available, however secondary reactants for chemicals like ethylene and propylene were found another way. The EIP database was used to find these values. The EIP used the data from the EPA to track the breakdown of emissions from petrochemical plants. To find the amount of emissions made from ethylene and propylene, a ratio was made between the total production and the total emissions that plant made. The total U.S. production of the product was multiplied by that ratio to get the total amount of secondary products for that chemical seen in Tables 7 and 8. Here, in Tables 7 and 8, there is a breakdown of each of the outputs for the plants that were used to calculate the ratio and find the total amount of secondary reactants for these products in the U.S.

Table 6: *Inputs and outputs of five refinery plants in the U.S. from 2019. These refineries are used to scale up the GHG based on the total crude oil produced in the U.S. The inputs represent the total crude oil, natural gas, and natural gas liquids. The outputs are the GHG secondary products from the refineries. These values are used in the Sankey diagram for the secondary reactants and products.*

Inputs/Outputs (Mt y^{-1})	**Refineries**						**Total (U.S.)**
	Kenai Refinery	Holly Tulsa Refinery East, West, and Loading Terminal	Corpus Christi Refinery	Valero McKee Refinery	Valero Port Arthur Refinery	Port Arthur Refinery	
Inputs							
Feedstock (Crude Oil, Natural Gas, NGL)	52.78	1246.1	252.89	1539.3	3151.9	769.65	7487.6
Outputs							7.26
NO$_x$	.054	835	.025	.291	.128	.1	1.43
SO$_2$	.007	38	.018	.218	.79	.157	1.23
CO	.037	1240	.118	.651	.364	.051	2.46
VOCs	.021	37	.559	.215	.535	.016	1.38
PM	.006	--	.025	--	.077	.032	.140
PM 10	.006	120	.015	.056	.061	.032	.29
PM2 5	.006	122	.014	.054	.063	.032	.291

Table 7*:* *Inputs and outputs of five propylene plants in the U.S. from 2019. These plants are used to scale up the GHG based on the total propylene produced in the U.S. The inputs represent the total ethane, naphtha, and crude oil. The outputs are the GHG secondary products from the plants. These values are used in the Sankey diagram for the secondary reactants and products.*

Inputs/Outputs (Mt y^{-1})	**Propylene Secondary Reactants**					**Total**
	Chocolate Bayou PDH Plant	Mont Belvieu Complex	Enterprise Products Operating LLC (second unit)	Equistar Chemicals, LP (LyondellBasell)	Flint Hills Resources Houston Chemical LLC	
Inputs						
Feedstock (ethane, Naphtha, crude oil)	1	.725	5.48	.32	.66	8.18
Outputs						2.53
NO$_x$	.053	.064	.011	.038	.022	.188
SO$_2$	.004	.031	.135	.014	.033	.217
CO	.324	.228	.200	.169	.061	.982
VOCs	.020	.077	.071	.161	.025	.354
PM	.046	.032	.089	.042	.033	.242
PM 10	.046	.027	.088	.034	.032	.227
PM2 5	.042	.024	.087	.032	.032	.217

Table 8: *Inputs and outputs of six ethylene plants in the U.S. from 2019. These plants are used to scale up the GHG based on the total ethylene produced in the U.S. The inputs represent the total crude oil, natural gas, and natural gas liquids. The outputs are the GHG secondary products from the plants. These values are used in the Sankey diagram for the secondary reactants and products.*

	Ethylene Secondary reactants						
Inputs/Outputs (Mt y^{-1})	Ethylene Plant	Lake Charles East, West, and Loading Terminal	Ethylene and Monoethylene Glycol Plants	Geismar Ethylene Plant	Lake Charles Chemical Complex-Cracker Project	Plaquemine Ethylene Plant 1 (PEP-1)	**Total**
Inputs							
Feedstock (Crude Oil, Natural Gas, NGL)	.342	.46	1	.885	1.5	669.956	4854.6
Outputs							10.5
NO$_x$	.064	.33	.043	.024	.925	.099	1.49
SO$_2$	.002	.028	.009	.033	.061	.007	.14
CO	.089	.526	.731	.074	2.646	.374	4.44
VOCs	.415	.202	.269	.024	2.223	.199	3.332
PM	--	--	--	--	--	--	--
PM 10	.022	.064	.069	.009	.37	.056	.590
PM2 5	.013	.064	.056	.008	.37	.043	.554

CREATING THE SANKEY

The structure for the Sankey diagram was created using the previously discussed tables wherein the total production amounts and reaction chemistry values were used to satisfy a mass balance for the petrochemical industry. The software program e! Sankey was used to create the flow structure and Adobe Illustrator was used to create the flow labels.

The most challenging part of creating the Sankey was determining the "branching", or distribution of the total production of one chemical to its constituent, downstream, chemicals. Take ethylene, for example. The total production of ethylene was known and the total production of the downstream chemicals that are made from ethylene (polyethylene, styrene, vinyl chloride, etc.) were also known. The challenge was determining how the total mass of ethylene (32.2 Mt yr^{-1}) was distributed to the downstream products. This process was aided by Table 15 in Appendix B, which provided a standard product to reactant ratio. Keeping with the example of ethylene, the ratio Table 9 allowed us to determine how much ethylene was required to make a known amount of vinyl chloride. Conceptualizing the branching methodology is, perhaps, aided by a mathematical representation shown below.

$$(Mass\ of\ product\ vinyl\ chloride) \times (Reaction\ Ratio) = (Mass\ of\ reacted\ ethylene)$$

$$(7.2\ Mt\ vinyl\ chloride) \times (0.49) = (3.5\ Mt\ ethylene)$$

In the above relationship above, the mass of vinyl chloride and the reaction ratio are known, and the mass of ethylene is solved for. Similar math was conducted for each of downstream products of ethylene to determine the comprehensive distribution of ethylene. For proof of concept, the individual contribution of ethylene to each of the downstream chemicals was summed and compared to a reported total of ethylene production. The comparison of these values is displayed in (Table 9).

The total ethylene production derived via the product-contribution method demonstrated good agreement with a reported total. For the purposes of the Sankey diagram, the difference was negligible and within the acceptable range for mass balance agreement. The process detailed above was repeated for each chemical in the Sankey diagram where most of the chemicals demonstrated acceptable agreement.

For the cases where there was a discrepancy between the product contribution and the reference total production, one of two methods was implemented. When the production-contribution method was less than the reference production, the remaining reference production was distributed into the "other" product flow on the Sankey diagram. In this sense, the

Table 9: *Sample mass balance calculation for ethylene production. The contribution row refers to the amount of ethylene required to make a known amount of product. The researched ethylene production (bottom row) simply refers to a researched total for ethylene production in a year.*

	Ethylene's Downstream Products					
	Polyethylene	Styrene	Vinyl Chloride	Vinyl Acetate	Ethylene Glycol	**Total**
Ethylene Contribution (Mt)	23.5	3.7	3.5	0.5	1.0	32.2
Researched Ethylene Production (Mt)	-	-	-	-	-	31.4

"other" product flow represents an unknown mass contribution. Conversely, for instances where the production-contribution method was greater than the reference production, the contributions were summed and calculated as a percentage of the total production. That is, if the reference ethylene production shown above was much lower than the product-contribution, 10.0 for example, then each contribution would be taken as a percentage of the whole and applied to research value. In the above table, 73% of the total ethylene was used to make polyethylene (23.5 / 32.2 = 73%). By the stated logic for a lower reference production, we would still assume that 73% of the ethylene is used to make polyethylene. We would then deduce that 7.3 Mt of ethylene was used in the production of polyethylene (73% x 10.0 Mt = 7.3 Mt).

A certain level of discretion was necessarily involved in the Sankey methodology as the data was retrieved from a diverse array of sources. Some of the high-production chemicals, particularly those upstream such as ethylene, were easy to find and had multiple sources to verify the production values. However, the production totals for some of the niche chemicals was difficult to find and individual, though reputable, sources were used for data collection. For those chemicals with less rigorous sources, extra consideration was given as to the validity of the data. In such cases, extra research was done beyond the primary source to further validate and contextualize the data.

CO_2 DATA

The CO_2 equivalent emissions were based off the EIP's paper and the database, *Greenhouse Gases from Oil, Gas, and Petrochemical Production*. The database was published on January 8, 2020 but the data on annual emissions were collected from 2018. The database used information from the EPA on all plants in the petroleum and natural gas systems, chemical manufacturing, and refineries in the U.S. Refineries contained a feedstock of crude oil and natural gas. The chemical manufacturing included chemicals produced from crude oil, coal, and natural gas. The plants in the chemical sector included nitric acid production, ammonia manufacturing, hydrogen production, petrochemical and plastics productions, and other chemicals including adipic acid. This data can be seen in Figure 6 organized from the lowest GHG emissions to the largest from 2018.

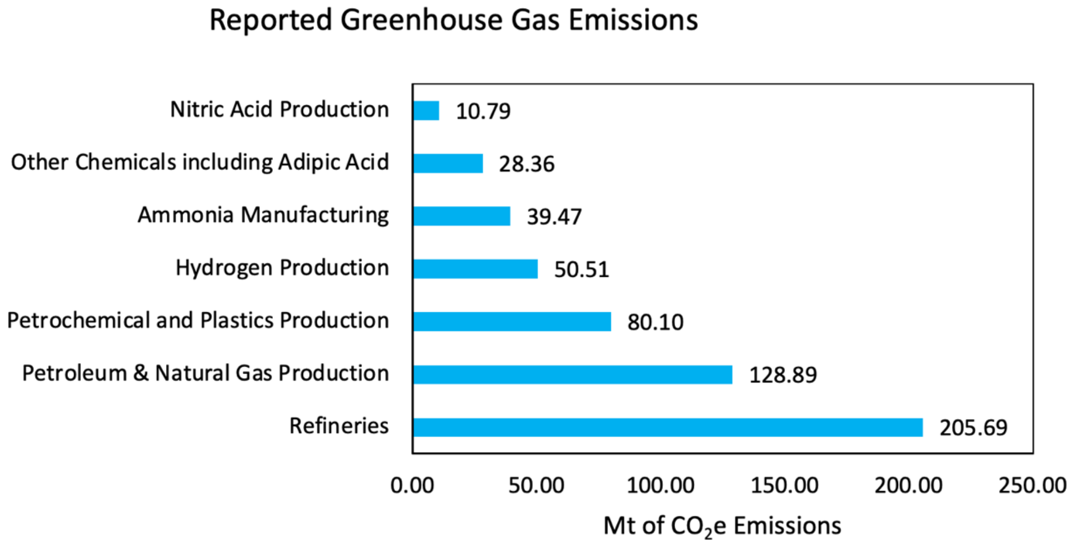
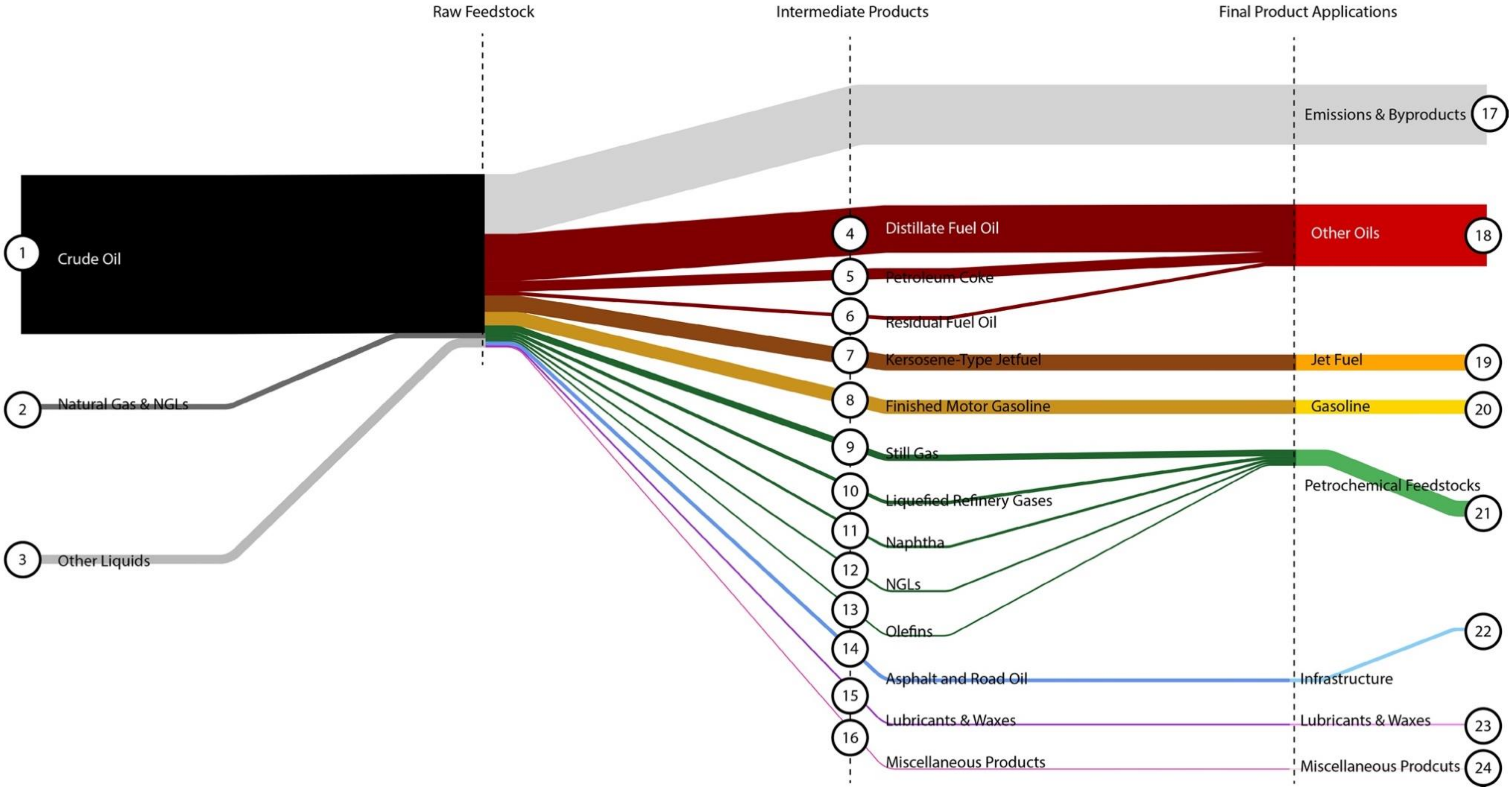


Figure 6: *Reported greenhouse gas emissions from the chemical manufacturing, petroleum and natural gas production, and refineries in the U.S. in 2018. These represent the kilotons of carbon dioxide equivalent of emissions gained from* the EPA in the greenhouse gas reporting system. [9]

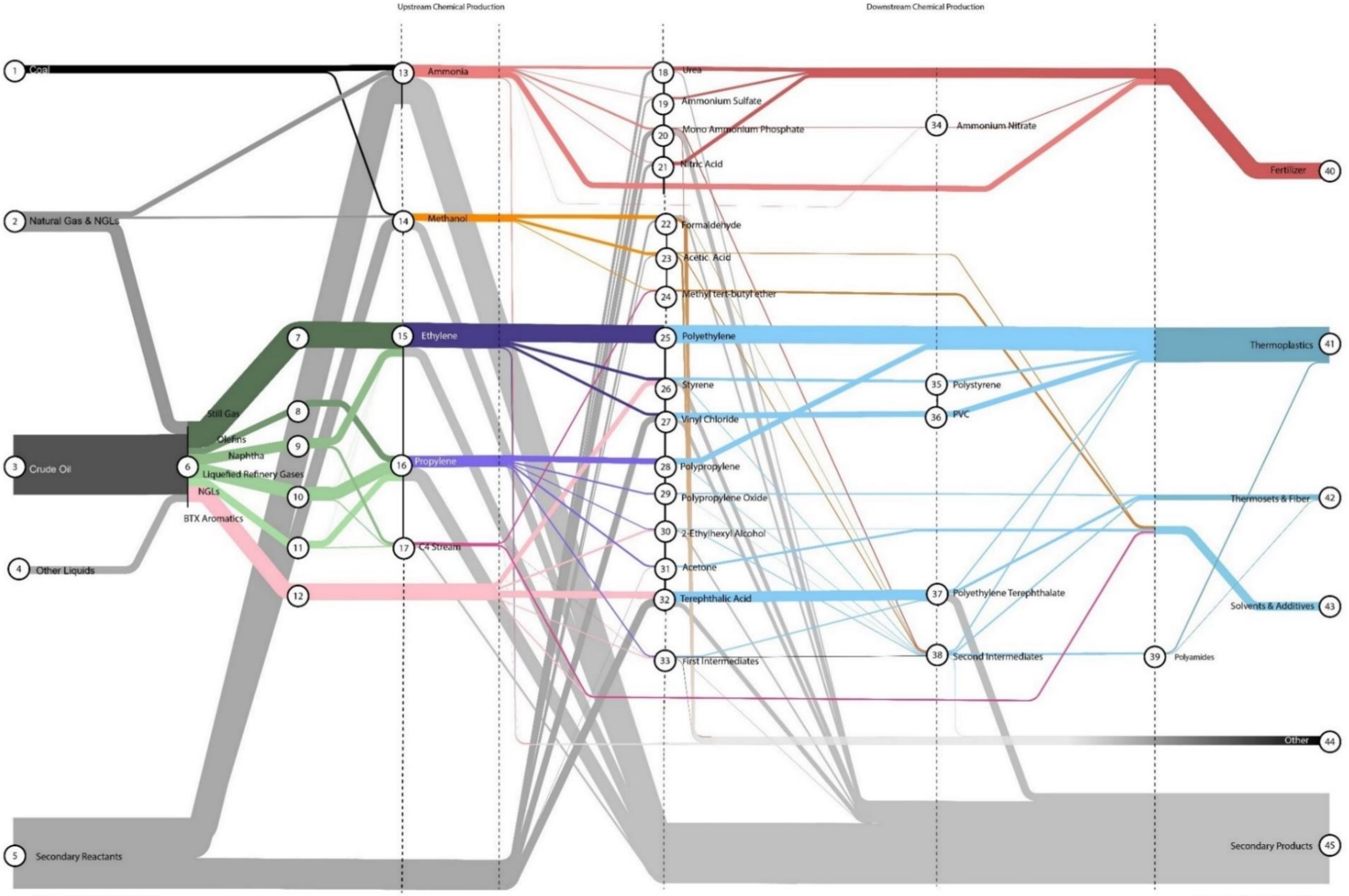
OVERALL SANKEY DIAGRAM

***Figure 7**: Sankey Diagram of Fossil Fuels used in the U.S. in 2019*



PETROCHEMICAL SANKEY DIAGRAM

Figure 8: *Sankey Diagram of the Petrochemical Flow in the U.S. from 2019*



Secondary Reactants include:
H_2O
O_2
CO_2
N_2
H_3PO_4

First Intermediates include: Polychloroprene, Isophthalic acid, Dimethyl terephthalate, Adiponitrile, Maleic anhydride, Phthalic anhydride, Acrylonitrile, Cyclohexane, and Phenol

Second Intermediates include: Nitrile butadiene, Hexamethylenediamine, Melamine, Polyacrylonitrile, Toluene diisocyanate, Dioctyl phthalate, Methyl methacrylate, Caprolactam, Aniline, Stryene butadiene, Bisphenol A, Vinyl acetate, Styrene acrylonitrile, and Acrylonitrile butadiene styrene

Secondary Reactants include:
H_2O
CH_4
CO_2
$CaCl_2$
HCl

SANKEY ANALYSIS

In this analysis, all estimates were from data published in 2019 unless otherwise mentioned. The analysis will focus on Figure 8, the petrochemical Sankey diagram since it contains the products of interest in this paper. It will start with the feedstocks into refineries, coal gasification plants, and petrochemical industry and finish with the four major categories of products.

FOSSIL FUEL FEEDSTOCK TO REFINERY AND COAL GASIFICATION

This study examined the mass flow rates in the U.S. of three fossil fuels from raw materials into products of interest. Two main processes that coal, crude oil, and natural gas are fed into are refineries and coal gasification plants. In the raw material production of natural gas and petroleum, 128.0 Mt of CO_2e of emissions are released annually in the U.S. Refineries break down crude oil, natural gas, and other liquids such as hydrogen, ethanol, renewable diesel fuel, and heavy gas oils. As of 2019, the input of crude oil into the 132 operating U.S. refineries was 836.2 Mt yr^{-1} or 6.05 billion barrels per year. This would fill about 385,000 Olympic swimming pools or 707 empire state buildings. Refineries also consume 17.0 Mt yr^{-1} of natural gas and 49.1 Mt yr^{-1} of other liquids. With these fossil fuels, there was 205.7 Mt of CO_2e of emissions from refineries in the U.S. in 2018. The four coal gasification plants operating in 2019 consumed 10.2 Mt yr^{-1} of coal and lignite. Coal gasification plants provide feedstocks for ammonia and methanol production. The 34 ammonia and 12 methanol plants also consume natural gas as feedstocks and were projected to consume 11.4 Mt yr^{-1} based on the world consumption (See appendix A).

REFINERY OUTPUTS/PETROCHEMICAL INPUTS

The largest product from a refinery in 2019 was distillate fuel oil that can be used as fuel for diesel engines in trucks, railroad locomotives, space heating, or electric power generation.[37] The next largest product was kerosene used for jet fuel and motor gasoline. Fuels and oils comprise about 71% of the total mass products made from refineries. The other products from refineries include petrochemical feedstocks, lubricants, waxes, petroleum coke, and asphalt/road oil. Petrochemical feedstocks comprise of naphtha's and other oils but portions of the olefins, liquified refinery gases, natural gas liquids and still gases are also sent to petrochemical plants. Lubricants contain oils such as spindle and cylinder oil as well as greases for machines. Petroleum coke can be used as fuel in cement kilns or electricity generation. Petcoke can also be used in aluminum manufacturing or in the production of steel, paint, brick, glass, paper, or fertilizer.[38] Asphalt and road oil is normally used in construction to make cement and concrete or sprayed on roads to settle dust and bind the gravel.[39] Refineries are the start to major products people rely on every day from gasoline to plastics.

Coal gasification plants, besides fertilizers, have the highest production of flaked residue also known as coal ash that can be used in construction in cement. Many fuels that are produced in refineries are also produced in coal gasification plants such as diesel, liquified petroleum gases, gasoline, naphtha, and jet fuel. Reformate is also produced which is a blending stock for gasoline.

MAJOR FINAL PRODUCTS

THERMOPLASTICS

Thermoplastics are plastics that can be remolded when heated, therefore can be recycled. As expected, thermoplastics were among the largest outputs of the petrochemical industry—49.6 Mt are produced annually. As previously mentioned, most of the thermoplastic contribution came from the production of ethylene (32.2 Mt yr^{-1}) where most of the ethylene produced was used to make thermoplastics. The contribution of polypropylene, via propylene, was similarly significant where 7.0 Mt yr^{-1} were produced. The 46.9 Mt yr^{-1} estimated in accordance with the Sankey Diagram was higher than the 35.7 Mt yr^{-1} thermoplastic estimate provided by the EPA for 2019. The discrepancy could be, in part, due to the number of assumptions that were made in the intermediate production process. For instance, while the production amount of polyethylene terephthalate was known (5.1 Mt yr^{-1}) the subsequent utilization and distribution of polyethylene terephthalate was relatively difficult to determine. That is, assumptions had to be made to determine where the 5.1 Mt yr^{-1} of polyethylene terephthalate would be distributed. While some of the downstream products, such as polyvinyl chloride (PVC), were easy to distribute, others were more challenging and necessarily required assumptions.

THERMOSETS AND FIBERS

Thermosets are plastics that are unable to be remolded after they are made. Thermosets contributed 7.0 Mt yr^{-1} to the overall 53.9 Mt yr^{-1} of plastic produced each year (13%). Much of the same logic that was applied to the thermoplastics can be applied to thermosets where a set of governing assumptions were used to establish the final production mass of thermosets. Polyethylene Terephthalate was the primary contributor to the thermoset production (3.4 Mt yr^{-1}) with Polypropylene Oxide (1.7 Mt yr^{-1}) being a large secondary contributor.

SOLVENTS AND ADDITIVES

Solvents are the final products that are used to dissolve in solution and additives are the final products used to preserve other products. The solvents and additives contribution to the Sankey is distinct from the fertilizer and plastics sections in that some upstream chemicals such as the C_4 and BTX aromatic streams contribute 2.1 Mt yr^{-1} and 1.7 Mt yr^{-1} to solvent and additive production, respectively.

A product of coal and natural gas is methanol, which has a production capacity of 6.9 Mt yr^{-1}.[36] There are a total of 12 methanol plants as of now that makes up this yearly capacity. Methanol can be the end product, but it can also make acetic acid and methyl-tert-butyl-ethane. All these products fall into the final solvent category.

FERTILIZER

Other production routes in the Sankey diagram look at coal and natural gas production. Most of these products are used to make fertilizers, which emits a large amount of GHG. The largest product made from coal is ammonia, which has a production capacity of 16.41 Mt yr^{-1}.[35] Ammonia can be sold as a finished product, but can also be made into urea, ammonium sulfate, mono ammonia phosphate, nitric acid, and formaldehyde. All these products can be put into the final fertilizer category. Ammonia fertilizer plants have a CO_2e of 39.5 Mt yr^{-1} and nitric acid production has 10.8 Mt yr^{-1} .[40]

Although there is a large production capacity of ammonia and methanol from coal and natural gas, there are only 4 coal plants now in the U.S. Both products can be made from natural gas, ultimately showing that coal plants in the U.S. are no longer needed. The production of ammonia and methanol are made from syngas, which can be made from an alternative method into order to lower the CO_2e of both fertilizers and solvents.

ALTERNATIVE PRODUCTION

FISCHER-TROPSCH SYNTHESIS (FTS)

HISTORY

Fischer Tropsch synthesis (FTS) is a long-standing and well researched method of converting syngas, a mixture of CO and H_2, to liquid hydrocarbon products. Historically, syngas has been produced through coal gasification. William Murdoch, a Scottish engineer and inventor, is credited with inventing coal gasification in the late 18th century, using the syngas to light his home and other buildings throughout England. Today, syngas is derived from other carbon sources including biomass, natural gas, shale gas, and garbage in addition to coal.[41]

After World War I, Germany sought to transform its abundant coal supplies into liquid transportation fuels to supplement its lacking petroleum supplies. This task was first taken on by a Friedrich Bergius, a German Chemist, in 1913. He developed the Bergius process for coal liquification, where powdered coal was mixed with heavy oil and reacted with high pressure and temperature H_2 gas to produce petroleum-like liquids.[42] German chemists Franz Fischer and Hans Tropsch furthered the cause in 1925 and developed the FTS process at the Kaiser-Wilhelm Institute for Coal Research. Fischer and Tropsch hydrocracked coal with steam to produce syngas. They developed a cobalt catalyst to convert the syngas to a synthetic crude oil, known as FT crude, under reasonable conditions of 1 to 10 atm and 453 to 473 K.[42] The FTS crude could then be further refined into gasoline, diesel, kerosene, and other petroleum products through typical refining methods. Germany exploited this process significantly during WWII; the first FTS plant began production in 1936, and soon Germany was operating twelve high-pressure coal hydrogenation plants alongside nine FTS plants.[43] These nine plants produced approximately 660,000 t yr^{-1} of synthetic petroleum products.[44]

In the years following WWII, FTS technology became the center of research efforts abroad in Europe as well as Japan, South Africa, and the U.S. In the 1940s, crude oil reserves were dwindling while there was still an ever-increasing demand for liquid fuels. Countries around the world thus began to focus on alternative methods to produce synthetic fuels, and large steps were made in catalyst and reactor development. Between 1945—1955, FTS was adapted to fluid-bed and fixed-bed multitubular reactors, as well as circulating catalyst and slurry processes.[45] Around 1955, there was an oil surge around the globe, providing a cheap and abundant supply of liquid fuels via traditional refining methods. Research interests thus turned away from FTS to crude oil refining with one major exception: Apartheid-era South Africa.

South Africa began its apartheid regime in 1948 and upheld it until the early 1990s. The South African government's policies sparked international opposition and led to strict trade embargoes which impacted the country's ability to import petroleum. However, it had an abundance of coal, leading to the formation of the state-owned South African Coal, Oil and Gas Corporation (Sasol) in 1950, an FTS based synthetic fuel company. Construction of the first Sasol FTS plant (Sasol 1) began in 1952; the plant housed four separate refineries to produce different product slates, including tar, high-temperature FT (HTFT) oil, low-temperature FT (LTFT) oil, and chemicals.[43] In 2004, the plant switched over from coal gasification to natural gas reforming. Construction of Sasol 2 began in 1976 and the plant came online in 1980. Sasol 3 was built alongside Sasol 2 and was commissioned in 1983. The two plants were later combined into a singular facility and renamed Sasol Synfuels, with the capacity to produce 160,000 bpd of


Figure 9: William Murdoch [46]


Figure 10: Friedrich Bergius [47]


Figure 12: Franz Fischer [48]

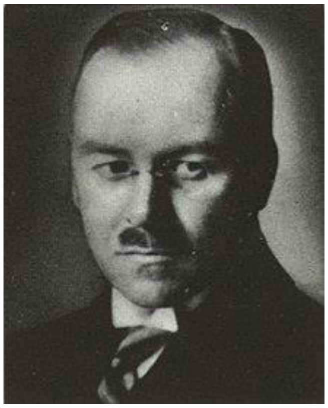


Figure 11: Hans Tropsch [49]

product.[43] There are additional commercial-scale FTS plants located in South Africa, Malaysia, Qatar, and China.

FTS was born from the unpredictability (due to economic or political circumstances) of fossil fuels. In the near future, it is likely FTS will have a place center-stage in dealing with the once unpredictable but now crucial consequences of burning fossil fuels in our effort to defossilize our energy systems.

REACTION

During FTS, CO and H_2 are polymerized on the surface of a catalyst.[42] There are at least 10 reaction steps to form the monomer CH_2 units necessary for forming the liquid hydrocarbon fuels. First, CO is adsorbed onto the catalyst and the C-O bond it split. Two H_2 molecules are also adsorbed and split into singular H atoms. Two of these H atoms bond with the split O to form and H_2O molecule, which then desorbs from the catalyst. The other two H atoms then bond with the lone C atom, forming the CH_2 monomer. This monomer then bonds with another monomer, building the hydrocarbon chain.[45] Depending on the catalyst used and the conditions of the reaction bed, FTS can produce a variety of molecules, from C_1 to C_{40} structures, and can be fine-tuned to produce specific product slates. These molecules take the form of alkanes, alkenes, alcohols, and carbonyls; generalized overall reactions for the synthesis of each of these groups are shown below.

Monomer Formation:

$$CO + 2H_2 \rightarrow (CH_2) + H_2O$$

Alkane:

$$nCO + (2n+1)H_2 \rightarrow H(CH_2)_{nH} + nH_2O$$

Alkene:

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O$$

Alcohol:

$$nCO + 2nH_2 \rightarrow H(CH_2)_{nOH} + (n-1)H_2O$$

Carbonyl:

$$nCO + (2n-1)H_2 \rightarrow (CH_2)_nO + (n-1)H_2O$$

CATALYST

Control over an efficient FTS process is highly dependent on the design of the catalyst. The active material in commercial FTS catalysts is either iron, cobalt, ruthenium, or nickel. These metals dissociatively adsorb CO and H_2 facilitating the hydrogenation of carbon to form the CH_2 monomers. Ruthenium has a high cost and nickel does not facilitate chain growth as well as other catalysts, which is necessary to produce higher molecular weight hydrocarbons for fuels. Thus, iron and cobalt catalysts are preferred.[42] There are tradeoffs between cobalt and iron catalysts. Cobalt is more expensive but has a higher selectivity for long chain alkanes and low selectivity for oxygenates and alkenes. It also has a higher deactivation resistance, giving it a longer lifetime.[42] Iron catalysts produce more water, which wastes CO feedstock and can lead to increased deactivation. However, they are cheaper and can produce naphthenes and aromatics whereas cobalt catalysts do not.[42] In traditional FTS, where syngas is sourced from coal and may contain sulfur, iron catalysts are preferred because of their tolerance to sulfur.[41]

The combination of catalyst and promoter, the relatively inexpensive material that is coated with the valuable catalyst to increase its reaction surface area, can help determine the FTS product slate. Common promoters include metal oxides such as aluminum oxide, silicon dioxide, and titanium dioxide or zeolites. Silica is also a popular promoter because it has an extremely large surface area and low density, which is ideal for creating a substantial number of reaction sites without the catalyst material being too heavy. [42] Lighter materials require less support in the reactor and reduce its cost. The choice of particle size, the type of support, and the metal-support interactions can also influence the performance of the catalyst. Sun et al. provide an excellent review of catalyst-promoter combinations that have been developed to induce particular product slates, such as jet fuel, olefins, aromatics, and oxygenated chemicals.[41]

SYNGAS PRODUCTION

HYDROGEN

There are multiple routes for H_2 production with various CO_2 emissions intensities. Brown hydrogen refers to H_2 produced from coal, whereas gray hydrogen is H_2 derived from natural gas or petroleum. When carbon capture is combined with either of these methods to offset emissions, the H_2 is referred to as blue hydrogen. Finally, the most sustainable is green hydrogen, or H_2 sourced completely from renewables. As of 2010, 52 $Mt_{H2}\ yr^{-1}$ were produced globally, primarily through steam methane reforming.[50]

Steam Methane Reforming & Water Gas Shift

Steam methane reforming is the partial oxidation of natural gas or light naphtha. High temperature steam (1300°F—1800°F) under pressures of 3—25 bar is reacted with the carbon stream (typically methane) over a nickel catalyst.[51] This produces a mixture containing primarily CO and H_2 much like the gasification processes, however the mixture has a higher H_2/CO ratio (3:1 to 5:1). The reaction is very endothermic (ΔH = 206 kJ/mol) and therefore requires a significant amount of additional heat energy. This is typically generated by external natural gas furnaces, which contribute a significant portion of the overall process CO_2 emissions. The syngas stream exits the reactor at 1500—1700°F, presenting the opportunity for heat recovery, which is typically used to preheat the syngas feed or in other applications around the plant.[52]

Steam Methane Reforming Reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

General Steam Reforming Reaction:

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m}{2} + n\right)H_2$$

Water Gas Shift Reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

When hydrogen is the desired product, the product stream from the steam methane reforming process is sent to a water gas shift (WGS) reactor where the remaining CO is converted to CO_2 and H_2. A variety of catalysts are used in this process under operating temperatures of 400—900°F.[53] When the WGS stage is completed before sulfur removal, cobalt-molybdenum catalysts are typically used. When located after sulfur-removal chromium or copper promoted iron-based catalysts or copper-zinc-aluminum catalysts are used.[53]

Electrolysis of Water

Electrolysis uses electricity to split water into H_2 and O_2; when combined with renewable energy it becomes a carbon neutral H_2 production method. Electrolysis applies an electric current to add or remove electrons from a species. Atoms and ions are then interchanged to generate the desired species. An electrolyzer replaces a traditional reactor; it consists of an anode and a cathode separated by an electrolyte. The anode provides a positive charge, causing negatively charged species to move toward it, while the cathode does the opposite and attracts positively charged species. Electrons are effectively removed at the anode (oxidation) and introduced at the cathode (reduction). There are three primary types of electrolyzers: polymer electrolyte membrane (PEM), alkaline, and solid oxide. An example of the PEM electrolyzer system with water as the solution can be seen in Figure 13.

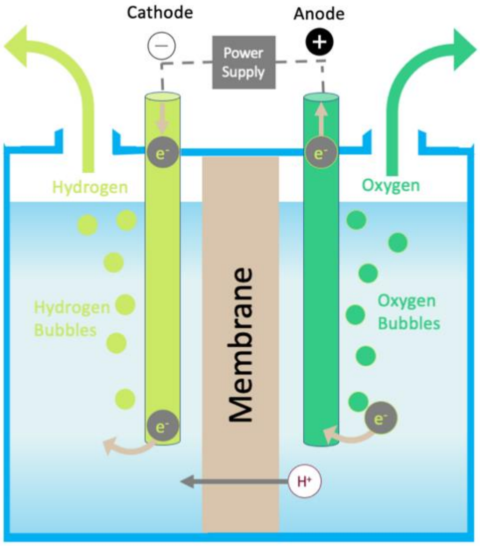


***Figure 13:** An example of an PEM electrolyzer with an anode and cathode removing electrons from water on one side of a membrane and moving them to the other side to produce hydrogen and oxygen gas.* [54]

In the case of water electrolysis, water molecules are split into O_2, hydrogen cations (H^+), and electrons (e^-) at the anode. In a PEM electrolyzer, the hydrogen cations travel across the membrane (a specialty plastic) to the cathode, where they receive the electrons to form H_2 gas. The H_2 and O_2 gases separate from solution at their respective sides of the electrolyzer and can then be collected. Alkaline electrolyzers operate by transporting hydroxide ions (OH) through the electrolyte, but the overall reaction remains the same. Solid oxide units use elevated temperatures to generate negative charged oxygen ions (O^{2-}), which pass through a solid ceramic membrane. Water electrolysis requires a minimum potential difference of 1.23 volts; for reference, new AA batteries supply 1.5 volts.[54]

Anode Side Reaction:

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$$

Cathode Side Reaction:

$$2H^+ + 2e^- \rightarrow H_2(g)$$

Overall Reaction:

$$2H_2O \rightarrow 2H_2 + O_2$$

CARBON MONOXIDE

Coal Gasification

During coal gasification, solid carbon (coal or petroleum coke) is partially oxidized to produce syngas, a gaseous mixture of CO and H_2. Typically, a fine particle form of the solid carbon source is fed into a reactor operating at high temperature and pressure. The particles are suspended in steam, and a limited supply of oxygen is introduced. The oxygen supplied is just enough to induce partial oxidation but not full combustion, which would only produce CO_2 and H_2O.[55]The mixture may contain sulfur byproducts, CO_2, and residual H_2O and carbon; these components are later separated leaving a syngas mixture with a final H_2/CO ratio between 1.6 and 1.8.[56]

Gasification Reaction:

$$3C + O_2 + H_2O \rightarrow H_2 + 3CO$$

Gasification processes in general are endothermal. The energy necessary to complete the reaction can be produced within the reactor through partial combustion of the carbon source (auto-thermal process), or by supplying energy from an outside source (allo-thermal process).[57] Different reactor configurations and gasification processes can be utilized based on the properties of the carbon source. In coal gasification, there are two primary systems, those for processing low-sulfur-content coal and those for high-sulfur content. Sulfur can poison catalysts used in the reactor bed, therefore catalytic partial oxidation (CPOX) can be only used for low-sulfur coals. These processes are run around 1475—1650°F, which reduces energy consumption. Thermal partial oxidation (TPOX) is used for high sulfur content and is conducted at >2200°F.[56]

Electrochemical Reduction of CO_2

The electrochemical reduction of CO_2 to CO via the reverse water-gas shift reaction is a developing field of research, with most efforts being directed towards catalyst development. The primary issues researchers are looking into include energy efficiency, reaction rates and selectivity, and the prevention of catalyst deactivation.

Reverse Water-Gas Shift Reaction:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

To be feasible, the reaction must have a high energy efficiency and a high reaction rate; this is difficult to achieve due to the high overpotential, or high electric energy, required to obtain reduction products. High overpotentials are caused by the instability of the $*CO_2^-$ radical ion in the rate limiting step of the reaction. Catalysts are thus designed to stabilize the radical intermediate while also promoting further reaction to achieve the desired product.

Hydrogen production also competes with the CO_2 reduction, and thus reduces the rate of the reaction.[58] This can be beneficial for syngas production since both species are needed, however it is more economically beneficial to aim for the highest possible CO selectivity.[59] Mass transfer of the CO_2 to the cathode surface also limits the reaction rate as CO_2 is relatively insoluble in most electrolytes. Gas diffusion electrodes (GDEs) have generally been used to alleviate this issue by creating a three-phase interface between the gaseous reactants, liquid electrolyte, and solid catalyst.[60]Additionally, reaction intermediates may poison some active sites of the catalyst. This both decreases the reaction rate and limits the longevity and stability of the reaction set up.[60]

Each of these issues may be alleviated by optimizing the electrolyte, reactor configuration, reaction conditions, and catalyst.[58] Researchers have sought ways to improve CO_2 reduction through varying the morphology, active sites, and the exposed faucets of the catalysts.[60] Different active materials have been combined to serve different reaction steps. Ag, Au, and Zn catalysts are most selective for CO production, while Sn, Cd, and Ti catalysts have been used for formic acid production; Cu catalysts are primarily being considered for making C_2 and C_{2+} products.[61] The catalysts used for CO production exhibit the highest energetic efficiencies, but the structure of the promoter material carrying the catalyst species can also influence their ability to increase current density, reaction rates, and energetic efficiencies.[61]

Little is known about the reaction pathways to making this product slate aside from how the initial C-C bond is formed and is thus a continuing area of research which may inform scientists about the possibility of other non-copper-based catalysts.[62]

Few groups have been able to test reaction set ups longer than a 24-hour period, either due to challenges in the reactor design which led to mass transfer limitations, or the failure of the catalyst.[50] A cascade system that combines the electroreduction if CO_2 to CO and CO to C_{2+} hydrocarbons is predicted to be more economical than generating CO separately for FT, so the attention of the research community has been directed more towards these efforts. However, the reaction schemes being studied for the production of C_{2+} product slates show low selectivity; in the future, this will need to be improved to reduce separation costs before the species are used to synthesize fuels and petrochemicals.[63] Thus far, the electrochemical reduction of CO_2 to CO has not been applied industrially because of the lack of stability and selectivity of the current catalysts.[60]

BIOMASS GASIFICATION

Biomass gasification utilizes biomass waste that would otherwise be discarded as a feedstock for syngas and energy production. The syngas composition is not greatly influenced by the biomass type used, making this process suitable for a wide range of feedstocks. Biomass may be sourced from forestry, agricultural, industrial, and waste sectors in the form of woodchips, straw, manure, sawdust, organic municipal waste, sewage sludge, etc.

In an auto-thermal process, partial oxidation of the biomass is first conducted to provide the energy needed for the endothermic stages of the process. The biomass is then dried by heating it to around 150°C; the energy required for this stage depends on the initial moisture content of the biomass. The next step is pyrolysis, where the biomass is subjected to high temperatures to break the chemical bonds and form smaller hydrocarbon species, much like the hydrocracking stage of a refinery. Pyrolysis can produce gas, liquid, and solid phase hydrocarbon species. The solid phase is known as char, the liquid phase is denoted as tar, and the gaseous phase, which makes up most of the product from this stage, is called pyrolysis gas. Pyrolysis gas is primarily CO, H_2, CO_2, and light hydrocarbons such as CH_4. In the final reduction step, the gas mixtures from the pyrolysis and oxidation stages react with the char to produce the syngas mixture. The temperature at which the reduction step is carried out determines the final composition of the syngas. When pure oxygen is used, process temperatures range from 500-1600°C; when air is used as an O_2 supply a temperature range of 800-1100°C is more common. CO formation is favored at higher reaction temperatures.[57]

BIOGAS

Biogas is generated through the breakdown of organic material in the absence of oxygen via anaerobic bacteria; this occurs naturally in the digestive tract of mammals, wetlands, swamps, and bogs. It can also be fabricated in anerobic digestion reactors, where the organic content of wastewater is broken down. The most common example of this is in municipal wastewater treatment plants where sewage is treated. Industrial wastewater from the meat and dairy, pulp and paper, brewing, and pharmaceutical industries, and municipal solid wastes can also be used.[64] In large scale anaerobic digesters, wastewater is fed continuously, where it is broken down by anaerobic bacteria to produce the biogas which is collected from the top of the reactor. Effluent water also exits and the left over biologic material called sludge is collected to be used as fertilizer.[65] A simplified example of a large scale anaerobic biogas system can be seen in Figure 14. Biogas is also produced by landfills, where it is typically vented to the atmosphere or burned off, but can be collected through underground piping networks.[64]

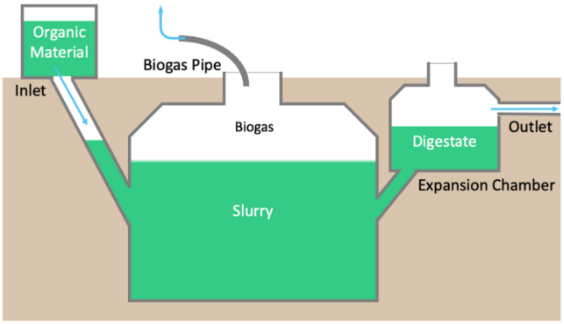


Figure 14: *Example Biogas System*

Biogas is a mixture of primarily methane and CO_2, with traces of H_2S, H_2, N_2, O_2, NH_3, and chlorine compounds. Anaerobic digesters can produce a stream of 50-70% methane with the remainder being CO_2; biogas from landfills is typically between 30-65% methane and 25-50% CO_2.[66] Biogas is typically used for heat and power generation, but the large percentage of CO_2 reduces its heating value compared to LPG. It can also be injected into natural gas pipelines after purification or compressed or liquified for use as a transportation fuel. The method chosen for removing impurities is application dependent and can include pressurized water scrubbing, pressure swing absorption, membrane permeation, and amine absorption.[66]

***Table 10:** Compositions of anaerobic digester and landfill biogas. Data obtained from Yang et al.[66]*

Compounds	Unit	AD Biogas	Landfill Biogas
CH_4	vol%	53—70	30—65
CO_2	vol%	30—50	25—47
N_2	vol%	2—6	<1—17
O_2	vol%	0—5	<1—3
H_2	vol%	NA	0—3
Higher HCs	vol%	NA	NA
H_2S	ppm	0—2000	30—500
NH_3	ppm	<100	0—5
Chlorines	mg/N m^3	<0.25	0.3—225
Siloxane	µg/g-dry	<0.08—0.5	<0.3—36

The route for producing syngas from biogas is slightly different than for natural gas. Because methane and CO_2 are present in syngas in around a 1:1.5 ratio, dry reforming is more suitable than steam methane reforming. Dry reforming subjects the biogas to high temperatures (700-900°C) to catalytically convert the mixture to syngas. However, side reactions also occur, including methane cracking, the Boudouard reaction, and the reverse water-gas shift reaction. Methane cracking and the Boudouard reaction produce coke which can deposit on the catalyst and reduce its activity. Methane cracking is more likely to occur at high temperatures because it is an endothermic reaction, whereas the Boudouard reaction is exothermic. Water produced from the RWGS must be separated from the syngas before it is used for methanol production. Nickel catalysts are generally preferred because of their low cost, but noble metal catalysts such as Pt, Pd, Rh, Ru, and Ir based catalysts reduce the occurrence of the unwanted side reactions.[66]

Dry Reforming:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247\frac{kJ}{mol}$$

Methane Cracking:

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H = 75\frac{kJ}{mol}$$

Boudouard Reaction:

$$2CO \rightarrow C + CO_2 \qquad \Delta H = -173\frac{kJ}{mol}$$

Reverse Water-Gas Shift:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H = 42\frac{kJ}{mol}$$

In 2019, methane emissions from manure management, municipal solid waste landfills, and wastewater treatment represented 9.4%, 16.4%, and 2.2% of the total U.S. methane emissions; the remainder is mostly attributed to coal and crude oil sources.[66] Collecting and utilizing biogas from these sources presents both an opportunity to reduce methane emissions, which is a far more potent GHG than CO_2, and produce fuels and goods from non-fossil feedstocks. Across the globe, biogas projects have already been installed, showing a promising outlook for biogas utilization. Of the 1250+ landfills in the US, 619 have been outfitted with biogas collection projects and approximately 480 are being considered for new projects. There are also 248 anaerobic digestion projects for livestock manure and 1,200+ wastewater treatment biogas collection projects (half of which only flare their biogas). The biogas collected from these sites is generally used for energy production or is combined with existed natural gas pipelines.[67] In a few instances, the biogas is compressed and used for transportation fuel at Bio-CNG stations, 11 of which exist in the US. A station in Fair Oaks, Indiana for example produced the Bio-CNG equivalent of 5.6 million liters of diesel in 2012, which was used for long-distance trucking.[66]

PRODUCTS

There are two primary categories of FTS processes: low-temperature Fischer Tropsch (LTFT) and high-temperature Fischer Tropsch (HTFT). A LTFT process typically runs between 200-250°C, while HTFT is operated at 330-350°C. Because the composition of the syngas remains within a very small range, FT refineries can control their product stream, also called syncrude, compositions within a narrow range. The composition of the syncrude produced is dependent on the reactor deign, operating conditions, and the catalyst used.[68] While each process produces a different syncrude, there is a general composition range for LTFT and HTFT processes.

HTFT syncrude generally has a very light hydrocarbon distribution, with a large percentage of C_2-C_4 and gasoline range molecules.[69] It is also characterized by a high olefin and oxygenate content with a small and very aromatic residue fraction. There is also a significant fraction of aqueous products including alcohols and aldehydes, carboxylic acids, and ketones.[68]

Table 11: *Syncrude compositions resulting from LTFT and HTFT processes, not including byproducts such as H_2O, H_2, CO, and CO_2. Data obtained from Klerk.*[68]

Compounds	FT Syncrude (wt %)		
	Fe-HTFT	**Fe-LTFT**	**Co-LTFT**
Gaseous Hydrocarbons			
Methane	12.7	4.3	5.6
Ethane	5.6	1.0	0.1
Ethene	4.5	1.0	1.0
Propane	11.5	3.5	2.0
Propene	1.6	0.9	0.9
Butanes	9.7	2.5	1.4
Butenes	1.4	0.8	0.8
Naphtha (C_5—C_{10})			
Alkanes	25.8	7.7	7.8
Alkenes	4.3	3.3	12.0
Aromatics	1.7	~0	~0
Oxygenates	1.6	1.4	0.2
Distillate (C_{11}—C_{22})			
Alkanes	4.8	5.7	1.1
Alkenes	0.9	13.5	20.8
Aromatics	0.8	~0	~0
Oygenates	0.5	0.3	~0
Residue/Wax Fraction			
Alkanes	1.6	0.7	~0
Alkenes	0.4	49.2	44.6
Aromatics	0.7	~0	~0
Oxygenates	0.2	~0	~0
Aqueous Products			
Alcohols	4.5	3.9	1.5
Aldehydes/Ketones	3.9	~0	~0
Carboxylic Acids	1.3	0.3	0.2

LTFT is used to produce wax and middle distillates, specifically diesel. C_{22+} waxes make up around 50% of the syncrude; this fraction is mainly paraffins.[68] The middle distillates are obtained from both distilling the product mixture and hydrocracking some of the wax fraction.[70] There is a very small fraction of aromatics and naphthenes. The small amount of oxygenates present in the syncrude are mainly alcohols and carboxylic acids. Fe catalysts generally produce more olefin compounds while Co catalysts give a higher paraffin content.[68]

When feedstocks are derived from non-fossil resources, FT is a clean synthesis method—it does not produce any of the harmful/carcinogenic byproducts resulting from petroleum refining such as nickel, lead, sulfur dioxide, and unwanted aromatics.[42] In a traditional FT refinery, the largest sources of waste are generated through poor syncrude recovery and separation.

PROCESS DESIGN

From 1955 to 1993, Sasol only used Arge tubular fixed bed reactors, in 1993 they introduced the first slurry phase reactor for FTS.[70] In this type of reactor, the slurry is made up of heavier hydrocarbons, mostly waxes, and is used to suspend the catalyst. The syngas is then bubbled through the slurry from the bottom, so it reacts to form hydrocarbons and water. The heavier hydrocarbons remain in the reactor as part of the slurry, some of which is separated from the catalyst and purged. The lighter hydrocarbons and water form a gaseous phase that exits the reactor.[70] The slurry phase is well mixed and near isothermal, and the pressure drop across the reactor is minimal, making it easier to control the reaction conditions compared to other reactor designs. Slurry-beds are the most common reactor type because of their improved mass-transfer capabilities for exothermic reactions when compared to fixed or fluidized bed reactors.[41]

The syngas H_2:CO ratio must be adjusted to a specified ratio through a combination of gas recycle loops and conversion technologies.[68] The FT process is highly exothermic, generating 165-180 kJ/ mol of CO converted. If heat is not removed from the reactor at the appropriate rate, there is the risk of catalyst deactivation and reduced product selectivity in addition to a possible runaway reaction.[71] Therefore most of the energy consumption in the reaction stage is attributed to cooling the reactor.

The separation and refining stages consume the majority of the energy in the plant. Reaction conditions are chosen to produce the largest amount of the desired product possible in just the initial reaction stage. HTFT synthesis produces syncrude with a higher straight-run gasoline (C_5-C_{10}) and light hydrocarbon (C_2-C_4) content than LTFT, reducing the amount of energy needed for separation and conversion. LTFT is often used when the desired products are diesel and other heavy fuels.[68] Many of the same conversion techniques (alkylation, hydrocracking, catalytic cracking, hydrogenation) are then used to convert syncrude to the desired product slate. Other measures such as the addition of small amounts of 1-olefins (e.g., 1-octene, 1-decene) to the original syngas feedstock have been shown to increase the selectivity of the FT reaction for jet fuel (C_8-C_{16}) to 65%.[41]

The synthesis process is energy intensive, which is counterproductive in the sense of reducing CO_2 emissions if clean, renewable energy is not used. Because the syngas production processes are collocated with the FTS plant, both processes will likely run on the same renewable energy supply in future refinery designs.

CURRENT SCALE

There are currently six FTS plants operating around the world: two in South Africa, two in Qatar, one in Malaysia, and one in Nigeria. All these plants source their syngas from coal or natural gas.

Table 12: *Information about the six FTS plants in operation.*

Name	Location	Ownership & Year	Capacity (bbl/d)
Secunda CTL	Secunda, South Africa	Sasol Sasol II—1980 Sasol III—1984	150,000
Mossel Bay GTL	Mossel Bay, South Africa	PetroSA 1992	45,000
Oryx GTL	Ras Laffan, Qatar	Sasol & Shell 2007	34,000
Pearl GTL	Ras Laffan, Qatar	Shell & Qatar Petroleum 2012	140,000 GTL products 120,000 NGL
Shell MDS	Bintulu, Malaysia	Shell 1993	16,000
Escravos GTL	Escravos, Nigeria	Chevron & NNPC 2014	33,000

Sasol operates one coal-to-liquids plant in Secunda, South Africa with a 150,000 bbl/d capacity. The Secunda CTL site contains both the Sasol II and Sasol III plants which were commissioned in 1980 and 1984. This is the only CTL plant operating today and is also largest single emitter of GHG emissions in the world. PetroSA operates another natural gas-to-liquids plant in Mossel Bay, South Africa with a 45,000 bbl/d capacity.[72,73]

The Oryx GTL plant in Ras Laffan, Qatar is a joint venture between Sasol and Shell. It began operation in 2007 at a 34,000 bbl/d capacity.[74] Shell and Qatar Petroleum co-operate the Pearl GTL plant in Ras Laffan, Qatar; it has a production capacity of 140,000 bbl/d of GTL products and 120,000 bbl/d of natural gas liquids and ethane. Full capacity operation was reached in 2012.[75]

Shell also operates the Shell MDS plant in Bintulu, Malaysia which began production in 1993. It has a capacity of 16,000 bbl/d and utilizes natural gas as a feedstock.[76,77] Chevron and the Nigerian National Petroleum Company (NNPC) co-operate the Escravos GTL plant in Escravos, Nigeria. The plant began operating in 2014 with a 33,000 bbl/d capacity; the plant is expected to expand to 120,000 bbl/d by 2024.[78] GTL plants have been proposed for sites in Lake Charles, LA; Karns City, PA; and Ashtabula, OH. Shell cancelled plans to construct a GTL plant in Louisiana in 2013.[79]

As of 2020, the water electrolysis market was worth $8.5 billion, which only made up 4% of the total hydrogen production market. The total hydrogen production market is worth $115 billion currently and is expected to grow to $155 billion by 2022. To become economically comparable to fossil fuel dependent hydrogen production, electricity costs must fall below 4 cents/kWh and energy efficiencies must be greater than 60% in a PEM water electrolyzer. This is within the realm of possibility as the average solar power plant was able to deliver electricity at 10 cents/kWh in 2017, a 73% cost decrease from 2010. Onshore wind was also available at 6 cents/kWh. In the near future, technology improvements and increased economies of scale should be able to drive these costs down more, making industrial processes run on renewable electricity preferable to fossil fuel dependent operations.[59] There are currently no large-scale projects for CO_2 reduction to CO.

DIRECT CO_2 FTS

Direct CO_2 FTS, or CO_2 hydrogenation, partnered with green hydrogen production would eliminate the need for separate CO_2 reduction to CO for syngas feedstock. The reaction still proceeds through a pseudo-syngas route, where the reverse water gas shift (RWGS) reaction converts CO_2 and H_2 to CO and water, then the FTS reaction proceeds to form hydrocarbon products.[80]

RWGS:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$
$$\Delta H = 41\frac{kJ}{mol}$$

FTS:

$$CO + 2H_2 \rightarrow (-CH_2-)_n + H_2O$$
$$\Delta H = -152\frac{kJ}{mol}$$

Overall:

$$CO_2 + 3H_2 \rightarrow (-CH_2-)_n + 2H_2O$$

These two reactions are not complementary however, as the RWGS reaction is favored at a higher temperature due to its endothermicity, and FTS is favored at lower temperatures due to its exothermicity.[81] CO_2 is also an extremely stable molecule and difficult to adsorb onto a catalyst surface, resulting in a low C/H ratio and a high probability of methane formation. Current studies are mainly focused on C_1 or short chain products (CH_3OH, CH_4, C_2—C_4 olefins) and very rarely pursue C_{5+} products.[81] High temperatures (>300°C) are often needed, but the equilibrium concentration of CO in the reactor is limited by the RWGS reaction, which in turn reduces the selectivity for higher order hydrocarbons.[81]

Fe-based catalysts are generally favored over Co, Ni, and Ru-based catalysts for direct CO_2 FTS because they have higher RWGS activity and greater selectivity for C_{2+} products. Studies have suggested that Fe catalysts can be improved with the addition of promoter metals or metal oxides such as Mn, Cu, Na, K, α-$Al_{2O}3$, or TiO_2. Recurring problems include catalyst deactivation due to the presence of water in the reactor and poor selectivity for higher-order hydrocarbons.[80] There are hundreds of research groups involved in developing catalysts for synthesis of a specific product slate, improved reactor designs, and optimum operating conditions. For example, Choi et al. developed a Cu-Fe catalyst from delafossilite-$CuFeO_2$ which gave a C_{5+} selectivity of approximately 65% and suppressed methane formation to 2-3%. It also gave an olefin-to-paraffin ratio of 7.3 in the product stream.[80] He et al. reported a process with a Co_6/MnO_x nanocatalyst with a relatively low operating temperature of 200°C. Selectivity towards normal C_{5+} hydrocarbons selectivity as high as 53.2%.[81] Specific processes for fuel and petrochemical production are therefore achievable, but industrial scales have yet to be realized. Traditional FTS technology has already been well studied, which gives direct CO_2 synthesis options a head start and makes them a desirable alternative.

METHANOL SYNTHESIS

HISTORY AND PRODUCTION FROM SYNGAS

Renewable methanol production is both a way to provide fossil-free feedstocks to petrochemical plants and transport renewable energy. Methanol is liquid at room temperature, making it easier to transport than gaseous alternative fuels such as hydrogen and methane. This presents the opportunity to distribute energy from areas with high capacities of renewable electricity to areas without renewables.[82]

The first records of methanol production come from ancient Egypt, where wood was pyrolyzed to produce embalming fluids. Commercialized production of methanol was catalyzed by the development of high-pressure catalytic processes for ammonia production in the early 20th century. In 1923, German chemists Alwin Mittasch and Matthias Pier developed the first high-pressure process for producing methanol from coal-derived syngas while working at Badische-Anilin & Soda-Fabrik (BASF).[83] The reaction conditions for this process were severe, operating at pressures above 300 atm and temperatures between 300-400°C with zinc-chromite catalyst.

Figure 18: *Alwin Mittasch* [84]

Figure 16: *Matthias Pier* [85]

Figure 15: *The first shipment of methanol produced via the BASF process.* [83]

Figure 17: *ICI's first low pressure methanol plant in Billingham, UK.* [83]

After World War II, syngas was increasingly produced with natural gas, which gave a feedstock stream with fewer sulfur impurities. This allowed for the use of more active catalysts because there was less risk of catalyst poisoning. These developments led the way for the UK's Imperial Chemical Industries (ICI) process, first patented in 1963, which operated at a much lower temperature and pressure (200-300°C & 30-120 atm) with copper, zinc, and chromium-based catalyst. The low-pressure process (currently called the Synetix process) was also much more selective for methanol production and is the basis for the processes used today. ICI began operating its first low-pressure plant in 1966 in Billingham, UK; only one high pressure plant was built after 1966, and the last remaining high-pressure plant closed in the 1980s. In the 1990s, ICI developed more active magnesium-copper-zinc-aluminum catalysts with selectivity's of >99.5%. Today, copper catalysts are used almost exclusively for methanol synthesis from syngas because of their high activity and selectivity. [64,83]

Methanol Synthesis:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H = -91\frac{kJ}{mol}$$

There are several possible reactor configurations for gas-phase processes including quench (ICI), tubular (Lurgi), and double-tube heat exchange (Mitsubishi) reactors.[86] Each reactor is designed to operate nearly isothermally by removing heat from the system or reducing the temperature of the reactants. Quench reactors inject cold streams of syngas at various places within the reactor while tubular reactors circulate water through cooling tubes, which is vaporized to absorb the heat of reaction. The most common type of reactor used in industry is the Lurgi methanol reactor, which supplies cooling water outside of a series of tubes housing the catalyst and reaction.[87] Both cases present the opportunity to recycle heat for other processes, such as the production of syngas. Single-pass conversions of the syngas is generally low, so the methanol and water is condensed from the product stream at the reactor outlet, and the separated syngas is recycled back to the reactor.[64] Air Products developed the Liquid Phase Methanol Process where a powdered catalyst is suspended in oil and the syngas is bubbled through the mixture. This process is more effective at controlling the temperature and has a higher syngas to methanol conversion per pass.[64]

Modern methanol plants generally produce a very pure product stream (99%), however there are still small amounts of impurities including water, CH_4, CO, CO_2, dimethyl ether, methyl format, acetone, alcohols, and other hydrocarbons. The type and amount of impurities varies depending on the reactor design, the type of catalyst, and the age of the catalyst. Due to the presence of both light and heavy byproducts, a series of distillation columns, including a light-ends unit, is necessary to separate any impurities. Some byproduct species may form an azeotropic mixture with methanol, which then requires pressure swing distillation.[82]

Like FTS, syngas for methanol production is typically sourced from natural gas, but can come from coal, biomass, or electrochemical routes. The choice of feedstock is generally dependent on what is available and most economical in the region of the plant. Electrochemical routes for producing syngas like those described in the FTS section will likely be preferred as renewable energy becomes readily available. Methanol from syngas is the only commercial production route used today, however there are other methods which may garner more attention in the future. These are discussed in the next sections.

OTHER METHANOL PRODUCTION PROCESSES

DIRECT METHANE TO METHANOL (DMTM)

The syngas route involves two steps which are highly energy-intensive: steam-methane reforming to produce syngas and conversion of the syngas to methanol. By directly synthesizing methanol from methane, the goal is to reduce the energy requirement and number of stages, both of which reduce the cost of production.[88] While a good idea in theory, this route is thermodynamically difficult in practice. There are four reaction pathways in methane oxidation, shown below. Methanol is the least stable product possible through methane oxidation, making the selectivity for methanol very low. Instead, methane is converted to more stable species such as CO or fully combusted to CO_2 and H_2O.

This production route has been intensely researched to identify suitable catalysts and reaction conditions, including gas or liquid-phase reaction with solid catalyst, liquid-phase reaction with soluble catalyst, and catalyst-free homogeneous routes. There has been no success in developing a commercial scale process, but progress in the field still continues.[64,88]

Methanol:

$$CH_4 + 0.5O_2 \rightarrow CH_3OH \qquad \Delta H = -30.4\frac{kcal}{mol}$$

Formaldehyde:

$$CH_4 + O_2 \rightarrow CH_2O + H_2O \qquad \Delta H = -66.0\frac{kcal}{mol}$$

Carbon Monoxide:

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \qquad \Delta H = -124.1\frac{kcal}{mol}$$

Combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H = -191.9\frac{kcal}{mol}$$

CO_2 HYDROGENATION

Since CO_2 reduction to CO is not a commercially available technology, alternative methods for captured CO_2 have been sought after. CO_2 hydrogenation is a route to methanol production that does not involve the production of syngas, but rather reacts hydrogen (preferably generated through electrolysis of water) with CO_2. CO_2 can be sourced from industrial capture (ammonia plants, power plants, cement works, and steel works) or from direct air capture (DAC). The CO_2 hydrogenation reaction (shown below) is slightly less exothermic than the traditional methanol synthesis reaction and produces water as a byproduct. This is important in terms of catalyst lifetime and process design.

CO_2 Hydrogenation:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H = -50\frac{kJ}{mol}$$

The catalyst typically used for CO_2 hydrogenation is the same as for traditional methanol synthesis (magnesium-copper-zinc-aluminum). However, the significant production of water decreases the catalyst activity and lifetime. Research has been conducted on improving catalysts for this process; PdZn alloy-based catalysts have shown promising methanol selectivity but are very expensive. Other materials such as Ni and Co, and different Cu-based catalysts have also been investigated, but there are no other catalysts that are commercially practical at this time.[89]

The production of other byproducts such as CH_4, CO, CO_2, dimethyl ether, methyl formate, acetone, alcohols, and other hydrocarbons is significantly reduced when CO_2 is used as a feedstock, therefore reducing the separation to primarily water and methanol. The high ratio of water in the product stream results in high energy expenditures for separation processes, but purification can often be achieved in a singular distillation column and gas stripping unit.[82] Other purification technologies such as membrane separation are also available.

CO_2 hydrogenation requires less heat removal than traditional methanol synthesis, so simpler, less expensive tube-cooled reactors can be used. Heat generated from the exothermic CO_2 hydrogenation reaction can be recovered and used for distillation, preheating the feed, or otherwise integrated into the production site.[89] The only disadvantage is that larger reactors are often needed because the CO_2/H_2 mixture is less reactive than syngas.[82] Large amounts of unreacted CO_2 and H_2 must be compressed and recycled back into the reactor.[89]

The first CO_2-to-methanol pilot plant was established by Mitsui Chemicals in Osaka, Japan in 2008; production began in May 2009. The pilot plant uses around 150-160 t_{CO2} yr^{-1} emitted from the company's nearby petrochemical plant to produce t_{MeOH} yr^{-1}.[90]

Carbon Recycling International (CRI) began operating the George Olah Renewable Methanol Plant in 2012 in Svartsengi, Iceland. It was the first industrial scale methanol synthesis facility to use captured CO_2 as a feedstock. The plant originally had a production capacity of 1300 t_{MeOH} yr^{-1} but was scaled up to 4000 t_{MeOH} yr^{-1} in 2016. CO_2 is captured from an adjacent geothermal power plant, and H_2 is produced via electrolysis using Iceland's renewable electricity grid. Distillation of the methanol is powered by geothermal steam.[91]

The pan-European MefCO_2 project in Niederaussem, Germany was completed in June 2019, and is a pilot plant for methanol production via CO_2 hydrogenation. The plant uses CO_2 captured from an adjacent coal-fired power plant via amine absorption and hydrogen from a PEM electrolyzer to convert 1.5+ tons of CO_2 per day and produce 1 t_{MeOH} day^{-1}. It is one of the largest flue gas CO_2-derived methanol synthesis plants in Europe.[92]

CRI is also constructing the Shunli CO_2-to-Methanol Plant in Anyang City, Henan Province, China. The plant will be commissioned in late 2021, with a production capacity of 110,000 t_{MeOH} yr^{-1}, making it the largest CO_2-to-methanol plant in the world. CO_2 and H_2 will be sourced from a coke-oven gas production facility where coal is converted to metallurgic coke for steel manufacturing. This process will recycle 160,000 t_{MeOH} yr^{-1}, helping to reduce the carbon footprint of steel production.[91]

METHANOTROPHY

Methanotrophic bacteria obtain their energy and carbon by performing a controlled partial oxidation of methane to methanol with high conversion and selectivity under ambient temperature and pressure conditions. This makes them a prime candidate for the bioproduction of methanol from methane.[64] Two types of methanotrophs exist: one depends on high methane concentrations (low affinity methanotrophs) while the other can survive on very low methane concentrations (high affinity methanotrophs). The latter has been identified but cannot be isolated, so research is primarily conducted on low affinity species. Methanotrophs use an enzyme known as methane monooxygenase (MMO) to catalyze the oxidation of methane to methanol. Industrial processes seek to utilize or mimic MMO enzymes to produce methanol from methane, either through whole cell methanotroph cultures, MMO enzyme isolates, genetically modified organisms, or synthetic MMO analogues. However challenges associated with mass transfer limitations, reactor design, overoxidation, methanol separation, and maintaining methanotroph viability limit the applicability of methanotrophy on an industrial scale.[93] Much research is being done in this field, which may prove fruitful in the future, but due to limited sources of non-fossil derived methane, methanotrophy will likely only be used in niche applications.

METHYL FORMATE

Another methanol synthesis method is via methyl formate. This route was proposed by Jens Anton Christiansen in 1919 as a way to convert CO/H_2 mixtures to methanol under milder reaction conditions.[64] Methyl formate is first produced through methanol carbonylation, which is a liquid phase reaction catalyzed by sodium or potassium methoxide.[65] This reaction chemistry is widely used for formic acid production.[64] The methyl formate is then reacted with hydrogen over a copper-based catalyst, either in the gas or liquid phase, to produce 200% of the original methanol input.[65]

Methanol Carbonylation:

$$CH_3OH + CO \rightarrow HCOOCH_3$$

Hydrogenolysis:

$$HCOOCH_3 + 2H_2 \rightarrow 2CH_3OH$$

Overall:

$$CO + 2H_2 \rightarrow CH_3OH$$

These reactions take place in a single reactor where syngas is used as a feedstock, therefore presenting the need for a combined catalyst such as CH_3ONa/Cu. Patents from Mitsui Petrochemicals, Brookhaven National Laboratory, and Shell proposed processes that operate at 80-120°C and 10-50 atm, significantly milder conditions than those used in the low-pressure Synetix process. The only drawback to this process is that any H_2O or CO_2 in the syngas stream reacts with the sodium methoxide to form byproducts which deactivate the catalyst, so these species must be removed from the gas feed.[64,65] Thus far methanol production via methyl formate is not a widely used process, but it presents a low-energy consumption route that could be compatible with renewable energy sources.

PRODUCTS FROM METHANOL

METHANOL TO OLEFINS (MTO)

Ethylene and propylene are the two largest volume chemicals produced by the petrochemical industry; the conversion of methanol to olefins could present a fossil-free pathway to these products. Today, most light olefins are produced through steam or catalytic cracking of naphtha and other gas liquids. Mobil Oil Corporation introduced the methanol-to-gasoline process in 1977, which was followed by the methanol to olefins (MTO) process by Union Carbide in 1981.[94] These first processes were developed during the energy crisis of the 1970s, much like FTS was developed during WWI oil shortages, but abandoned as the oil boom began.

The MTO reaction proceeds by first dehydrating methanol to dimethyl ether (DME), which is then further reacted to form ethylene and propylene. Small amounts of butenes, higher olefins, alkanes, and some aromatics are also produced.[64] There are four MTO technologies being used today: 1) D-MTO/D-MTO-II, 2) S-MTO, 3) MTO by UOP/Norsk Hydro, 4) MTP by Lurgi.[94]

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \rightarrow H_2C{=}CH_2 \;\&\; H_2C{=}CH_2{-}CH_3$$

The most popular catalyst is SAPO-34, a type of zeolite molecular sieve made from silicoaluminaphosphate. Zeolite catalysts are 3-D structures which have pores and channels supporting the actual catalyst element(s). The sizes of these pores control the size of the molecule formed within the zeolite structure. SAPO-34 has pore sizes of 3.8 Å, which are just right for producing primarily propylene and ethylene. SAPO-34 was preceded by ZSM-5 catalysts, an aluminosilocate zeolite with pore openings of 5.5 Å, which make it less selective towards propylene and ethylene.[64]

The MTO reaction over SAPO-34 catalyst is very exothermic (-196 kcal/kg methanol feed), thus sufficient heat removal in the reactor is important. Catalyst regeneration must also be integrated into the process as coke byproduct can also poison the catalyst. The DICP, Sinopec, and UOP/Norsk Hydro processes are run in a fluidized bed reactor, which allows for the catalyst to be cycled between the reactor and a regenerator and has excellent heat removal.[95] The Lurgi process is similar but the MTO reactor is a fixed bed. A series of separation stages including water condensation, CO_2 scrubbing, and several distillation stages produce polymer-grade ethylene and propylene, along with small amounts of methane, ethane, propane, and C_4's.[96]

MTO technology is widely used in countries with vast coal sources such as China. The largest single-train MTO plant in the world is owned by the Jiangsu Sailboat Petrochemical Company, Ltd., located in Lianyungang City in the Jiangsu Province of China. It has a production capacity of 833,000 Mt of ethylene and propylene per year and sources its syngas for methanol production from coal.[97] There are several other plants located in China with production capacities ranging from 200,000-600,000 Mt/y.[94] Additionally, a demonstration MTO plant was built by Total Petrochemicals in Feluy, Belgium in 2008.[98] Eurochem Technologies Corporation also owns an MTO plant in Lekki, Lagos State, Nigeria that further converts ethylene and propylene to polyethylene and polypropylene at a rate of 400,000 t yr^{-1}each.[99]

METHANOL TO GASOLINE (MTG)

The methanol to gasoline process was the precursor to the MTO process and was the first major development in synthetic hydrocarbon production since the advent of Fischer-Tropsch Synthesis. The primary difference between MTG and MTO is the selection of catalyst; zeolites with larger pore sizes, such as ZMS-5, produce larger hydrocarbon molecules. The reaction mechanism is the same: methanol is first dehydrated to a mixture of DME and methanol, this mixture is then converted to light olefins (propylene and ethylene) which can be further converted to higher olefins, C_3-C_6 alkanes, and C_6-C_{10} aromatics.[64] Methanol is converted to DME over an alumina catalyst at around 310-320°C and 26 bar, then the second stage of the reaction is completed at 350-400°C and atmospheric pressure.[96] A catalyst regeneration unit is also included to remove coke from the catalyst. The exact product composition can be altered by the reaction conditions and choice of catalyst, but the mixture generally lands in the range of gasoline. If heavier hydrocarbons were desired, a catalyst with larger pore sizes such as ZSM-12 could be used. Just the same as MTO, water is condensed from the mixture, CO_2 is removed, and the various species are separated through fractionation.[64]

The first MTG plant began operating in 1986 in Motunui, Taranaki, New Zealand. Methanol was produced via two ICI low-pressure units, each with a capacity of 2,200 Mt_{MeOH} per day, with natural gas from an offshore Maui field.[64] Crude methanol was then fed into the MTG unit, finally producing gasoline that needed little refining before use. The site produced around 570,000 t yr^{-1} of gasoline, supplying approximately 1/3 of New Zealand's gasoline until gasoline production was halted in 1997 and the plant began solely producing methanol.[96] A demonstration plant was also constructed in Wesseling, Germany by Mobil Oil Corporation, Union Rheinische Braunkohlen Kraftstoff AG, and Uhde GmbH; from 1982-1985 the plant produced 15.9 m^3/day of gasoline.[96] Due to low oil prices, there are no other MTG plants operating today, but these two instances show that industrial scale MTG is feasible and could be a piece to the puzzle in de-fossilizing the transportation fuel sector.

CHEMICAL PRODUCTION

Methanol is predominantly used in the production of petrochemicals. Around 35% of the methanol produced globally is catalytically oxidized to formaldehyde. The synthesis of methyl tert-butyl ether (MTBE) by reacting methanol and isobutylene consumes about 19% of global methanol supply, while acetic acid production from methanol and carbon monoxide consumes around 10%. The remaining methanol supply is split between the production of methylamines, methyl methacrylate (MMA), fuel additives, and other chemicals seen in Figure 19.[100]

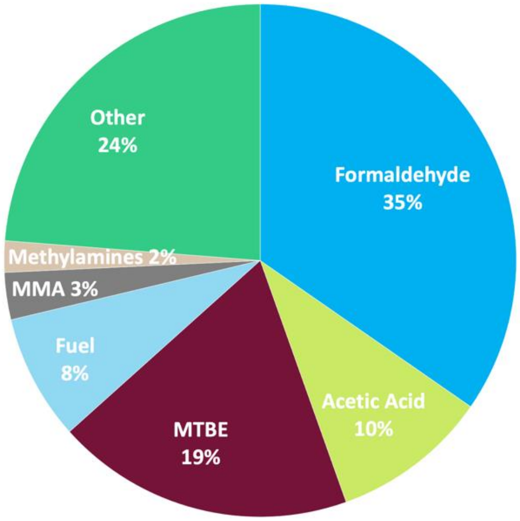


Figure 19: *Chemical products from methanol.* [100]

In the 1970s, Monsanto introduced a process for producing acetic acid from methanol instead of ethylene, which has since become the primary process used today. Other processes using ethylene as a feedstock, including acetaldehyde and ethanol, may be able to convert to methanol. Progress has been made in obtaining ethylene glycol from dimethyl ether, a secondary product of methanol. Other large volume chemicals produced from ethylene and propylene, including styrene and ethylbenzene, may also be manufactured from methanol in the future.[64]

CURRENT SCALE OF METHANOL SYNTHESIS

There are over 90 methanol synthesis plants around the globe with a combined production capacity of approximately 110 Mt_{MeOH} yr^{-1}. China produces over 50% of the world's methanol almost exclusively from coal feedstock and consumes more methanol than any other country, primarily for olefin and petrochemical production, even causing the country to import 5 Mt_{MeOH} in 2015. The U.S. is one of the world's largest importers of methanol due to its lack of production capacity, and also imported 5 Mt_{MeOH} in 2015, primarily from the Middle East and Latin America.[101]

In 2019 and 2020, three new methanol plants were brought online in the U.S., increasing total U.S. methanol capacity from 6.1 to 9.4 Mt_{MeOH} yr^{-1}. These facilities are almost exclusively located in the Gulf Coast region, seen in Figure 20, which is both connected to the Permian Basin's natural gas pipelines and close to overseas shipping ports allowing the U.S. to export methanol to China.[36]

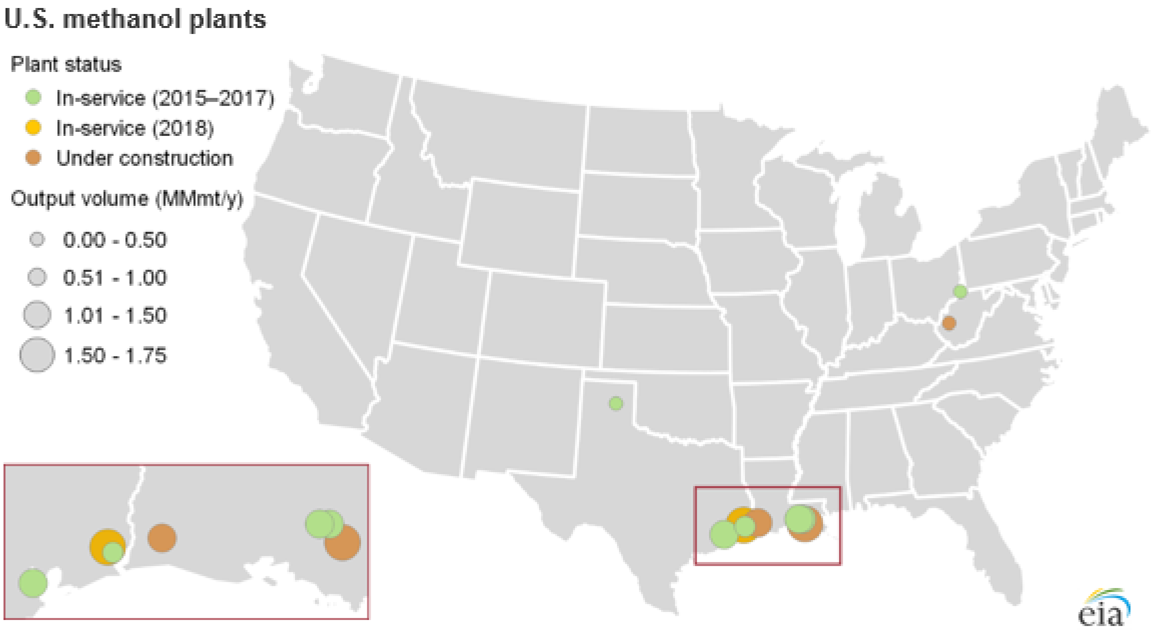


***Figure 20:** Locations of U.S. methanol plants in 2018.*[36]

Trinidad houses the largest singular methanol production sites in the world. The Atlas plant is jointly owned by Methanex Co. and BP Oil was commissioned in 2004 at Point Lisas, Trinidad. The plant has a production capacity of 1.7 Mt_{MeOH} yr^{-1}, which is mainly exported to Europe and North America. Approximately 164 million ft^3/day of natural gas is fed into the facility from BP Oil fields located on the eastern coast of Trinidad. The Atlas plant is collocated with Methanex Co.'s Titan methanol plant, which has a production capacity of 850,000 t_{MeOH} yr^{-1}.[102]

In 2005, the M5000 methanol plant, also located in Point Lisas, Trinidad, overtook the Atlas plant as the largest methanol production facility in the world with a capacity of 1.9 Mt_{MeOH} yr^{-1}. The M5000 plant is owned by Methanol Holdings (Trinidad) Limited, which operates 4 additional methanol synthesis plants in the same industrial park; the company produces a total of 4 Mt_{MeOH} yr^{-1}, making it one of the largest methanol producers in the world.[103]

In 2020, Ningxia Baofeng Energy Group Co. Ltd. Commissioned the world's largest single-train (meaning only one set of equipment instead of multiple parallel sets) in Yinchuan City, Ningxia Province, China, with a 600,000 t_{MeOH} yr^{-1} capacity produced from coal-derived syngas.[104]

ETHYLENE AND PROPYLENE SYNTHESIS

STEAM CRACKING AND FLUID CATALYTIC CRACKING

Ethylene ($C_2^=$) and propylene ($C_3^=$) are homologues of one another and are two of the largest-volume petrochemicals produced globally. Ethylene was the first to emerge as a large-volume intermediate when oil and chemical companies began separating it from refinery waste gases and producing it from ethane to replace acetylene in many processes.[105] Because propylene is a byproduct of ethylene production, it too became a widely used petrochemical intermediate.[106]

Today's commercial production of ethylene is based on thermal cracking of heavier petroleum feeds with steam, also called steam cracking. Feedstocks are typically ethane or naphtha, but can also include propane, butane, and gas oil. In the process, the petroleum stream is mixed with steam and heated to 500-680°C depending on the feedstock composition. The mixture then enters a fired tubular reactor where it is further heated to 750-875°C; the mixture only spends 0.1-0.5 seconds in the reactor, during which time the heavier molecules are cracked into ethylene and other olefins/diolefins such as propylene. Within 0.02-0.1 seconds, the product stream temperature is brought down to 550-650°C to prevent further reactions. Then the mixture is separated into major products; the ratio of ethylene to propylene produced can be altered by changing the cracking conditions and the feedstock used. This reaction is very endothermic, and thus requires large energy inputs even when heat is recovered effectively in the process.[105,106]

Propylene is also recovered from the off gases of other refinery operations such as fluid-catalytic cracking (FCC). FCC's are used to break down heavy gas oils into gasoline and light gas oil, but in the process generates lighter byproducts including propylene.[106] Steam cracking accounts for around 60-65% of global propylene production, FCC produces around 30%, and the remainder comes from metathesis or propane dehydrogenation.[107]

PROPANE DEHYDROGENATION

Propane dehydrogenation was designed to make use of natural gas feedstocks through the catalytic removal of hydrogen atoms from propane to convert it to propylene. Side reactions can include cracking propane to methane and ethylene, hydrogenolysis to ethane and methane, and coke production; the goal of catalyst and process design is to limit these side reactions to effectively produce propylene.[108]

Propane Dehydrogenation:

$$C_3H_8 \leftrightarrow C_3H_6 + H_2 \qquad \Delta H = 124.3\frac{kJ}{mol}$$

There are many different process technologies available for propane dehydrogenation, but the most widely used are the Catofin and Oleflex processes. The Catofin process was developed by the ABB Lummus company. It uses a CrO_x-based catalyst (K(Na)-CrO_x/Al_2O_3) in a fixed-bed gas phase reactor with a pressure and temperature of 0.5 bar and 650°C. Honeywell UOP commercialized the Oleflex process in 1990. The process operates at 700°C and 3 bar in a moving bed reactor with a Pt-based catalyst (K(Na)-Pt-Sn/Al_2O_3). Both processes have a propylene selectivity of around 87%.[108]

The reaction is very endothermic and requires large energy inputs. Much research is being done on catalyst and process improvements to both increase propylene selectivity and improve energy consumption. As recently as 2016, Dow Chemical Company announced their new fluidized catalytic dehydrogenation (FCDh) technology, which has a 93% propylene selectivity, 20% capital savings, and reduced energy demand per pound of propylene produced.[108]

METATHESIS

Olefin metathesis, also called Olefins Conversion Technology (OCT), is a process that converts ethylene and butene to propylene. Two reactions occur simultaneously: any 1-butene is isomerized to 2-butene, which is consumed in the metathesis reaction that converts 2-butene and ethylene to propylene.[109]

Isomerization:

$$CH_2{=}CHCH_2CH_3 \rightarrow CH_3CH{=}CHCH_3$$

Metathesis:

$$CH_2{=}CH_2 + CH_3CH{=}CHCH_3 \rightarrow 2CH_2{=}CHCH_3$$

This reaction takes place over a rhenium- and molybdenum-containing catalyst in a fluidized fixed-bed reactor. Around 60% of the ethylene is converted per pass with a greater than 90% selectivity for propylene; any unreacted ethylene and butene is separated in recovery towers and recycled to the reactor. OCT presents a way to recover and convert dilute streams of ethylene from refinery off gas that would otherwise be used for fuel gas. It can also be used to increase the ratio of propylene to ethylene from steam cracking operations.[109]

OCT was originally developed by Phillips Petroleum and was called the Phillips Triolefin Process. ABB Lummus Global acquired the technology in 1996. The first OCT propylene production unit was commissioned by Lyondell Petrochemical in the USA in 1985, but has since closed.[109] In 2003, ABB Lummus Global also constructed an OCT unit in Port Arthur, Texas as part of BASF Fina's olefin plant.[110]

NOVEL PROCESSES

OXIDATIVE COUPLING OF METHANE (OCM) TO ETHYLENE

Work on the oxidative coupling of methane began in the 1980s, and was originally sought after as a way to produce ethylene directly from methane sourced from natural gas.[111] The OCM reaction begins by contacting a methane molecule with an oxide catalyst surface to remove a hydrogen and form a methyl radical (CH_3*). Two methyl radicals then couple to form an ethane molecule which is then dehydrogenated to form the ethylene molecule. The overall reaction is shown below and illustrated in Figure 21.

OCM:

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \qquad \Delta H = -280\frac{kJ}{mol}$$

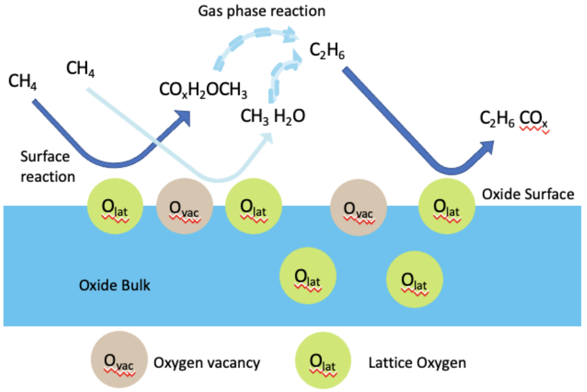


Figure 21: *The oxidative coupling methane (OCM) reaction on the metal oxide catalyst surface.* [111]

While a desirable process in theory, there have been issues with improving the process catalytically, causing OCM to be a well-studied research topic but not an industrially applied process. The catalyst works by replenishing empty oxygen sites on the surface with oxygen from the bulk of the catalyst. This happens very slowly, which limits the activity of the catalyst and allows gaseous phase oxygen species to attach to the catalyst surface and later form CO and CO_2. Additionally, the catalyst properties necessary to form the methyl radical also activate the ethane intermediate to form CO and CO_2 instead. Perhaps the biggest setback is that full combustion of the methane stream is very likely due to the high temperature required for the OCM reaction (around 800°C).[112] To summarize, OCM catalysts must be stable at high temperatures, offer high amounts of oxygen, and replenish oxygen quickly enough to minimize CO and CO_2 side reactions.[111]

The Na_2WO_4/SiO_2 system is considered the best OCM catalyst at the moment because of its relatively high C_2 yield and long-term stability, but it still needs to be further perfected before it can be considered for industrial use.[112] Research into OCM catalysts will no doubt continue as we move away from crude oil petrochemical production. While ultimately, we would also like the to avoid the use of natural gas, OCM may be a bridge technology and could be further utilized with biogas or FTS sources of methane.

ELECTROCHEMICAL REDUCTION OF CO_2 TO OLEFINS

The electrochemical reduction of CO_2 to ethylene coupled with renewable energy sources could become a pathway to completely fossil-free and possibly carbon-negative petrochemical feedstocks. In this process, CO_2 would be selectively converted to ethylene at the cathode while H_2O would be converted to O_2 at the anode. At a mechanistic level, electrons are delivered to the CO_2 molecule, which is then protonated to form a format (COOH) radical; two format radicals are then reductively coupled to form various intermediates which eventually result in ethylene.[113] The overall process is shown by the following reactions and illustrated in Figure 22:

Cathode:

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$$

Anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Overall:

$$2CO_2 + 2H_2O \rightarrow C_2H_4 + 3O_2$$

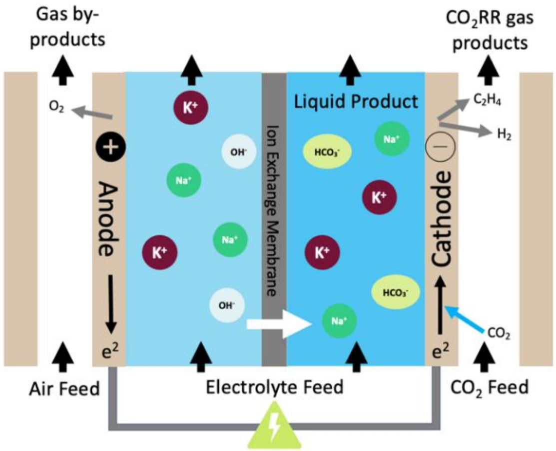


Figure 22: *Using electrochemical reduction of CO_2 to produce olefins.* [113]

Acidic solution is needed at the cathode to provide the necessary protons, but CO_2 is very insoluble in aqueous solutions. This presents a problem as transport of CO_2 from the bulk solution to the surface limits how quickly the reaction can occur. To overcome this issue, partially submerged cathodes are used to create a gas-solution-solid interface, so CO_2 does not have to be transported through the solution but is instead readily available in the gas phase. This keeps the concentration of both CO_2 and protons high at the reaction interface so it can proceed at a reasonable rate. The low pH of the acidic solution also accelerates the formation of H_2 from the hydrogen protons, which would deplete the protons in solution necessary for the reaction. This is alleviated by the addition of halide ions which adsorb onto the cathode and suppress the production of H_2.[113]

There is a very large energy expenditure needed to ionize three very stable molecules—the energy required to convert one mole of CO_2 is 666 kJ/mol-CO_2, which means each mole of ethylene requires 1332 kJ/mol-C_2H_4.[113] There are many research groups working to improve and scale up this technology through optimizing the reactor conditions and design, electrode materials, and reaction mechanism. There are currently no industrial scale applications of this technology, but with further progress in the field we may soon be able to produce ethylene directly from CO_2 and H_2O.

ADVANCES IN MTO

Electrochemical reduction of CO_2 is just one approach in converting CO_2 to olefins—work has also been done in advancing MTO by combining it directly with CO_2 hydrogenation to methanol. For example, Gao et al. designed a bifunctional catalyst system of indium-zirconium composite oxides and SAPO-34 zeolites for conversion of CO_2 to lower olefins ($C_2^{=}$—$C_4^{=}$). They were able to achieve 80% $C_2^{=}$—$C_4^{=}$ selectivity with only 4% methane selectivity and a CO_2 conversion of 35%. Reaction conditions were also relatively mild at 400°C and 3.0 MPa and their catalysts showed no deactivation over an extended run time of 150 hr. The CO_2 was hydrogenated to methanol with the oxide catalyst, then coupled within the pores of the SAPO-34 catalyst, essentially carrying out methanol production from CO_2 and MTO simultaneously.[114]

CYANOBACTERIA

Cell factories of cyanobacteria could present a way to convert solar energy to ethylene. Cyanobacteria are photosynthetic microorganisms which convert CO_2 and water to biomass and energy-rich organic compounds. Plants naturally synthesize ethylene and use it as a signal molecule to regulate growth and development; some can be genetically or metabolically engineered to hold synthetic pathways that target specific products such as ethylene.[115,116]

The contents of the reactor are mixed by the gas flow carrying the CO_2 to continuously expose the cyanobacteria to the light source; the ethylene produced is also removed in the gas phase, then purified.[116] Red light LED illumination generated from renewable energy sources is used instead of direct sunlight because it allows the process to run continuously and reduces the overall scale of the photobioreactor.[116] However there is a trade-off between efficiency losses during the electricity-generation and light-generation stages and increased growth of the cyanobacteria. In a study by Zavřel et al. engineered *Synechocystis* sp. PCC 6803 cyanobacteria were used to produce ethylene. Assuming conversion efficiencies of 20% and 50% for solar-to-electricity and electricity-to-light generation, only 0.36% of the original solar energy was converted to ethylene product.[116] A study by Vajravel et al. showed that when *Synechocystis* sp. PCC 6803 cells were entrapped in a thin biofilm later, the solar-to-product efficiency was increased to 1.54%, and production was viable for up to 38 days.[115]

The cost of ethylene production via cyanobacteria is around \$15/kg, whereas the global price of ethylene is around \$1.06/kg.[116] Reducing this gap is essential to making this technology economically feasible. These processes are currently at the proof-of-principle stage, and current efforts are being directed at increasing yields and reaction rates, upscaling production, and designing photobioreactors of various configurations. The greatest challenges are designing space-efficient reactors and increasing energy conversion efficiencies. While much needs to be done to reach industrial scale, cyanobacteria present a CO_2 to ethylene route that is completely dependent on biological catalysis and could be a promising field in the near future.

AMMONIA SYNTHESIS

HABER-BOSCH PROCESS

The Haber-Bosch process was developed in response to dwindling fixed-nitrogen reserves for agricultural fertilizers and explosives in the late 17th and early 18th century. At this time, ammonium sulfate was obtained as a byproduct of the destructive distillation of coal, and sodium nitrate was also exported from Chile to Europe. These two non-renewable sources made up the global fixed-nitrogen supply but were not enough to sustain growing populations and industrial expansion.

Ammonia Synthesis:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta H = -92.4\frac{kJ}{mol}$$

Molecular nitrogen is too inert to react with hydrogen at moderate temperatures, but at high temperatures ammonia decomposes, which is why a catalyst is required to complete the reaction. Fritz Haber, a German chemist, began working on the thermodynamic equilibria between ammonia, hydrogen, and nitrogen in 1904. He initially achieved the synthesis of ammonia, but even under severe reactor conditions of 600°C and 200 bar, only saw an equilibrium concentration of 8% ammonia. By 1909 Haber and his assistant, a British chemist named Robert Le Rossignol, were finally able to achieve an acceptable conversion rate using an osmium catalyst at 175 bar and 550°C. Haber received the Nobel Prize in 1919 for his work.[117]

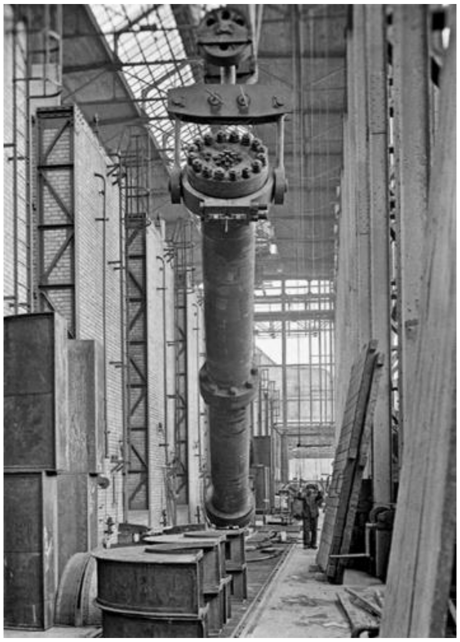


Figure 23: *The first reactor at the Oppau, Germany plant in 1913.*[118]

Two German chemists/engineers from BASF, Carl Bosch and Alwin Mittasch (who also developed high-pressure methanol synthesis) then became involved in the development of high-pressure technology and catalysts for the process. Mittasch and his group tested over 2,500 catalysts, finally arriving at an iron catalyst promoted by alumina and potassium in 1910. The high temperature and pressure conditions combined with the presence of hydrogen corroded the carbon steel reactor, giving it a lifetime of only a few days. By March 1911, Bosch designed a double-tube reactor, where hydrogen diffused from a low-carbon iron tube filled with catalyst to an outer pressure-bearing steel tube through small holes, which prevented corrosion of the steel reactor. In 1931, he received the Nobel Prize for his work on high-pressure technology.[117]

Figure 24: *Fritz Haber*[119]

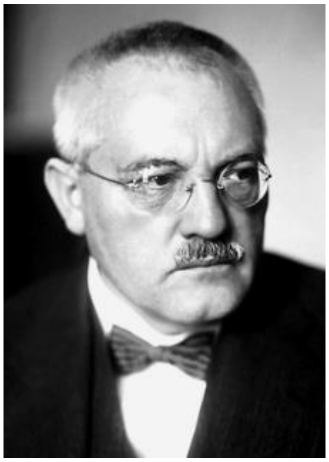
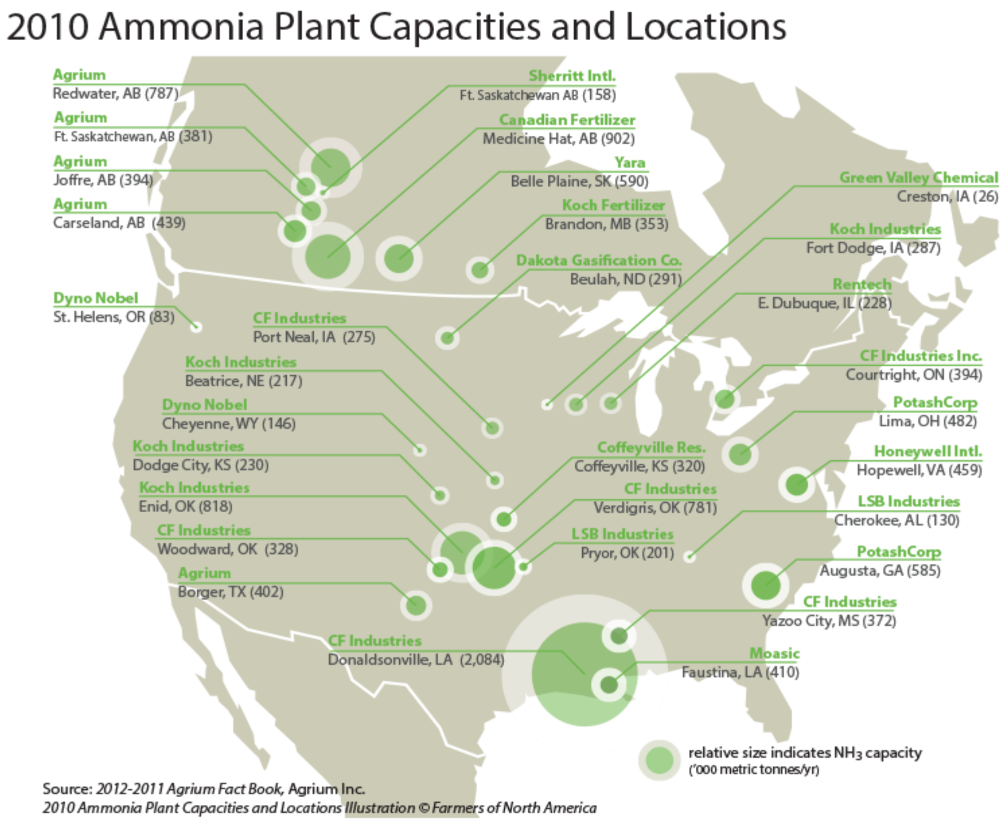


Figure 25: *Carl Bosch*[120]

Figure 26: *Robert Le Rossingnol*[121]



Source: *2012-2011 Agrium Fact Book*, Agrium Inc.
2010 Ammonia Plant Capacities and Locations Illustration © Farmers of North America

Figure 27: *Map and relative scale of North American ammonia plants as of 2010.* [122]

BASF built the first industrial scale ammonia synthesis plant in Oppau, Germany in 1913 using the combined Haber-Bosch technology. Initially it produced 3-5 t_{NH3} day^{-1} but by 1917 it had been expanded to generate 230 Mt_{NH3}/day.[117] In 1921 4,500 tons of a mixture of ammonium sulfate and ammonium nitrate fertilizer exploded and destroyed the plant.[123]

Modern ammonia plants produce more than 3,000 t_{NH3} day^{-1} in one production line. Hydrogen is sourced from either natural gas or coal, and nitrogen is separated from ambient air. Today's reactors are made of hydrogen-resistant chromium-molybdenum steels which allow for single wall designs. Besides the reactor, gas compression and preheating stages, several recycle loops, and product cooling stages to liquidate the ammonia are also part of the process. KBR (Kellogg Brown Root), Haldor Topsøe, and ThyssenKrupp Industrial Solutions (TKIS) technologies currently dominate the market. These processes integrate heat recovery, enhanced conversion schemes, improved catalysts, hydrogen recover systems, and lower energy consumption equipment to make the process as efficient as possible.[124] In 2020, 14 Mt_{NH3} were produced in the US at a 35 different facilities. The largest single-train facility in the world is currently under construction in Karratha, Western Australia. Perdaman Chemicals and Fertilisers will use Haldor Topsøe's technology in its $4 billion plant to produce 3,500 t_{NH3} day^{-1}.[125] Because of its high temperature/pressure reaction conditions and multiple gas separation processes, and the sheer amount of ammonia produced worldwide, the Haber-Bosch process accounts for around 2% of global energy use and 1.44% of global CO_2 emissions.[5,6] Thus ammonia synthesis with renewable energy sources stands to have a large impact on carbon emissions from the petrochemical industry.

GREEN HYDROGEN

An intermediate step to achieving more sustainable ammonia production is using green hydrogen, which was discussed in the FTS section. This would allow the world's ammonia production facilities to simply convert to a new H_2 source and keep existing plants online until they are decommissioned. While installing electrolyzers and renewable energy hookups is expensive, they can further be connected to completely green NH_3 synthesis processes should they become available in the future. Thus, no existing equipment would be rendered obsolete as we transition to more sustainable production methods.

Multiple projects are already underway in Australia, New Zealand, Spain, and the U.S. In February 2018, the state of

South Australia awarded AU$12 million in grants and loans to a renewable ammonia project.[126]

Yara, one of the world's largest ammonia producer, operates an 850,000 t_{NH3} y^{-1} facility in Western Australia's Pilbara Desert.[126] In collaboration with ENGIE, a global energy company, Yara developed a 4-phase sustainability plan to implement green hydrogen production in its existing Haber-Bosch process. In 2019, a pilot plant was started next to the existing plant, producing H_2 via water electrolysis with a 2.5-megawatt solar array and a bank of electrolyzers. This feasibility study, has a budget of AUD$3.6 million with the goal of determining the scale of solar power generation and electrolyzers needed to produce green H_2.[127] Yara plans to complete Phase 0 by 2022, where green H_2 will make up 3% of the plant's H_2 consumption. Phase 1 will increase this to 20%, Phase 2 will see the construction of a dedicated green ammonia plant and a 20% increase in green hydrogen production, all between 2025-2030. Yara hopes to complete Phase 3 by 2030, scaling up to reach a total green NH_3 production capacity of 720,000 t_{NH3} y^{-1} in addition to the current capacity. In 2020, the project received AU$995,000 in aid from ARENA.[127]

A similar project is underway in New Zealand with Balance-Agri Nutrients and Hiringa Energy. In 2019, they announced that 16 MW of wind-energy would be used to produce green H_2 and decarbonize 2% of the Kapuni ammonia-urea plant capacity by 2021. The Provincial Growth Fund provided NZ$19.9 million in 2020 for the project.[127]

Spanish power company Fertiberia SA and ammonia fertilizer producer Iberdrola SA plan to build an 800 MW green H_2 plant, the largest such project in Europe, by 2027. The project has a total investment budget of €1.8 billion and has the potential to decarbonize 25% of Spain's hydrogen production.[128]

Lastly, CF Industries, one of the largest ammonia producers in the world, committed to reaching net-zero emissions by 2050, beginning with building a 20,000 t_{NH3} y^{-1} plant in Donaldsonville, Louisiana. The plant will be situated in CF Industries' 4 Mt_{NH3} yr^{-1} ammonia plant; by 2030 they hope to reduce the overall CO_2 emissions from the complex by 25%.[129] These are all exciting examples of how the CO_2 intensity of the petrochemical industry can be reduced, and will likely be a catalyst for further progress towards sustainability in the ammonia industry in the years to come.

ELECTROCHEMICAL SYNTHESIS

Electrochemical ammonia synthesis is a desirable alternative to the traditional Haber-Bosch process because it can occur at atmospheric pressure and lower temperatures. With a lower energy demand, renewable energy sources can be applied, reducing the carbon footprint of ammonia production drastically. The rate determining step in ammonia synthesis is breaking the incredibly strong $N \equiv N$ bond in molecular nitrogen so atomic N can be adsorbed and reacted on the catalyst. Plants already take an electrochemical approach when fixing atmospheric nitrogen, using energy from the sun and nitrogenase metallo-enzymes as a catalyst.[6] Like most electrochemical processes, the biggest challenge is developing a catalyst with an acceptable NH_3 production rate and selectivity. The efficiency of electrochemical ammonia synthesis is impacted by the configuration of the reactor, reaction conditions (temperature, pressure, pH, electrolyte, etc.), the applied voltage, and choice of catalyst.[130]

There are two types of electrochemical synthesis being studied: one is an adaptation of the Haber-Bosch process where methane is used as a hydrogen source, and the other relies on water electrolysis.

Kyriakou et al. recently proposed an electrochemical Haber-Bosch process illustrated in Figure 28. On one side of the process, a protonic ceramic membrane reactor (PCMR) powered with renewables is used. Hydrogen is generated from methane over an Ni-composite anode at around 550°C. It is then purified through a $BaZrO_3$-based electrolyte and CO_2 and H_2O byproducts leave the reactor. Ammonia synthesis then occurs on a VN-Fe cathode at around 550°C. NH_3 is condensed from the product stream, and residual H_2 is directed to a protonic ceramic fuel cell (PCFC) operating at 600°C to generate electricity to purify the N_2 used in the PCMR.[6]

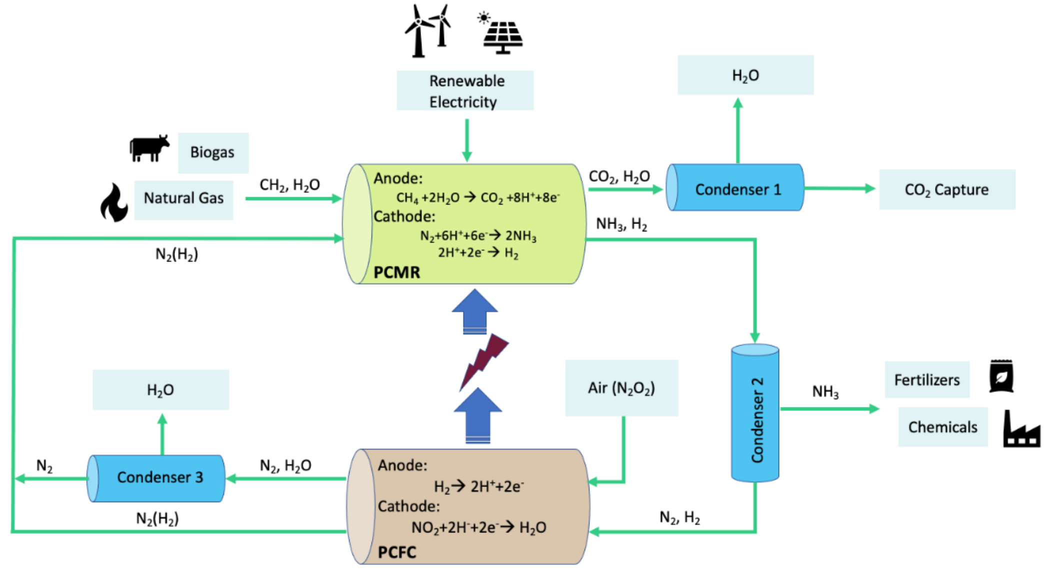


Figure 28: *Electrochemical synthesis of ammonia using biogas or natural gas with renewable electricity.* [6]

This process eliminates the need for a water gas shift reactor typically used in the Haber-Bosch process because it directly converts methane to CO_2 and reduces energy consumption by utilizing the excess H_2 to purify the N_2 stream. It could also be redesigned to eliminate the use of methane, instead opting for water electrolysis, but at the cost of increased energy consumption. Kyriakou et al. estimated the energy consumption for methane route was 289.5 kJ/mol NH_3, while the water electrolysis route was 1,158 kJ/mol NH_3.

Kong et al. developed an anion exchange membrane (AEM) using γ-Fe_2O_3 nanoparticles as a catalyst. An AEM transfers OH^- anions instead of H^+ protons across the membrane. They tested this set-up with both aqueous KOH solution saturated with N_2 and gaseous N_2 at the γ-Fe_2O_3 anode. The group concluded that mass transfer of N_2 was limited in the aqueous solution, but selectivity towards NH_3 was decreased in the gas phase variation, and that further research into catalyst activity, reaction temperature, and acidity were needed.[5] The overall process is shown by the following reactions and illustrated in Figure 29:

Cathode:

$$N_2 + 6H_2O + 6e^- \rightarrow 2NH_3 + 6OH^-$$

Anode:

$$6OH^- + 6H^+ \rightarrow 3H_2O + 1.5O_2$$

Overall:

$$N_2 + 3H_2O \rightarrow 2NH_3 + 1.5O_2$$

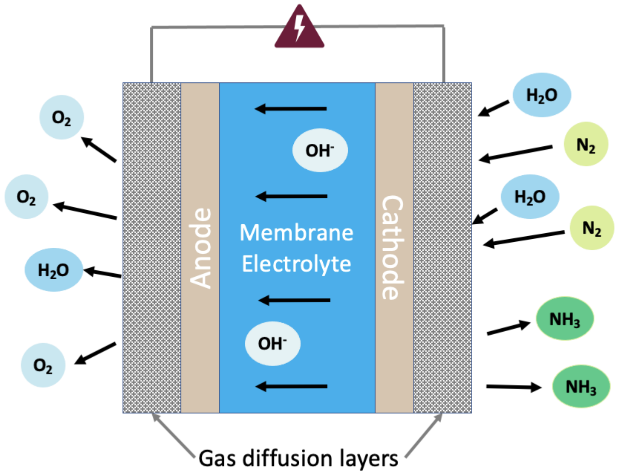


Figure 29: *An anion exchange membrane (AEM) to produce ammonia from nitrogen gas and water.* [5]

To improve scalability, research groups are also trying to design reactors more similar to PEM-type fuel cells, with an anode and cathode on opposite sides of the proton-conductive membrane. One side of the reactor contains a dilute aqueous solution for water electrolysis to generate the H^+ protons and electrons, which are used on the gas-phase side where N_2 is electrocatalytically converted to NH_3. NH_3 exits the reactor in the gas phase, then is condensed and collected.[130] Chen et al. completed a thorough investigation of a PEM-type reactor with an Fe_2O_3-carbon nanotube catalyst. They found that the choice of electrolyte generally impacts selectivity for NH_3 while the choice of catalyst and applied voltage determined the rate. They also found that NH_3 crossover from the cathode (gas-phase) side to the anode (liquid-phase) side of the reactor must be inhibited, as it consumes the NH_3 produced and decreases the NH_3 collection rate.[130]

Bicer et al. designed a photoelectrochemical reactor, where solar energy was used to produce a hydrogen supply. NH_3 synthesis occurred in an NaOH-KOH molten salt mixture at 170°C, where a nano-Fe_3O_4 catalyst is present. N_2 is dissociated to N^{3-} at nickel cathode, then combined with H_2 at the anode to form NH_3. A gaseous mixture of the reactants and NH_3 exits the reactor whereupon the NH_3 is separated.[131]

These are just a few examples of research pursuits, but most groups conclude that efficient electrochemical NH_3 synthesis is not yet available on an industrial scale mainly due to the slow rate of the N_2 dissociation step.[5] The hydrogen evolution reaction also competes with NH_3 synthesis, decreasing efficiency and selectivity. Many groups are interested in developing catalysts that contain abundant materials such as iron instead of noble metals to avoid the use of scarce and expensive raw materials.[130] Other primary goals include improving reactor design and optimizing reaction conditions to improve the rate of NH_3 production and reduce energy requirements. Like most new processes, there is much work to be done to reach the point of industrial scalability.

BTX AROMATICS SYNTHESIS

DIRECT CO_2 TO BTX SYNTHESIS

BTX aromatics are produced directly from naphtha hydrotreating and catalytic reforming stages in a refinery. The most desirable feedstock to sustainable BTX synthesis is CO_2 as it would provide a utilization scheme for captured carbon and avoid the use of other resources such as biomass. The reaction schemes being studied in this area are essentially a modified Fischer-Tropsch synthesis, which requires a bifunctional catalyst to convert CO_2 to CO to olefins through FTS, and a zeolite catalyst to convert olefins to aromatics.

Cui et al. reported considerable success using a catalyst system of sodium-modified spinel oxide $ZnFeO_x$, which provided Fe_3O_4 sites for CO_2-to-CO conversion and Fe_5C_2 sites for CO-to-olefins; HZSM-5 zeolites were then used to aromatize the olefins. They reported a 75.6% aromatics selectivity and 41.2% CO_2 conversion when operated at 320°C, and an overall selectivity towards CH_4 and CO of less than 20%. Suppressing the formation of these undesired byproducts means that most of the CO_2 is converted to either olefins or aromatics both of which are highly sought after. They also reported up to a 75% selectivity for para-xylene out of the total xylenes produced[132]

Xu et al. conducted a similar study with Fe_3O_4 catalyst and HZSM-5 zeolites. They saw a 94% selectivity for aromatics, and when the HZSM-5 was coated in SiO_2, they were able to increase specifically the selectivity for para-xylene from 25% to 70% of total xylenes.[133] Wang et al. prepared a Na-Fe@C catalyst by pyrolyzing Fe-based metal organic frameworks. When used in conjunction with HZSM-5 zeolites, they too were able to achieve high aromatics selectivity of 50.2% and a 33.3% CO_2 conversion.[134]

Each of these groups have shown that direct CO_2 to BTX synthesis is possible, but there has not yet been a demonstration of the technology on a larger scale. Because FTS has already been applied on large scale, it is likely that this process could be modeled after existing facilities. All that is left to solidify is optimal catalyst combinations and reaction conditions that ensure an appropriate rate of reaction and selectivity/yield of aromatics.

THERMOCHEMICAL PRODUCTION FROM BIOMASS

Pyrolysis is the thermal decomposition of biomass in an oxygen-free environment.[135] Fast pyrolysis produces a mixture of small oxygenates by rapidly heating biomass (>500°C/s) to temperatures between 350-650°C at atmospheric pressure, followed by rapid cooling (1-2 s).[135,136] The mixture of oxygenates, also called bio-oil, has a low-heating value, poor stability, and high viscosity and therefore is not a desirable alternative fuel.[135] However through catalytic cracking, it can be converted to a mixture of volatile aromatics, CO, CO_2, H_2O, and coke. Both steps can occur simultaneously in the same reactor, and with short residence times.[136]

There are several challenges associated with catalyst deactivation from coke formation, and undesirable yields and selectivity towards BTX aromatics.[136] The key to improving these aspects of the reaction lies in the characteristic of the catalyst and the reaction conditions. Brønsted acid sites must be present for catalytic cracking, and pore size/structure determine the products produced. Zeolite catalysts are frequently used because the pore structure and active sites can be tuned to control product selectivity; zeolites doped with metals can also promote high yields of aromatics. HZSM-5 catalysts have been investigated heavily, and have shown promising results.[135]

Selectivity and yield can also be improved by optimizing heating rates, catalyst to feed ratio, and reaction time.[136] The composition of the feedstock bio-oil can also be refined to remove less reactive compounds which produce excessive coke (e.g. 2-methoxyphenol and acetaldehyde). The addition of hydrogen-donor species to the feedstock can be used to further reduce coke formation on the catalyst.[135]

Biomass feedstocks can come from many sources, including agricultural, industrial, and household waste. Growing crops specifically for fuel/chemical production, like corn and soybeans for ethanol, is highly controversial because they occupy arable land that would otherwise be used for food production. These crops also require nitrogen fertilizers, which currently have a high carbon footprint and can cause other environmental harm. Some strains of microalgae are of great interest because of their ability to deliver bio-oil yields per hectare that are 60 times greater than other crops. Pyrolysis of microalgae yields not only hydrocarbon species but also ammonia that can be recycled as fertilizer.[137]

Thermochemical production of BTX from biomass is a promising route to sustainable chemical feedstocks that could utilize existing refinery equipment to reduce capital costs.[135] In fact, the field is already progressing. A Dutch company called BioBTX is planning to build a pilot plant for biomass-based aromatics in 2023, using their Integrated Cascading Catalytic Pyrolysis (ICCP) process. In showcasing their process, BioBTX was able to create the world's first 100% bio-based PET for cosmetics container lids.[138,139]

However, there are CO_2 emissions associated with land usage and fertilizer application for biomass growth which must be accounted for. If this process could be fed entirely with waste biomass from different sectors, it could be a way of repurposing materials that would otherwise end up in a landfill into value-added chemicals.

BIOLOGICAL PRODUCTION FROM BIOMASS

The transformation of isobutyraldehyde (IBA) or other oxygen containing compounds, obtained through the microbial fermentation of biomass, into aromatics via a zeolite catalysts is one possible approach to fossil-free aromatics production.[140] IBA can be sustainably produced from biomass by *Escherichia coli* cell factories, or produced photosynthetically from CO_2 with a genetically engineered strain of *Synechococcus elangatus*.[141,142]

Deischter et al. developed an IBA conversion to aromatics process using a continuous, fixed bed tubular reactor tested with several zeolite catalysts doped with SiO_2/Al_2O_3 at varying ratios. They were able to obtain up to a 93% aromatic yield in the product slate, with a maximum BTX yield of 79% when HZSM-5(30) catalyst was used. They determined that HZSM-5 catalysts gave superior results but were deactivated due to coke deposits. Regenerating the catalyst through calcination allowed for multiple uses with minor declines in BTX yields.[140]

The processes to produce isobutyraldehyde and BTX aromatics have been testing in long term stability but not in the feasibility large scale reaction which would be needed to replace the traditional fossil fuel production.

ANALYSIS OF ALTERNATIVES

The previous section discussed many petrochemical production methods including fossil-fuel dependent practices and newer alternatives which rely on renewables. The chosen categories (FTS, methanol, ethylene, propylene, ammonia, and BTX aromatics) comprise the most consumed petrochemical intermediates; implementing renewables-based processes for these intermediates stands to have the biggest impact on reducing the fossil-fuel dependency and emissions intensity of the petrochemical industry. The alternatives presented are not an exhaustive analysis (there are thousands of proposed ideas and research projects) but instead just those that show the most potential currently. This analysis shows that there is always a route to use waste resources (CO_2, biogas, biomass) and renewables (energy and H_2) to synthesize valuable and essential chemicals.

There are several things that will determine the feasibility of these processes: their technological readiness, ability to reduce emissions, the status of renewable energy and carbon capture, economics, and policy. The next section gives a brief discussion of these factors.

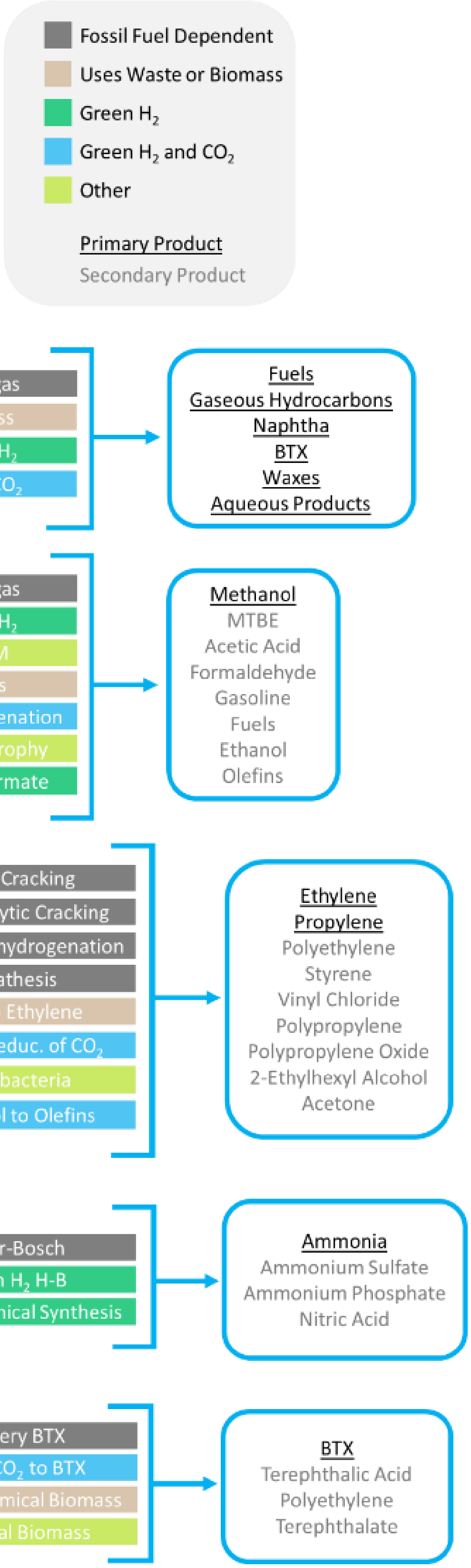


Figure 30: *Overview of alternative processes and the products they create.*

TECHNOLOGICAL READINESS AND EMISSIONS REDUCTIONS

Some of the alternative production methods presented have already entered the pilot scale phase while others are only at proof of concept. Ranking these alternatives based on their technological readiness can give an idea of how far away the U.S. is from being able to switch over from fossil fuels. This is done in Figure 31, where industrial scale processes rank at a 10 and proof of concept ventures rank at a 1. The five most consumed petrochemicals all have green processes which are being implemented on a pilot scale somewhere in the world. This is encouraging because some companies and governments are showing interest in reducing emissions from the petrochemical industry and demonstrating their capability of achieving these goals.

There are also many ongoing lab-scale projects which are on the brink of success. With further improvements in reaction selectivity and kinetics, many of these processes have the potential to reach pilot scale size in the near future. Biological petrochemical production is a relatively new field and has generally only reached the proof-of-concept stage, whereas biomass and biogas routes tend to only be applicable in niche situations where a viable feedstock is available.

The question then becomes how much impact will these alternatives have in reducing emissions? CO_2 conversion is inherently difficult because of the stability of the molecule; the same is true for N_2 to NH_3 and H_2O to H_2. More energy is required with complex catalysts and sometimes intense reaction conditions. When crude oil or natural gas feedstocks are replaced by CO_2 and H_2O, but the energy source for the process is still fossil-reliant, it is very possible that many of these alternatives emit more CO_2 than the processes used today. Thus, an overall carbon balance considering the origin of feedstocks and energy is needed to determine which alternatives, if any, can bring us closest to our goal of carbon neutrality.

Some of this work has already been done in published Life Cycle Analysis (LCA) studies which look at these processes in conjunction with CO_2 Capture and Utilization (CCU) schemes and renewable energy sources. These studies investigate the CO_2e emitted by each method to evaluate if there are any emissions reductions compared to fossil-fuel based production.

Liu et al. investigated using CO_2 from direct air capture (DAC) and H_2 from renewables-powered water electrolysis for FTS fuel production. They found that while DAC emitted 0.51 gCO_2e per g of CO_2 captured, the fuel produced had a carbon intensity that was 75 gCO_2e/MJ lower than conventional petroleum diesel. This analysis was dependent on an entirely carbon neutral electricity supply.[143]

Kajaste et al. conducted a study on methanol synthesis with CO_2 captured from a coal-fired power plant and H_2 produced from water electrolysis. They showed that the green alternative had the potential to reduce emissions by 0.54 t_{CO2e}/t_{MeOH} compared to the traditional process; combined with the utilization of CO_2 which would otherwise be emitted, the CO_2e avoided were 2.0 t_{CO2e}/t_{MeOH}. This also represented a small reduction (8%) of the total emissions from the power plant, making it a potential route to decarbonize fossil-fuel power plants while producing valuable chemicals.[144]

Khoo et al. studied the emissions impact of transitioning to electrochemical ethylene synthesis with captured CO_2 and renewable H_2. Their analysis included energy sources from natural gas, renewable hydrogen, and bioenergy. They found that the process was carbon negative when renewable H_2 and bioenergy electricity sources were used, resulting in emissions reductions of 3.0 $tCO_2e/t_{Ethylene}$ and 0.65 $tCO_2e/t_{Ethylene}$, respectively. When electricity from the natural gas powered grid was used, the process emitted 0.25 $tCO_2e/t_{Ethylene}$.[145] Although this is not negative, this is still a significantly lower value than that associated with ethylene production from fossil-fuel feedstocks.

Electrochemical ammonia synthesis using solar energy and green H_2 has been shown to greatly reduce CO_2 emissions. Bicer et al. estimated that fossil fuel powered ammonia plants emit 2.0—2.5 kg_{CO2e}/kg_{NH3}, whereas an electrochemical approach emits around 1 kg_{CO2e}/kg_{NH3}.

Some groups have even completed an LCA for a complete transition to sustainable petrochemical production on a national scale. A study by Rosental et al. considered Germany. Eliminating fossil-fuel petrochemical production would reduce the industry's emissions by 88—97%, and Germany's total emissions by 5.8—6.3%. However, achieving this would increase total electricity demand by 2—7%, putting further pressure on green energy scale-ups.[146] Given that this study only considered Germany, a similar analysis for the U.S. would likely show a larger relative emissions reduction because of the size of the U.S. petrochemical industry.

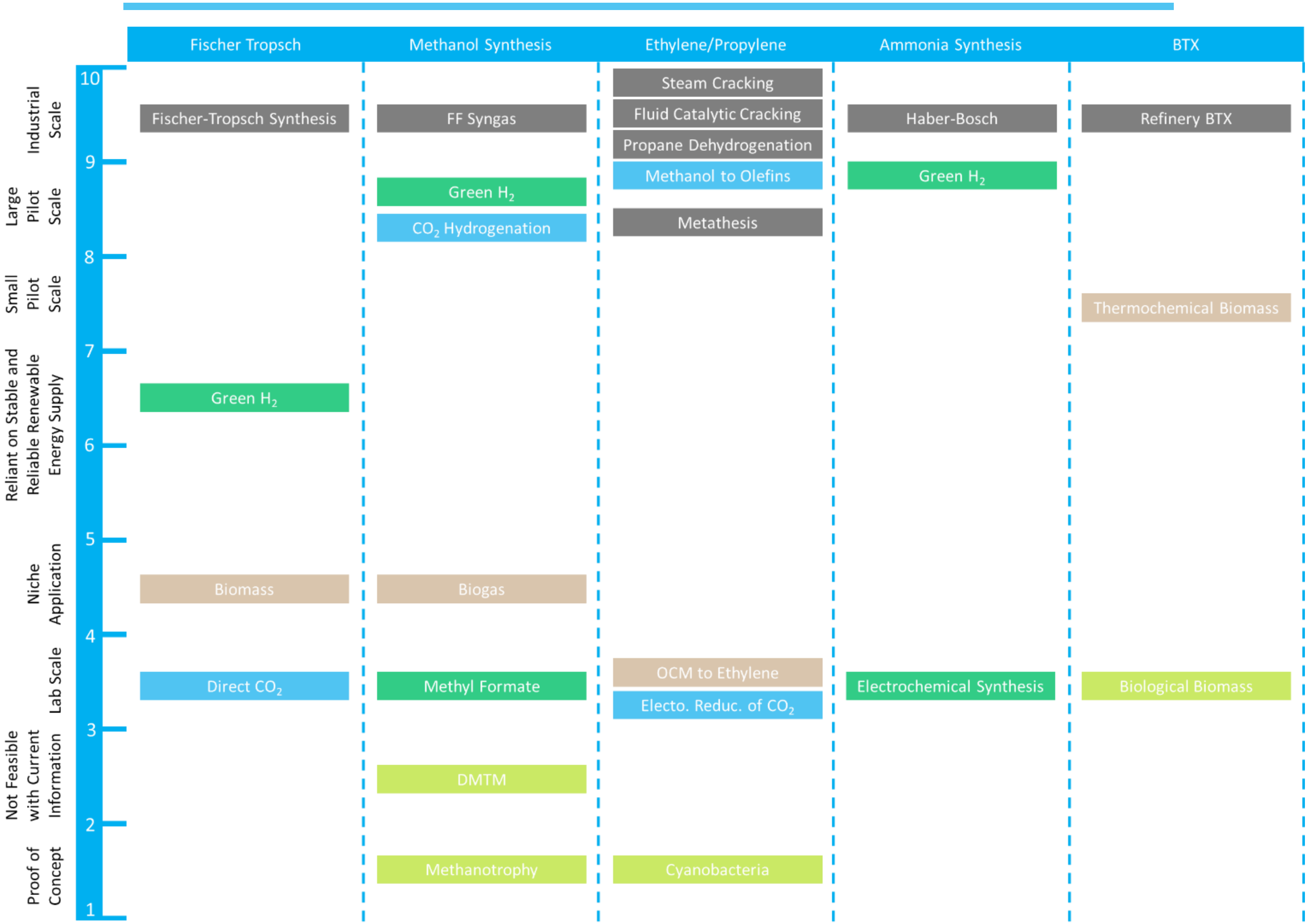


Figure 31: *Ranking alternative processes with the industrial scale ability ranked at a 10 and the basic proof of concept ventures rank at a 1.*

Although these studies show that there is the potential to greatly reduce CO_2 emissions by defossilizing the petrochemical industrial, they also highlight the need for massive expansion of renewable energy sources and carbon capture projects. The growth of these projects is primarily governed by policy and economics and will likely need legislative support and funding.

STATUS OF RENEWABLES, POLICY, AND ECONOMICS

A study by Kätelhön et al. estimated that while 3.5 Gt CO_2e could be avoided by switching the petrochemical industry over to these alternative processes, it would require 55% of the projected global electricity production in 2030.[7] Thus emissions reductions via carbon capture and utilization in the petrochemical industry can only realistically occur with a joint massive expansion of renewable electricity to supply both process energy and feedstocks. Perhaps the most influential factors are government intervention and support, costs, and electrical grid storage capacities.

There are obstacles in implementing alternative processes due to current policies and funding mechanisms. Huge tax subsidies are allocated to the fossil fuel industry. The global direct fossil-fuel subsidies in 2017 totaled at $447 billion, not accounting for externalities such as climate and health impacts. When these factors were accounted for, the actual price of fossil fuel usage exceeded $3.1 trillion, which exceeded subsidies for renewable energy by a factor of 19.[147] These subsidies remain largely attached to domestic policy, meaning that while governments are increasingly committing to emission reduction goals, growth of the fossil fuel industry continues to be supported.

Even though the fossil-industry still has a large political influence, renewable energy has successfully entered the market. Globally, $166 billion dollars were allocated to renewables in 2017, with $23 billion spent in the U.S. alone. In recent years, renewable energy production has become much more cost competitive with fossil fuels due to technological improvements and economies of scale. The cost of solar electricity fell 82% between 2010 and 2019, while onshore and offshore wind fell by 47% and 39% respectively.[148] New solar and wind projects are producing cheaper electricity than existing coal-fired powerplants, making them a cost-competitive replacement for new fossil-fuel power plants. In 2019, 72% of new energy projects globally were renewables-based. From a climate perspective however, renewable energy has the greatest emissions reduction when used for heating and transportation, and these sectors will likely take priority.[7]

In an ideal scenario, we could build an entirely renewable energy grid that could support the industrial sector. An alternative process would be available for each major intermediate, and the entire petrochemical industry would be carbon neutral at the least. But we are very far out from achieving this. While there are proven ways to generate renewable energy, the greatest technological obstacle is electricity storage to provide a continuous, reliable supply of energy. This is a large undertaking which will require intense technological improvements and huge changes to our energy distribution infrastructure. Strong government backing on state and national levels will be necessary to transition the U.S. and therefore petrochemical production to renewable energy.

In addition to renewable energy, carbon capture projects will be needed for processes which require CO_2 feedstocks. CO_2 could potentially be sourced from existing power plants and ammonia plants, until they are decommissioned, steel and concrete production facilities, as these sites will have unavoidable emissions due to the characteristics of the process, and direct air capture.

Lastly, many refineries and petrochemical plants have plant lifetimes that extend decades from now. On average, only 4% of existing production capacities are replaced annually.[7] Because monetary investments have already been made, these facilities will not be decommissioned before their technically feasible lifetime. This is perhaps a good thing because it gives time for the energy sector to switch over to renewables as industrial demand for renewables gradually increases.

Table 13: *Price comparison of different energy sources. Data obtained from Dudley.* [149]

Energy Source	Oil/Gas	Hydroelectric	Solar Photovoltaic (PV)	Biomass	Geothermal	Onshore Wind	Offshore Wind
Price Per kWh	$0.05-$0.15	$0.05	>$0.10	>$0.10	>$0.10	>$0.10	$0.13

CONCLUSIONS

The production and combustion of fossil fuels is the largest contributor to GHG emissions, causing unprecedented global warming. CO_2 emissions must be reduced significantly in the next 30 years and eliminated completely by 2100. Approximately 80% of all U.S. energy consumption is from fossil fuels.[150] While there are ways to transition away from fossil heat and transport fuels through renewable energy, the petrochemical industry is not so easily replaced. A full transition away from crude oil, natural gas, and coal cannot be made until solutions are identified for every sector.

The goal of this study was to characterize current U.S. petrochemical production amounts, identify the most produced intermediates, and describe possible alternative production methods which rely entirely on renewable feedstocks. In 2019, the U.S. processed 836.2 Mt y^{-1} of crude oil, 10.22 Mt y^{-1} of coal and lignite, 16.95 Mt y^{-1} of natural gas and 49.1 Mt y^{-1} of other liquids. While most of these feedstocks were either transformed into fuels or emissions, a significant portion was used to generate petrochemical feedstocks.

The largest petrochemical product categories are thermoplastics and fertilizers. Moreover, >95% of all petrochemical end products were derived from five main intermediates: methanol, ethylene, propylene, ammonia, and BTX aromatics. Finding alternative processes for these major intermediates, rather than individual end products, is the simplest way to defossilize the petrochemical industry.

These intermediates may be produced through numerous thermocatalytic, biocatalytic, and electrocatalytic routes. Processes such as Fischer Tropsch Synthesis, CO_2 hydrogenation to methanol, and water electrolysis are well characterized and have been demonstrated on large scales. These processes should be implemented wherever possible. Newer research pursuits such as the electrocatalysis and biocatalysis of CO_2 are less developed and have only been tested in a lab environment. With further developments in catalyst and reaction design, some of the technologies will likely replace fossil-based production.

Many of these alternative processes only show an emissions improvement when they are powered with renewable electricity. They also have the capability of being net negative CO_2e when combined with carbon capture. This highlights the need for massive expansions in the renewable electricity grid and carbon capture projects. Expansion of these resources is dependent on policy, funding, economics, and technological feasibility. Renewable energy storage must be improved to provide reliable electricity; additionally, renewable energy, captured CO_2, and green H_2 feedstocks must be cost competitive with current fossil fuel feedstocks. This can be made possible with economies of scale and government support.

Phasing out fossil fuels will not happen overnight. There are dedicated emissions from refineries and petrochemical plants that are still within their operational lifetimes, and this infrastructure will take years to develop. However, sooner steps are taken to intervene with the projected global warming, the better off people and the planet will be in the future. This study shows that it is possible to both defossilize the world and still support essential sectors such as petrochemicals.

FURTHER RESEARCH RECOMMENDATIONS

This project presents an overview of U.S. refinery operations with a concentration on petrochemical plants. For further research, a similar study could be conducted on other refinery products such as oils and fuels since distillate fuel oil was the largest product produced in the U.S. in 2019. An additional Sankey diagram can be made to track specifically where the fuels, oils, and infrastructure products go and their related emissions. The analysis on alternative processes should be expanded to include the different types of biofuels and bio-oils that are currently being researched and produced.

The fertilizer industry, which can be grouped into the petrochemical sector, does not have annual data on feedstocks and products collected and presented to the public. This can make it difficult to determine what specific fossil fuels are fed into ammonia or methanol plants. This paper used a generalized fossil fuel breakdown; the specific ratios of coal, natural gas, and crude oil used by U.S. ammonia and methanol plants are needed for more accurate accounting. By knowing what feedstocks are used, the CO_2 emissions associated with the fossil fuels can also be estimated more accurately.

CO_2 emissions are the driving factor for the divergence away from fossil fuels. This paper reported the CO_2e emissions generated by each major sector (petroleum, natural gas, coal, refineries, and petrochemical plants). However, the carbon lifecycle of each end product was not explored. Some materials such as plastics can sequester carbon, whereas fuels are at best carbon neutral because they are burned almost immediately after production. A more thorough CO_2 analysis should be conducted to account for the emissions from production and the emissions related to the lifetime of that product.

The remaining industries that use coal to produce hydrogen gas, such as ammonia and methanol plants, should switch to natural gas. This would reduce carbon dioxide emissions by about 50% since coal produces the most CO_2 when burned compared to other fossil fuels.[151] Besides using fossil fuels as feedstocks, they are also used to produce energy for the chemical industry. This should be switched to renewable energy sources to lower the overall emissions produced.

Most alternative processes have higher cost of production compared to the traditional fossil fuel route which makes it difficult to move toward the more sustainable options. Government policies and subsidiaries could help lower cost of renewable options. The analysis of this project could be improved by looking into current government efforts and policies that improve the progress of alternative pathways. Policies and funding surrounding carbon capture should also be explored.

Finally, advances in the technological readiness of the reported alternatives should be reported. Many of these processes are currently only lab-scale but reporting on the progress of these ventures could help secure the funding and support they need to reach industrial scale.

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APPENDICES

APPENDIX A: ANNUAL PRODUCTION ESTIMATES

***Table** 14: The annual production estimates from 2019 either directly cited or projected amounts. It is noted if the production amount obtained is not from 2019. If values of a chemical could not be found, a balance was created using calculations from other chemicals such as the feed or products.*

Ref	Chemical	Mega Tons/year	Source(s)	Notes
1	Coal	10.22	30	
1 or 3	Crude Oil	836.2	152	
2	Natural Gas & NGL	28.43	152	
3 or 4	Other Liquids	49.05	152	
6 or 12	Natural Gas Liquids	10.1	37	
13	Refinery Olefins	8.28	37	
10	Liquefied Refinery Gases	18.14	30,37	
8	Finished Motor Gasoline	70.12	30,37	
7	Kerosene-Type Jet Fuel	84.89	30,37	
4	Distillate Fuel Oil	250.63	37	
6	Residual Fuel Oil	19.06	37	
21	Petrochemical Feedstocks	13.67	30,37	
11	Special Naphthas	1.41	37	
15	Lubricants	8.69	37	
15	Waxes	.21	37	
5	Petroleum Coke	56.002	37	
9	Still Gas	34.27	37	
16	Miscellaneous Products	4.38	37	
12	Ammonia	16.41	153	
14	Methyl Alcohol (Methanol)	9.4	154	Projected Total Methanol Capacity from an increase in 2019/2020 with three new plants
15	Ethylene	31.4	153	
16	Propylene	15.6	153	
12	p-Xylene	2.68	153	
12	Toluene	5.03	153	
12	Benzene	4.74	153	
18	Urea	5.87	155	From 2018
20	Mono Ammonium Phosphate	4.82	155	From 2018
19	Ammonium Sulfate	2.95	155	From 2018
21	Nitric Acid	8.96	156	2016 projected amount
25	Polyethylene	22.67	153	

27	Vinyl Chloride	7.2	153	Obtained by using the amount of polyvinyl chloride produced in the US since direct conversion of vinyl chloride to PVC
26	Styrene	4.68	153	
28	Polypropylene	7.65	153	
32	Terephthalic Acid	13.72	157	2019 Forecasted Estimate
33	maleic anhydride	.3	153	
33	phthalic anhydride	.255	153	
33	acrylonitrile	1.08	153	
33	cyclohexane	.860	153	
23	acetic acid	3.1	153	
33	phenol	1.11	153	
31	Acetone	1.64	158	Total Capacity of Seven Largest Acetone Production Facilities in 2017
30	2 ethylhexyl alcohol	.410	159,160	Estimate from Largest two Plants in 2014 and 2018
22	formaldehyde	4.5	161	From 2006
24	Methyl tert-butyl ether	2.72	162	Total Capacity of Six Largest MTBE Plants in 2018
29	Propylene oxide	2.445	163	Total Capacity of Three Largest PO Plants in 2011
33	Polychloroprene	.1	164	Total Capacity of Two Largest Polychloroprene Plants in 2005
34	Ammonium Nitrate	1.195	155	From 2018
36	Polyvinyl chloride	7.200	153	
35	Polystyrene	2.527	153	
37	Polyethylene terephthalate	5,121	165	From 2017
38	Acrylonitrile butadiene styrene	8.64	166	From 2016
39	Polyester	1.275	153	
38	Toluene diisocyanate	.193	167	From 2011
38	Aniline	.845	153	
38	Styrene butadiene	.89	153	
38	Bisphenol A	1.025	153	
38	Vinyl acetate	1.535	153	
38	Methyl methacrylate	.99	168	Total Capacity of Five Largest MMA Plants in 2018
39	Polyaminds	.6	153	Used production amount of Nylon
38	Polyvinyl acetate	1.535	153	Assumed to be the same as Vinyl acetate, the primary feedstock.

APPENDIX B: INPUT REQUIREMENTS FOR PROCESS REACTIONS

Table 15: *The input requirements for each process reaction in the petrochemical industry. The input value are the tones of primary reactant(s) required per ton of primary reactant. These were sourced from the paper, Mapping the Global Flows of Chemicals.*

Reference	Primary Product	Primary Reactant	Input (t/t)
16 to 30	2-ethyl hexyl alcohol	propylene	0.8
14 to 23	Acetic Acid	Methyl Alcohol	0.542
16 to 31	Acetone	Propylene	0.81
16 to 33	Acrylonitrile	Propylene	1.1
13 to 33		Ammonia	0.445
33 to 38	Acrylonitrile butadiene styrene	Acrylonitrile	0.256
26 to 38		Styrene	0.562
33 to 38		Butadiene	0.203
13 to 33	Adiponitrile	Ammonia	0.332
13 to 34	Ammonium nitrate	Ammonia	0.216
21 to 34		Nitric Acid	0.803
13 to 19	Ammonium sulphate	Ammonia	0.26
12 to 38	Aniline	Benzene	0.88
21 to 38		Nitric Acid	0.71
33 to 38	Bisphenol A	Phenol	0.88
31 to 38		Acetone	0.29
33 to 38	Caprolactam	Cyclohexane	1.03
13 to 38		Ammonia	0.417
12 to 38	Cyclohexane	Benzene	0.94
12 to 33	Dimethyl terephthalate	Para-xylene	0.64
14 to 33		methyl alcohol	0.386
14 to 22	Formaldehyde	methyl alcohol	1.135
15 to 33	Ethylene Glycol	Ethylene	0.6
33 to 38	Hexamethylenediamine	Adiponitrile	1.095
12 to 33	Isophthalic acid	Meta-xylene	0.67
12 to 33	Maleic anhydride (1)	Butane	0.941
12 to 33	Maleic anhydride (2)	benzene	0.905
16 to 38	Methyl methacrylate	Acetone	0.718
14 to 38		methyl alcohol	0.396
13 to 38		Ammonia	0.21
35 to 21	Methyl tert-butyl ether	Methyl alcohol	0.37
		Isobutene	0.653
13 to 20	Monoammonium phosphate	Ammonia	0.212
13 to 21	Nitric Acid	Ammonia	0.29
12 to 33	Phenol	Benzene	0.945
37 to 33		Propylene	0.486
12 to 33	Phthalic anhydride	Ortho-xylene	0.96

15 to 25	Polyethylene (high density)	Ethylene	1.05
32 to 37	Polyethylene terephthalate (1)	Terephthalic acid	0.87
33 to 37	Polyethylene terephthalate (2)	Dimethyl terephthalate	1.02
16 to 28	Polypropylene	propylene	1.02
26 to 35	Polystyrene	Styrene	1.02
26 to 35	Polystyrene (high impact)	Styrene	1.05
27 to 36	Polyvinyl chloride	Vinyl Chloride	1.03
16 to 29	Propylene oxide	Propylene	0.85
12 to 32	Purified Terephthalic acid	Para-xylene	0.67
15 to 26	Styrene	Ethylene	0.788
12 to 26		Benzene	0.283
12 to 26		Ethylbenzene	1.06
33 to 38	Styrene acrylonitrile	Acrylonitrile	0.255
26 to 38		Styrene	0.791
26 to 38	Styrene butadiene	Styrene	0.255
33 to 38		Butadiene	0.765
12 to 38	Toluene diisocyanate	Toluene	0.65
21 to 38		Nitric Acid	0.889
13 to 18	Urea	Ammonia	0.58
15 to 38	Vinyl acetate	Ethylene	0.33
23 to 38		Acetic Acid	0.73

APPENDIX C: PRIMARY FLOW CALCULATIONS

Table 16: *The flow quantities, that represent the line thickness, used to create Figure SANKEY. In the additional information, it contains the calculations.*

Origin	Terminus	Composition	Mt yr^{-1}
1	13	Coal	7.8
1	14	Coal	2.5
2	6	Natural Gas & NGL	16.9
2	7	Natural Gas & NGL	6.8
2	8	Natural Gas & NGL	2.8
3	6	Crude Oil	78.2
4	6	Other Liquids	10.1
6	7	Still Gas	34.3
6	8	Olefins	8.3
6	9	Petrochemical Feedstocks	13.6
6	10	Liquefied Refinery Gases	18.0
6	11	Natural Gas Liquids	10.1
6	12	BTX Aromatics	21.1
7	15	Still Gas	34.3
8	16	Olefins	8.3
9	15	Petrochemical Feedstock	10.0
9	17	Petrochemical Feedstock	3.6
10	15	Liquified Refinery Gases	0.2
10	16	Liquefied Refinery Gases	16.3
10	17	Liquified Refinery Gases	1.5
11	16	Natural Gas Liquids	8.2
11	17	Natural Gas Liquids	1.7
12	26	BTX Aromatics	6.3
12	31	BTX Aromatics	2.6
12	32	BTX Aromatics	9.2
12	33	BTX Aromatics	1.4
12	44	BTX Aromatics	1.7
13	18	Ammonia	3.4
13	19	Ammonia	0.8
13	20	Ammonia	1.0
13	21	Ammonia	2.6
13	34	Ammonia	0.3
13	41	Ammonia	7.4
13	45	Ammonia	1.0

14	22	Methanol	5.1
14	23	Methanol	3.5
14	24	Methanol	1.0
15	25	Ethylene	23.6
15	26	Ethylene	3.7
15	27	Ethylene	3.5
15	45	Ethylene	1.5
16	28	Propylene	7.8
16	29	Propylene	2.1
16	30	Propylene	2.3
16	33	Propylene	1.7
17	24	C4 Stream	1.8
17	44	C4 Stream	2.1
18	41	Urea	5.3
19	41	Ammonium Sulfate	2.9
20	41	Ammonium Phosphate	4.8
21	34	Nitric Acid	1.0
21	39	Nitric Acid	1.4
21	45	Nitric Acid	0.9
22	39	Formaldehyde	0.6
22	45	Formaldehyde	4.5
23	39	Acetic Acid	1.2
23	44	Acetic Acid	1.2
23	45	Acetic Acid	2.5
24	44	Methyl-tert-butyl-ether	2.8
25	42	Polyethylene	23.6
26	36	Styrene	3.7
26	39	Styrene	1.0
27	37	Vinyl Chloride	7.4
28	42	Polypropylene	7.0
28	39	Polypropylene	0.8
29	43	Polypropylene Oxide	1.7
30	44	2-Ethylhexyl Alcohol	2.9
31	39	Acetone	0.4
31	44	Acetone	1.2
32	38	Terephthalic Acid	13.7
33	39	First Intermediate Chemicals	0.6
33	42	First Intermediate Chemicals	1.8

33	43	First Intermediate Chemicals	1.9
33	45	First Intermediate Chemicals	0.9
34	41	Ammonium Nitrate	1.2
35	42	Polyethylene	23.6
36	42	Polystyrene	3.7
37	42	Polyvinyl Chloride	7.4
38	42	Polyethylene Terephthalate	1.7
38	43	Polyethylene Terephthalate	3.4
39	40	Second Intermediate Chemicals	2.7
39	42	Second Intermediate Chemicals	1.8
39	43	Second Intermediate Chemicals	1.9
39	45	Second Intermediate Chemicals	0.9
40	42	Second Intermediate Chemicals	1.8
40	43	Second Intermediate Chemicals	0.9

APPENDIX D: BALANCING SECONDARY REACTANTS AND PRODUCTS

Table 17: *The secondary reactants and products used to balance the petrochemical industry section of the Sankey diagram. Calculations were used based on the moles of the primary product to determine the amount of kilo tons per year of water, oxygen, and carbon monoxide to name a few.*

Primary Product	Inputs	Mega tons/year	Outputs	Kilo tons/year	Moles of Product
2-ethyl hexyl alcohol	C_3H_6	.37	$C_8H_{18}O$	288	2.2
$2C_3H_6 + 2CO + 4H_2 \rightarrow C_8H_{18}O + H_2O$	CO	.248	H_2O	39.8	
	H_2	.071			
Acetic Acid	CH_4O	1.651	$C_2H_4O_2$	3100	51.6
$CH_4O + CO \rightarrow C_2H_4O_2$	CO	1.44			
Acrylonitrile	C_3H_6	.857	C_3H_3N	1080	10.2
$2C_3H_6 + 2NH_3 + 3O_2 \rightarrow 2C_3H_3N + 6H_2O$	NH_3	.347	H_2O	3301.1	
	O_2	1.466			
acrylonitrile butadiene styrene	$n(C_3H_3N)$		$(C_3H_3N)_n(C_4H_6)_{0.8n}(C_8H_8)_{1.1n}$	880	4.2
$n(C_3H_3N)+0.8n(C_4H_6)+1.1n(C_8H_8) \rightarrow (C_3H_3N)_n(C_4H_6)_{0.8n}(C_8H_8)_{1.1n}$	$n(C_4H_6)$				
	$n(C_8H_8)$				
Adipic acid	C_6H_{12}		$C_6H_8N_2$	810	5.5
$C_6H_{12}+O_2+HNO_2+HNO_3+H_2O \rightarrow C_6H_{10}O_4+N_2O+3H_2O$	O_2	.177	N_2O	243.9	
	HNO_2	.261	H_2O	131463	
	HNO_3				
	H_2O	.1			
Adiponitrile	C_4H_6		$C_6H_8N_2$	392.7	3.6
$C_4H_6+2CH_4+2NH_3+3O_2 \rightarrow C_6H_8N_2+6H_2O$	CH_4	.233	H_2O	392.3	
	NH_3				
	O_2	1.046			
Ammonium nitrate	HNO_3		$N_2H_4O_3$	1195	14.9
$HNO_3+NH_3 \rightarrow N_2H_4O_3$	NH_3				
Ammonium sulphate	NH_3		NH_8SO_4	2946	22.3
$2NH_3+H_2SO_4 \rightarrow NH_8SO_4$	H_2SO_4	2.19			
Aniline	C_6H_6		C_6H_7N	845	9.1
$C_6H_6+HNO_3+3H_2 \rightarrow C_6H_7N+3H_2O$	HNO_3		H_2O	1473.1	
	H_2	.16			
Bisphenol A	C_6H_6O		$C_{15}H_{16}O_2$	1000	4.4
$2C_6H_6O+C_3H_6O \rightarrow C_{15}H_{16}O_2+H_2O$	C_3H_6O		H_2O	78.8	
Cyclohexane	C_6H_6		C_6H_{12}	860	10.2
$C_6H_6+3H_2 \rightarrow C_6H_{12}$	H_2	1.55			
Dioctyl phthalate	$C_8H_4O_3$		$C_{24}H_{38}O_4$	122	0.31
$C_8H_4O_3+2C_8H_{18}O \rightarrow C_{24}H_{38}O_4+H_2O$	$C_8H_{18}O$		H_2O	5.6	
Formaldehyde	CH_4O		CH_2O	4500	74.9
$2CH_4O+O_2 \rightarrow 2CH_2O+2H_2O$	O_2	1.2	H_2O	2695.5	
Hexamethylenediamine	$C_6H_8N_2$		$C_6H_{16}N_2$	392.7	3.4

$C_6H_8N_2+4H_2\rightarrow C_6H_{16}N_2$	H_2	.12			
Maleic anhydride (benzene route)	O_2	1.98	H_2O	220.6	
$2C_6H_6+9O_2\rightarrow 2C_4H_2O_3+4H_2O+4CO_2$			CO_2	538.5	
Maleic anhydride (butane route)	C_4H_{10}		$C_4H_2O_3$	300	1.5
$2C_6H_6+7O_2\rightarrow 2C_4H_2O_3+8H_2O$	O_2	1.2	H_2O	882.4	
Methyl methacrylate	C_3H_6O		$C_5H_8O_2$	990	4.9
$2C_3H_6O+2CH_4O+2CH_4+2NH_3+3O_2+2H_2SO_4\rightarrow 2C_5H_8O_2+2NH_5SO_4+6H_2O$	CH_4O		NH_5SO_4	1138.4	
	CH_4	.16	H_2O	1603.7	
	NH_3				
	O_2	.712			
	H_2SO_4	.97			
Methyl tert-butyl ether	CH_4O		$C_5H_{12}O$	2720	30.8
$CH_4O+C_4H_8\rightarrow C_5H_{12}O$	C_4H_8				
Methylene diphenyl diisocyanate	C_6H_7N		$C_{15}H_{10}N_2O_2$	1490	6
$2C_6H_7N+CH_2O+2COC_{l2}\rightarrow C_{15}H_{10}N_2O_2+4HCl+H_2O$	CH_2O		HCl	3471.7	
	COC_{l2}	2.36	H_2O	107.2	
Monoammonium phosphate	NH_3		NH_6PO_4	4819.92	41.9
$NH_3+H_3PO_4\rightarrow NH_6PO_4$	H_3PO_4				
Nitric acid	NH_3		HNO_3	8958.32	71.1
$2NH_3+4O_2+H_2O\rightarrow 2C_2H_6O_2$	O_2	18.2	H_2O	5769.6	
	H_2O	.64			
Phenol & Acetone	C_6H_6		C_6H_6O	1110	11.8
$C_6H_6+C_3H_6+O_2\rightarrow C_6H_6O+C_3H_6O$	C_3H_6		C_3H_6O	1638	28.2
	O_2	0.000881			
Phthalic anhydride	C_8H_{10}		$C_8H_4O_2$	255	1.7
$C_8H_{10}+3O_2\rightarrow C_8H_4O_2+3H_2O$	O_2	.496	H_2O	279.4	
Polyamide-6	$n(C_6H_{11}NO)$		$(C_6H_{11}NO)_n$	600	5.3
$n(C_6H_{11}NO)\rightarrow (C_6H_{11}NO)_n$					
Polyamde-66	$n(C_6H_{10}O_4)$		$(C_{12}H_{24}N_2O_2)_n$	600	2.7
$n(C_6H_{10}O_4)+n(C_6H_{16}N_2)\rightarrow (C_{12}H_{24}N_2O_2)_n+2n(H_2O)$	$n(C_6H_{16}N_2)$		$n(H_2O)$	190.9	
Polybutadiene	$n(C_4H_6)$		$(C_4H_6)_n$	530	9.8
$n(C_4H_6)\rightarrow (C_4H_6)_n$					
Polycarbonate	$n(C_{15}H_{16}O_2)$		$(C_{16}H_{14}O_3)_n$	775	3.04
$n(C_{15}H_{16}O_2)+n(COC_{l2})\rightarrow (C_{16}H_{14}O_3)_n+2n(HCl)$	$n(COC_{l2})$		$2n(HCl)$	444.3	
Polyethylene	$n(C_2H_4)$		$(C_2H_4)_n$	11337	403.45
$n(C_2H_4)\rightarrow (C_2H_4)_n$					
Polyethylene terephthalate (DMT route)	$n(C_2H_6O_2)$		$(C_{10}H_8O_4)_n$	5070	26.4
$n(C_2H_6O_2)+n(C_{10}H_{10}O_4)\rightarrow (C_{10}H_8O_4)_n+2n(H_2O)$	$n(C_{10}H_{10}O_4)$		$n(CH_4O)$	3381.8	
Polyethylene terephthalate (PTA route)	$n(C_2H_6O_2)$		$(C_{10}H_8O_4)_n$	5070	26.4
$n(C_2H_6O_2)+n(C_8H_6O_4)\rightarrow (C_{10}H_8O_4)_n+2n(H_2O)$	$n(C_8H_6O_4)$		$n(H_2O)$	1899.3	
Polypropylene	$n(C_3H_6)$		$(C_3H_6)_n$	7650	181.7
$n(C_3H_6)\rightarrow (C_3H_6)_n$					
Propylene oxide	C_3H_6		C_3H_6O	2445	21.04

$2C_3H_6+2HOCl+CaO_2H_2 \rightarrow 2C_3H_6O+CaCl_2+2H_2O$	$HOCl$	2.21	$CaCl_2$	1167.8	
	CaO_2H_2	.78	H_2O	757.5	
Polystyrene	n(C8H8)		(C8H8)n	2530	24.3
$n(C_8H_8) \rightarrow (C_8H_8)_n$					
Polyvinyl acetate	$n(C_4H_6O_2)$		$(C_4H_6O_2)_n$	1540	17.9
$n(C_4H_6O_2) \rightarrow (C_4H_6O_2)_n$					
Polyvinyl chloride	$n(C_2H_3Cl)$		$(C_2H_3Cl)_n$	7200	115.2
$n(C_2H_3Cl) \rightarrow (C_2H_3Cl)_n$					
Styrene	C_2H_4		C_8H_8	4680	44.9
$C_2H_4+C_6H_6 \rightarrow C_8H_8+H_2$	C_6H_6		H_2	89.8	
Styrene acrylonitrile	$n(C_8H_8)$		$(C_8H_8)_{1.5n}(C_3H_3N)_n$	1.4	0.00675
$1.5n(C_8H_8)+n(C_3H_3N) \rightarrow (C_8H_8)_{1.5n}(C_3H_3N)_n$	$n(C_3H_3N)$				
Styrene butadiene	$n(C_8H_8)$		$(C_8H_8)_n(C_4H_6)_{5.8n}$	890	2.1
$n(C_8H_8)+5.8n(C_4H_6) \rightarrow (C_8H_8)_n(C_4H_6)_{5.8n}$	$n(C_4H_6)$				
Terephthalic acid	C_8H_{10}		$C_8H_6O_4$	13718	82.6
$C_8H_{10}+3O_2 \rightarrow C_8H_6O_4+2H_2O$	O_2	23.79	H_2O	5946.4	
Toluene diisocyanate	C_7H_8		$C_9H_6N_2O_2$	300	1.7
$C_7H_8+2HNO_3+6H_2+2COCl_2 \rightarrow C_9H_6N_2O_2+4HCl+6H_2O$	HNO_3		HCl	1004.4	
	H_2	.125	H_2O	1116.991	
	$COCl_2$	.68			
Urea	NH_3		CH_4N_2O	5873.17	97.7
$2NH_3+CO_2 \rightarrow CH_4N_2O+H_2O$	CO_2	4.3	H_2O	1759.02	
Vinyl acetate monomer	C_2H_4		$C_4H_6O_2$	1540	8.94
$2C_2H_4+2C_2H_4O_2+O_2 \rightarrow 2C_4H_6O_2+2H_2O$	$C_2H_4O_2$		H_2O	321.95	
	O_2	.143			
Vinyl chloride	C_2H_4		C_2H_3Cl	7200	28.8
$4C_2H_4+2Cl_2+4HCl+O_2 \rightarrow 4C_2H_3Cl+4HCl+2H_2O$	Cl_2	2.042	HCl	4199.04	
	HCl	4.2	H_2O	518.4	
	O_2	.23			