Atmospheric Methanol Technology

Atmospheric Methanol is the process where renewable power (e.g., solar, wind, hydro, geothermal) is used to create liquid methanol and pure oxygen out of the air. Unlike typical methanol production methods stem from carbon-heavy fossil fuels (such as coal or natural gas), or mostly carbon-neutral fuels (such as biomass or municipal solid waste), Atmospheric Methanol is a renewable negative-carbon process and represents the pinnacle of the clean methanol production methods, called e-methanol. Because Atmospheric Methanol pulls its required materials out of the air, it can be place anywhere renewable power is available, unlike typical methanol production facilities that need to be co-located with its source fuel or suffer from additional transportation costs.

What differentiates Atmospheric Methanol process above other e-methanol processes is that it is extremely efficient, generating the lowest levelized cost per ton of e-methanol. Atmospheric Methanol achieved this goal by applying systems engineering to the overall process, optimizing the techniques used in each subsystem and energy recycling between these subsystems. The electrolyzers are the most energy intensive portion of the system, being an endothermic process. The methane generation step is exothermic, releasing lots of excess heat. The Atmospheric Methanol process uses the waste heat from the methane generation step to power most of the atmospheric water generation and direct air capture steps, saving lots of electricity and its cost.

Atmospheric Methanol achieves a $400/ton levelized cost of methanol, assuming otherwise baseline costs and conditions. 74% of this plants cost is in the CO2 capture system. On the other hand, if the Atmospheric Methanol system could piggyback on a high-carbon exhaust stream, such as 10% CO2, the resulting levelized cost would drop to $250/ton. Since the current contract price in the USGC is $593/ton and spot price is $375/ton, this leaves plenty of room for profit for the Atmospheric Methanol process. These values all assumed a 60000 ton per year plant for scale.

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Table of Contents

Table of Figures

1 Background

1.1 Methanol

Methanol is a common organic chemical with the formula CH_3OH, often abbreviated to MeOH, and known as methyl alcohol or wood spirit. It is the simplest aliphatic alcohol, consisting of a methane molecule, CH_4, with one of the hydrogen atoms replaced by a hydroxyl group, -OH. Methanol is a light, volatile, colorless, flammable liquid with a distinctive alcoholic odor like that of ethanol (potable alcohol). A polar solvent, methanol acquired the name wood alcohol because it was once produced chiefly by the destructive distillation of wood. Today, methanol is mainly produced industrially by hydrogenation of carbon monoxide. Besides being used as a gasoline additive, methanol is also used as a reagent for chemical, plastics, biodiesel, and synthetic oil production, and as a hydrogen carrier supporting the hydrogen economy.

1.1.1 Methanol Market

As of 2019, global methanol production of about 98.3 million metric tons per year is valued at $29.4B USD.

About 65% is produced from produced from natural gas, 35% from coal, and the remaining <1% e-methanol. Roughly 40% of methanol produced is used in the energy sector with 14% directly used as a fuel, and the other 60% is used manufacturing (See Figure 1: Breakdown of Current Methanol Production Uses).

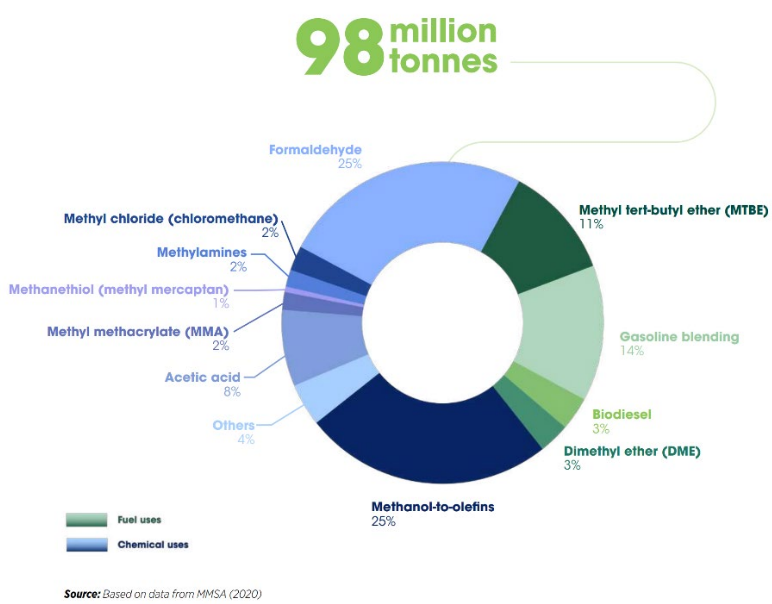


Figure 1: Breakdown of Current Methanol Production Uses

Methanol production processes are color-coded to denote the resulting carbon footprint (See Figure 2: Methanol Types):

- “Black” Methanol is produced from coal and has the highest carbon footprint.
- “Grey” Methanol is produced from natural gas and has a lower carbon footprint.
- “Blue” Methanol is between “Grey” and “Green” including some renewable and some non-renewable sources and has an in-between carbon footprint.

- "Green" Methanol is all renewable. Some is generated from renewable biomass, and hence has a slight carbon footprint. Other "Green" methanol is produced from renewable power and renewable carbon dioxide sources and hence has a zero or negative carbon footprint. Atmospheric Methanol is an example of this last category.

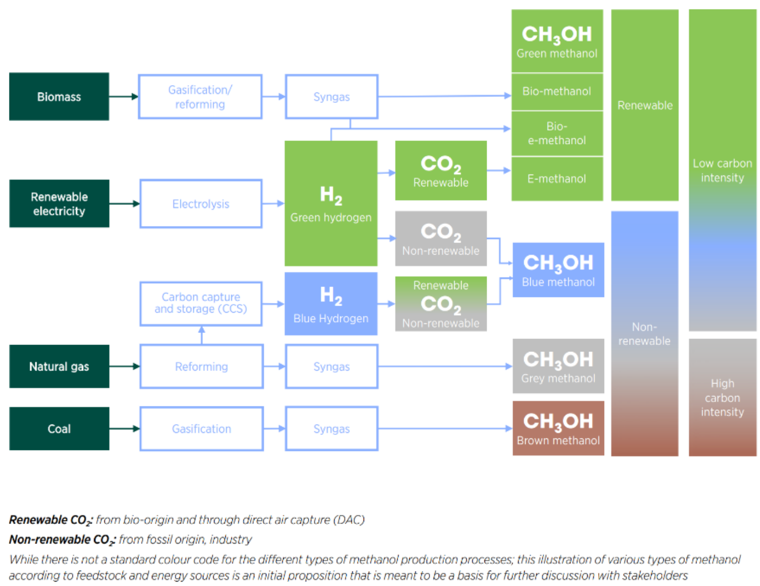


Figure 2: Methanol Types

Methanol is used in the creation of many other chemicals. Figure 3 shows some of those chemicals, such as biodiesel, formaldehyde, MTBE, and acetic acid.

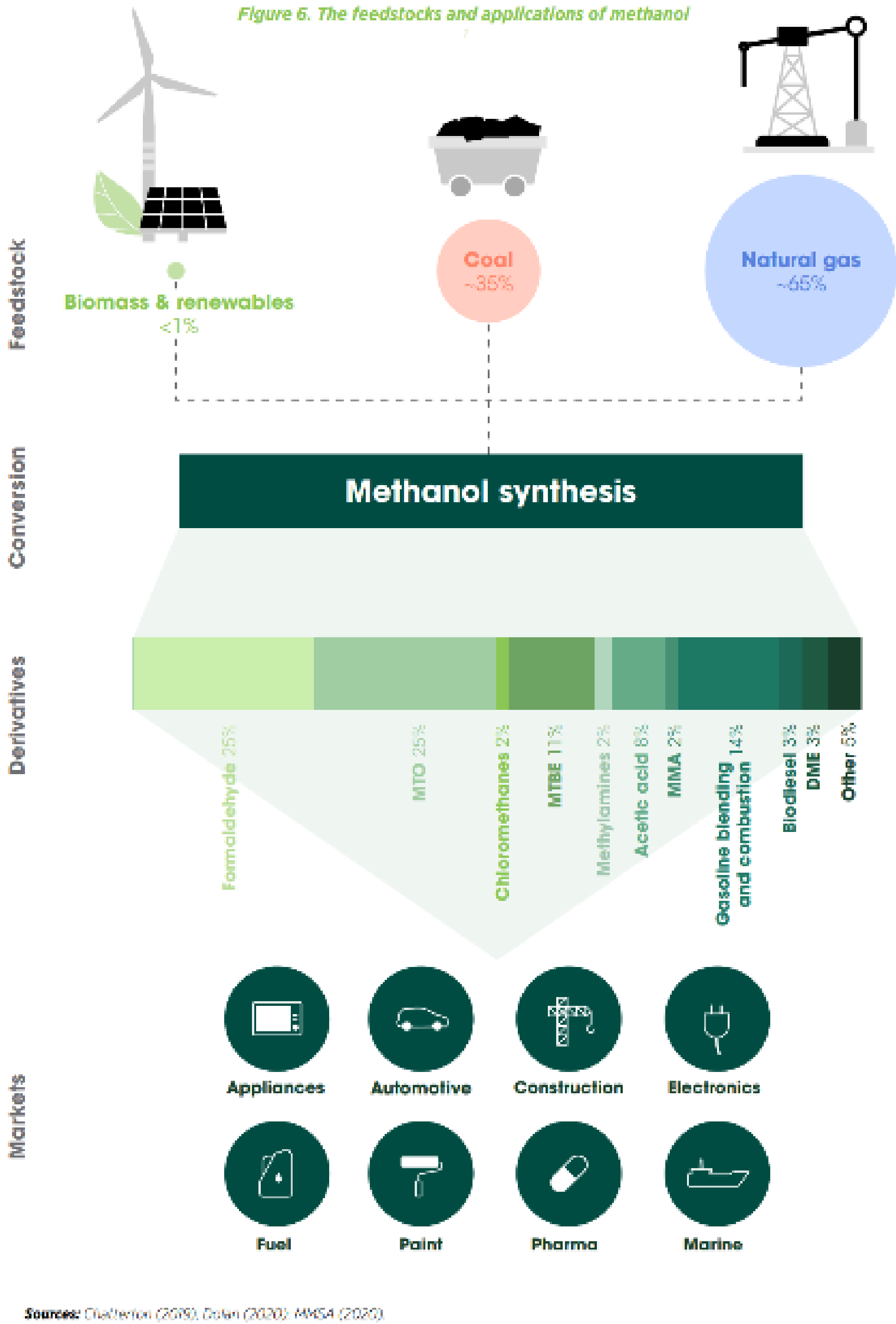


Figure 3: Methanol Sources and Uses

1.1.2 Methanol Production Mechanism

Typically, Methanol is produced by combining CO_2 with H_2 in the presence of a catalyst in a reactor at high pressure and temperature. In basic terms, each pass through the reactor converts about 10% of the carbon dioxide and hydrogen into methanol and water and release a bunch of heat.

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

The real process is a bit more complex. For example, the chemical process is really accomplished in two steps. The carbon dioxide and hydrogen gas first react to create carbon monoxide and water, in what is called the reverse water shift reaction, then the carbon monoxide reacts with the hydrogen to create methanol. That extra step explains the rapid buildup of carbon monoxide in the reactor gases. The reverse water gas shift reaction absorbs energy, hence the requirement to preheat the reactor. The later methanol production releases more energy than the reverse water gas shift reaction required, hence the overall release of energy. The whole reaction occurs at high pressure as it greatly increases the speed of the overall reaction.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \text{(Reverse Water Gas Shift)}$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \text{(Carbon Monoxide Hydrogenation)}$$

Secondly, the methanol production process occurs in small chunks, with only about 10% of the carbon dioxide and hydrogen reacting to produce methanol in each reactor pass. Hence, the reaction gases are typically looped to revisit the reactor in multiple passes to maximize the conversion rate.

There are other concurrent reactions that produce tiny amounts of other byproducts in the reactor. This is typically handled by bleeding a small percentage of the reaction gases allowing those gases to escape before they build up. These gases, which include hydrogen, are typically burned to recycle their heat energy and to limit emissions.

Finally, the resulting methanol is soluble in water, so a final distillation step that separates the methanol from the water is required.

2 Atmospheric Methanol Production Process

Atmospheric Methanol draws its components, carbon dioxide (CO_2) and water (H_2O), from the air, and its power from renewable sources, such as solar, wind and hydro. Atmospheric Methanol produces methanol, oxygen, and carbon credits.

2.1 Basic Process

The Atmospheric Methanol process is divided into four subprocesses, atmospheric water generation, water electrolysis, atmospheric carbon capture, and methanol generation.

2.1.1 Atmospheric Water Generation (AWG)

The first step is the sourcing of pure water. If impure liquid water is available (such as from surface water or municipal water), it is easier to purify that water. In the worst case when no liquid water is available, water can be condensed from the humidity in the air, which is called atmospheric water generation (AWG). When the methanol generation step distills and separates the methanol from the remaining water, the remaining water is recycled back to this step to reduce the amount of water that needs to be collected.

Independent of how the liquid water is obtained, that liquid water is then purified by distillation, filtering, and/or reverse osmosis. Once the water is pure, it is sent to the water electrolysis step.

The AWG process can be achieved via refrigeration (dehumidification), or desiccant-based systems. Atmospheric Methanol typically prefers desiccant-based systems over refrigeration because the desiccant-based system can be partially powered by the waste heat captured from the other steps. A desiccant-based AWG absorbs water out of the air into desiccant, then uses heat to release that water and rejuvenate the desiccant to capture more water.

Humid Air + Power -> Drier Air + Water

The performance of any AWG process is highly dependent upon the temperature and humidity in the air at various points of the day. The AWG water is combined with the recycled water from the methanol generation process and then filtered prior to being sent to the water electrolysis step.

The desiccant-based AWG process requires. The following chart show the performance effects of humidity and temperature (SunToWater is a desiccant-based AWG, Watergen is a refrigeration-based system). The next chart shows the economics of such systems, requiring about .3 kWh/liter of operational costs and capital and maintenance costs of about $50 and $2.5 per liter/day, respectively. About 50% of this power can be provided as heat energy instead of electrical for desiccant-based AWG systems.

The following website calculates the absolute humidity (lbm water/lbm air) based on temperature and relative humidity: http://www.hvac-calculator.net/index.php?v=2. NOAA provides data regarding expected temperatures and humidity levels for many locations worldwide.

Higher output, fewer impurities

Comparison of SunToWater's superior operating range over leading competitors

Green indicates greater operational range

SunToWater | Watergen and other AWGs

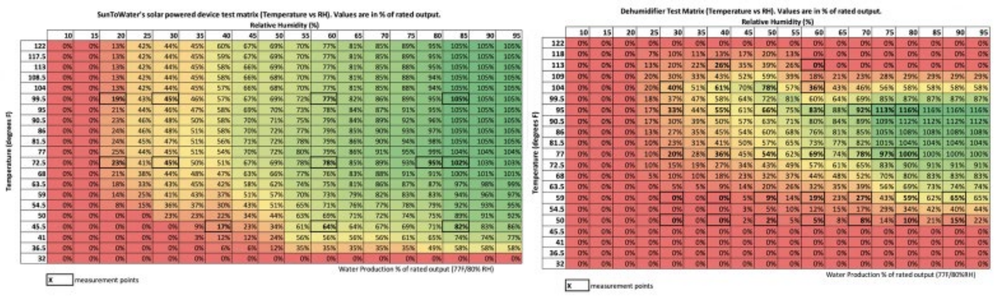


Figure 4: AWG Output Effects

Vendor	Scale	Weight (kg)	Volume Generated (L per day)	Electricity per Volume Produced (Wh/L)	Unit Cost (2018 USD)§	Maintenance Cost per Year (2018 USD)*
Watergen	Large	2,870	3,000‡	350	$115,000	$7,866
Watergen	Medium	800	400	330	$55,000	$2,500
Watergen	Home/Office	50	25	300	$1,250	-
EcoloBlue	Large	3,800	3,000	420	$159,700	$3,767
EcoloBlue	Medium	1,000	600	410	$30,750	$870
EcoloBlue	Home/Office	50	30	300	$799†	-

*Maintenance cost of AWGs includes filters replacement and disinfection of internal tanks.

†The default parameters for the EcoloBlue home/office unit are associated with Ecoloblue30E, there are two other units produced in this category called Ecoloblue30X and Ecoloblue30X Alkaline and their unit costs are $1299 and $1499 respectively.

‡ This volume is reported in multiple sources and selected as per the data provided directly to ERG by Watergen and the Watergen large scale AWG brochure available at the time of the project. Maximum water production for the large scale unit is modeled as up to 5,000 liters/day in a sensitivity analysis as specified in Table 6.

§Unit cost includes the cost of external tanks that are purchased with the large-scale units.

Figure 5: AWG Plant Specifics

Product	Type	Unit cost ($)	Annual maintenance cost ($)	AWG (kWh/L)	Electricity Cost per Liter*	Total cost per liter ($)
AWG – Watergen	Large	115,000	7,866	0.35	0.04	0.09
AWG – Watergen	Medium	55,000	2,500	0.33	0.04	0.14
AWG – Watergen	Home/Office	1,250	288	0.3	0.03	0.13
AWG – Ecoloblue	Large	159,700	3,767	0.42	0.05	0.06
AWG – Ecoloblue	Medium	30,750	870	0.41	0.04	0.06
AWG – Ecoloblue	Home/Office	799	288	0.3	0.03	0.07
Bottled water	Single-serve†	4.49	-	-		0.38§
Bottle water	Multi-serve†	7.49	6.95‡	-		0.49

*U.S. average price of electricity for commercial use in June 2018 was 10.82 cents per kWh (EIA, 2018)
§Includes water transportation cost based on the U.S. government standard mileage reimbursement rate (IRS, 2018)
†Price of single-serve bottles is calculated for a 24 pack/12L and price of multi-serve jug is for 5gallons/18.9L
‡ Monthly delivery cost which is a flat rate, we assumed monthly consumption of 4 jugs

Figure 6: AWG Economic Performance

2.1.2 Water Electrolysis

In the second step, water generated from the AWG step and recycled from the methanol generation step is broken into hydrogen and oxygen components. The hydrogen is sent to the methanol generation step, while the oxygen is produced as a product.

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

Atmospheric Methanol expects to use polymer electrolyte membrane (PEM) electrolyzers. Electrolysis is a very electric-hungry process, and heat cannot be used as a substitute. This puts the levelized cost of hydrogen at about \$6.5/kg-H_2 assuming \$0.06/kWh.

As alternatives, the water can be made to be alkaline prior to electrolysis, which lowers the electrical power required at the added expense of alkaline reagents that are added and need to be taken back out afterwards. Alkaline electrolysis does not end up improving the capital or operational costs despite adding to its complexity. Another recent alternative is Solid Oxide Electrolysis, but this has not progressed beyond lab scale.

2.1.2.1 Excess Hydrogen

Excess hydrogen generated at this step can be sold as fuel for hydrogen-powered cars, trucks, and busses, which require the fuel to be dispensed to them at standardized pressures, such as 350Bar for busses and 700Bar for cars. The current price for such hydrogen is about $12/kg. The process of using renewable energy to electrolyze water to create hydrogen is typical for “Green” hydrogen, a current and vibrant market.

2.1.3 Atmospheric Carbon Capture (ACC)

In the third step, carbon dioxide is captured from the air and sent to the methanol generation step.

$$Air + Power \rightarrow CO_2 + Air \text{ (with less } CO_2\text{)}$$

ACC can be achieved with adsorption, membrane, cryogenic, or amine methods. The optimum method depends on the scale at which the CO2 need to be generated, and the starting and desired ending concentrations of CO2. Adsorption and amine methods are preferred as they allow for 75%+ of the energy required to be provided via heat instead of electricity. Therefore the excess heat from the exothermic methanol generation step can be used to provide this heat for free.

2.1.4 Methanol Generation

In the last step, carbon dioxide is combined with hydrogen to create methanol and water. Methanol is purified prior to being output as a product, while the recaptured water is returned to the water electrolysis step.

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

2.2 Process Inputs

2.2.1 Renewable Power

For every ton of methanol produced, 14690 kWh of electrical power will be required as modeled in DWSim. The remainder of the energy requirements are fulfilled by recycling waste heat from the methanol generation step.

2.2.2 Air

For every ton of methanol produced, 0.56 tons of air will need to process to remove its carbon dioxide and water.

2.3 Process Outputs

2.3.1 Methanol

The Atmospheric Methanol process outputs high-purity distilled methanol

2.3.2 Oxygen

The Atmospheric Methanol process outputs 1.63 tons of O_2 per ton of methanol produced. This O_2 is medical quality.

2.3.3 Carbon Credits

The Atmospheric Methanol process produces 1.65 tons of carbon credits per ton of methanol produced.

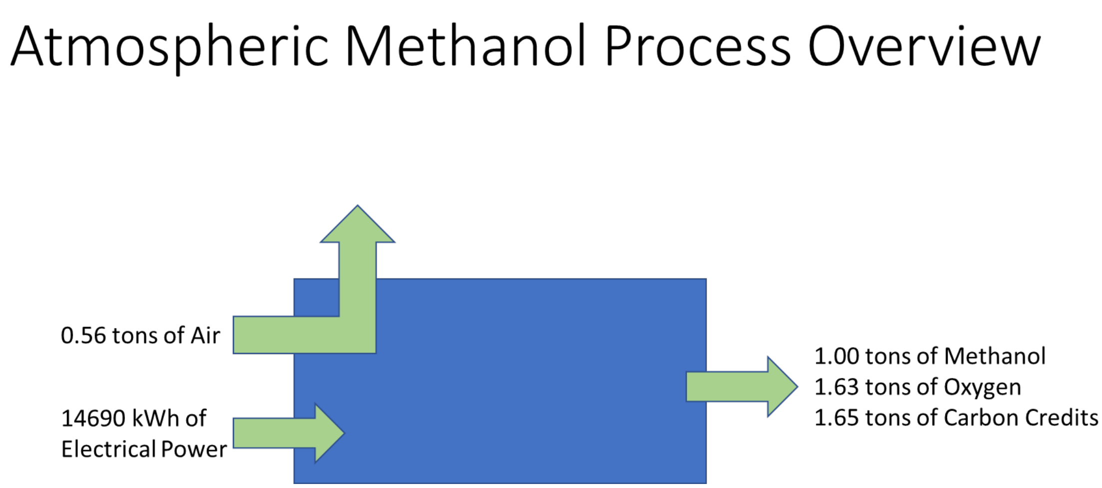


Figure 7: Overview of the Atmospheric Methanol Process

3 Market Analysis

3.1 Source Materials

3.1.1 Carbon Dioxide

In the case of Atmospheric Methanol, carbon dioxide is captured from the air. Today, air contains about 300ppm carbon dioxide. This carbon dioxide is available free of charge. To concentrate this carbon dioxide, the Atmospheric Methanol process uses an DAC system, which consumes a combination of heat and electrical power, the cost of the carbon dioxide source. The electrical power is sourced from renewable power, and the heat from the waste heat generated by the methanol generation step. The baseline Atmospheric Methanol process uses either a “Global Thermostat” carbon adsorption, or an amine based system, depending on scale.

The only way to reduce the cost of the carbon dioxide is to find a purer source that does not take heat and electrical power to concentrate. One such source is combustion exhaust gases, which include high concentrations of carbon dioxide, water, and heat energy. The source would have to be consistently available to ensure that the captured CO_2 is constantly available for the Atmospheric Methanol process and to avoid storage costs.

3.1.2 Water

Like carbon dioxide, the Atmospheric Methanol process collects its water from the humidity in the air, typically a few grams per cubic meter of air. The Atmospheric Methanol process uses a desiccant-based process to collect this water requiring heat and electrical power. Refrigeration based systems are also viable depending on the local climate.

3.1.3 Renewable Power

Renewable power is the main cost of the Atmospheric Methanol process. The cost of renewable power varies, based on its source. For example, renewable power from the grid utility providers in the New England states or Hawaii can be well over $0.20/kWh, but typically is only $0.10 to $0.15/kWh elsewhere in the USA. These prices cover the cost of producing that power (the cost of the PV array, wind turbines, or dam) plus the cost of transporting that power from the source to the destination. On the other hand, a local, dedicated PV solar facility should be able to provide power at about $0.05/kWh.

The best renewable power source for Atmospheric Methanol is hydro or geothermal, because these power sources are relatively constant, not suffering through pulses of availability.

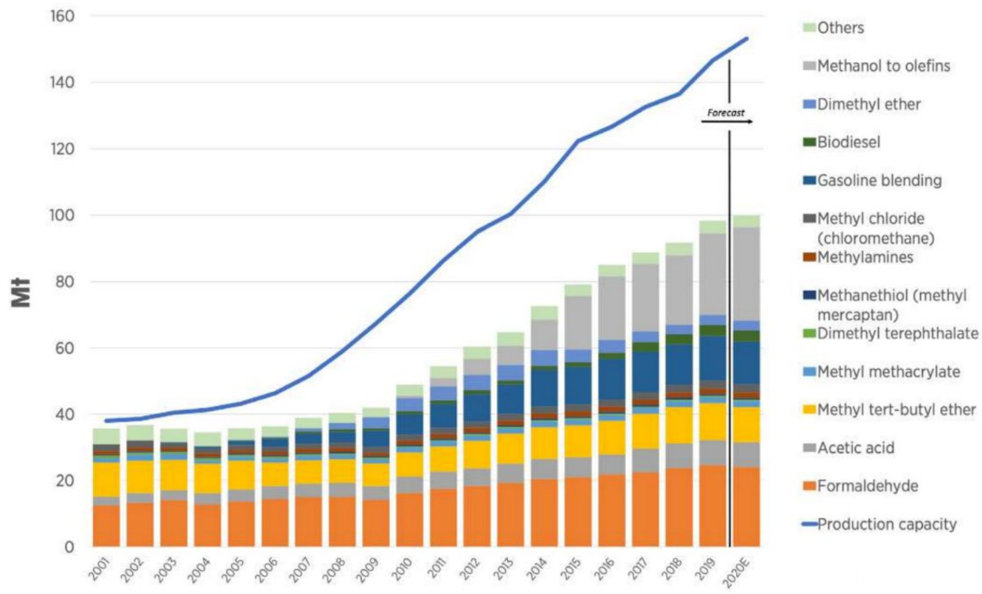
3.2 Produced Materials

3.2.1 Methanol

Methanol is a common fuel used as a gasoline additive, as a reagent for the creation of other chemicals, biodiesel, or plastics, or recently, as a hydrogen carrier. The methanol market is worldwide, which is divided between renewable and non-renewable production and regionally around the world.

In 2022, the global methanol market size is about 98.3MT/year in 2019 and forecasted to be 120MT/year in 2025 and 500MT/year in 2050. In 2019, global production capacity was about 140MT/year. The global Methanol Market was valued USD 29.4 Billion in 2021 and is all set to surpass USD 37.8 Billion by 2028, exhibiting a CAGR of 4.3% during the forecast period 2022-2028. The China and India markets for methanol are the largest.

The following chart shows historical production capacity, demand, and end uses of methanol. Roughly 25% of methanol production is devoted to formaldehyde, and other 25% is devoted to the production of olefins. Non-renewable methanol makes up the majority of this production, with renewable methanol representing only a small percentage of the market.



Source: *Based on data from MMSA (2020).*

Figure 8: Global Methanol Production, Demand and End Uses

List of Prominent Players in Methanol Market:

- Methanex Corporation (Canada)
- HELM Proman Methanol AG (Switzerland)
- SABIC (Saudi Arabia)
- Yanzhou Coal Mining Co. (China)
- Zagros Petrochemical Company (Iran)
- Celanese Corporation (Texas)
- BASF SE (Germany)
- PETRONAS (Malaysia)
- Mitsubishi Gas Chemical Company Inc. (Japan)
- Mitsui & Co. Ltd. (Japan)
- LyondellBasell Industries B.V. (U.S)
- OCI N.V. (Netherlands)
- Metafrax Chemicals (Russia)
- SIPCHEM (Saudi Arabia)

The following chart documents the historical spot prices for methanol in the various markets around the world. Typical current prices are as follows:

- Europe - $555 USD/metric ton
- North America (US Gulf Coast) - $585 USD/metric ton

- Asia Pacific - $410 USD/metric ton
- China - $375 USD/metric ton

	Methanol US MMSA Contract Index FOB USGC USD/metric ton	Methanol US MMSA Spot Barge Wtd Avg FOB USGC USD/metric ton	Methanol Europe MMSA Contract FOB Rotterdam T2 USD/metric ton	Methanol Europe MMSA Spot Avg FOB Rotterdam T2 USD/metric ton	Methanol NEA/SEA MMSA Contract Net Transaction Reference Wtd Avg USD/metric ton	Methanol China MMSA Spot, Avg. CFR China Main Ports USD/metric ton
Aug-19	340	233	342	235	234	231
Sep-19	340	261	338	236	240	238
Oct-19	340	259	307	228	249	247
Nov-19	340	274	308	228	236	235
Dec-19	340	259	309	227	233	231
Jan-20	341	288	301	255	275	273
Feb-20	397	330	295	264	247	244
Mar-20	397	252	300	224	217	215
Apr-20	356	211	278	166	188	187
May-20	312	185	278	161	182	181
Jun-20	287	154	287	175	175	174
Jul-20	271	195	258	189	195	194
Aug-20	277	230	266	222	205	203
Sep-20	289	308	266	241	234	233
Oct-20	339	287	309	271	243	241
Nov-20	375	314	311	304	268	266
Dec-20	402	377	320	399	301	299
Jan-21	485	357	481	400	344	333
Feb-21	492	370	478	412	348	330
Mar-21	497	393	471	383	346	329
Apr-21	521	402	499	380	342	326
May-21	539	367	503	370	348	338
Jun-21	539	354	505	371	345	336
Jul-21	539	377	479	395	348	338
Aug-21	539	428	476	462	359	348
Sep-21	594	438	478	444	381	373
Oct-21	608	487	571	509	455	445
Nov-21	681	446	554	446	406	379
Dec-21	646	370	548	408	380	353
Jan-22	615	388	561	426	359	344
Feb-22	617	405	562	414	375	361
Mar-22	617	431	546	453	409	396
Apr-22	660	379	593	396	400	380
May-22	634	329	581	378	368	349
Jun-22	610	357	583	392	362	345
Jul-22	600	348	534	367	325	308
Aug-22	593	375	529	374	326	315

Figure 9: Historical Methanol Prices by Market

3.2.1.1 Renewable Methanol

The renewable methanol market, which consists of both e-methanol and bio-methanol, is only a small percentage of the global non-renewable methanol market. To be specific here, renewable methanol is green methanol with all material sources (water, CO_2, and electrical power) being renewable. Bio-methanol gets its power and feedstock components from biomass, and thus has a larger carbon footprint.

The global production capacity of renewable methanol is only 200k tons per year. By 2027, it is expected that there will be roughly 80 renewable methanol plants, capable of producing 8MT/year.

Figure 10: E-Methanol and Bio-Methanol Production Rate and Locations

As of 2022 in the USA, there is only 1 bio-methanol plant and only 1 e-methanol plant. These are the following:

Company Name	Location	Capacity	Methanol Type
Air Company (2020)	Brooklyn NY	400 tons/year	E-methanol
Geismar (2021)	Louisiana	110k tons/year	Bio-methanol

The typical price performance of renewable methanol production is shown in the following figures:

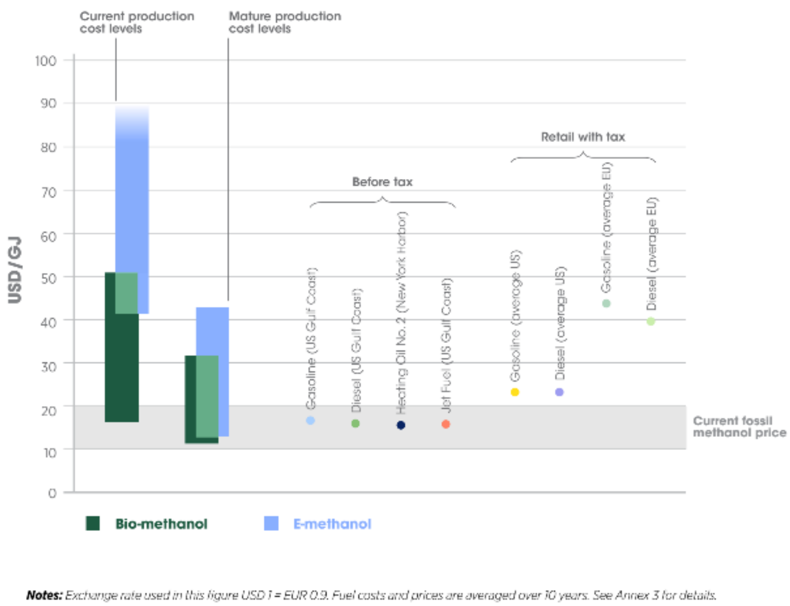


Figure 11: Typical Price of E-Methanol and Bio-Methanol vs Other Fuels

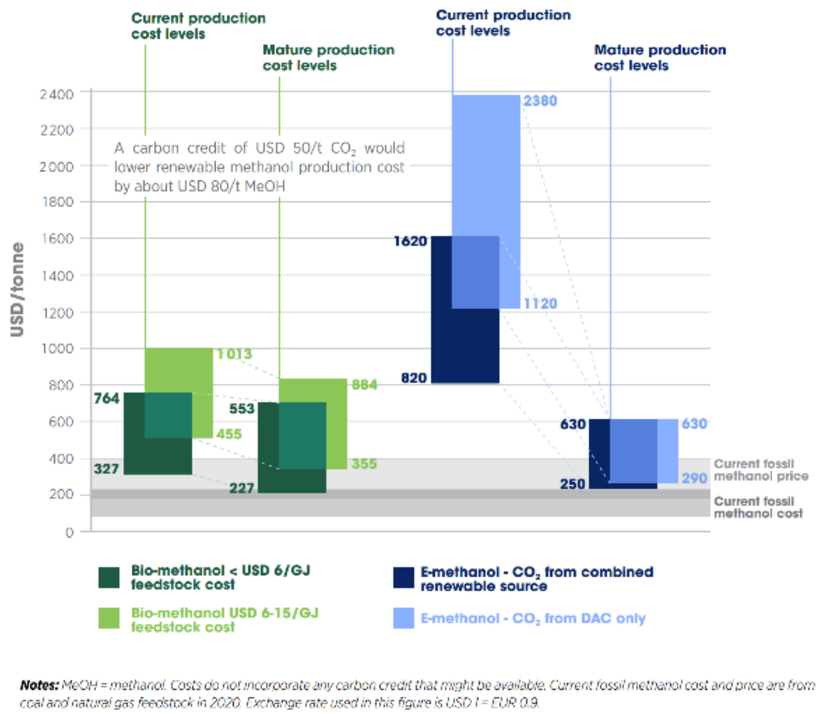


Figure 12: Comparison of E-Methanol vs Bio-Methanol Price

3.2.1.2 Renewable Methanol Driving Factors

Growth in the market is attributed to the increasing awareness of carbon emissions and environmental protection all over the world. Attributing to the increasing trend of sustainability, recycling, and bio-based chemicals have been witnessing a heavy surge in demand. Methanol is known as a key blending agent in conventional fuels to reduce their emissions, due to which it is witnessing rapid growth. Renewable methanol produced with the help of renewable feedstocks is expected to gain traction in the market. In addition to that, the rapid implication of strict regulations across emissions from vehicles and industries is anticipated to be the key factor driving the growth in the market.

As compared to gasoline, the application of methanol in internal combustion engines reduces greenhouse gas emissions by 15 to 20%. In addition, it also burns with clean fumes and can be used in spark ignition port injected gasoline engines without any modification. This makes renewable methanol a superior liquid motor fuel. Favorable government regulations in various countries, such as the U.S., China, India, and European countries, that require over 10% of renewable fuels in motor fuels by the end of 2025 is expected to drive demand for second-generation biofuels such as renewable methanol over the forecast period. The low greenhouse gas emissions and renewable feedstocks methanol fall under the next-generation fuel solutions which can adjust to strict governmental norms that are tightening their noose over various vehicle manufacturers regarding emissions.

Fuel cell technology is known as another key application of methanol. Fuel cell technology is trending due to its booming electric vehicle sales across the globe. Demand for electric vehicles has surged exponentially over the past few years, and according to a study, the market is expected to follow this trend over the upcoming assessment period of 2022– 2032. Plug-in hybrid electric vehicles extract their power from high-performance batteries rather than from fuel. Renewable methanol, which is anticipated to be environment-friendly and cost-effective, can be used in fuel-cell vehicles.

Furthermore, renewable methanol can also be fed directly to the fuel cell without its reformation with hydrogen.

Synthesis gas is a mixture of carbon dioxide, hydrogen and carbon monoxide which is used to create liquid methanol. These basic elements are utilized from a variety of feedstocks and by employing various technologies. Some of the most preferred feedstocks comprise natural gas and biomass to produce methanol. In accordance with the growing trend of sustainability and high growth in recycled and bio-based chemicals, the global renewable methanol market is anticipated to witness a surge in demand over the forthcoming decade.

3.2.1.3 Biodiesel

Methanol is a key ingredient in the transesterification of vegetable oils and fats into bio-diesel and glycerin. 20 pounds of methanol are required for the production of every 100 pounds of bio-diesel.

3.2.1.4 Methanol as a Hydrogen Carrier

The USA and Europe are subsidizing the development of the infrastructure for hydrogen-fueled vehicles, specifically hydrogen refueling stations. In the USA, all of these stations do not produce any fuel, relying on the fuel to be created at a central facility and distributed (usually by truck) to the refueling stations. While gaseous hydrogen can be produced at $4/kg, the distribution of gaseous hydrogen fuel from the centralized production facility to the refueling station costs about $5/kg because gaseous hydrogen must be stored at extremely high pressure with very thick-walled vessels and even then, it has an extremely low density. In California where most of the US Hydrogen market exists, individual trucks drive hundreds of miles to deliver a day's worth of hydrogen to an individual refueling station and drive back empty.

Methanol is a better carrier of hydrogen. It is a liquid, and hence much denser and less expensive to transport. Compared to electrolysis, which has a carbon footprint of 21 kgCO_2eq/kg of H_2 because electrolysis requires 50 – 55 kWh/kg to produce, bio-ethanol requires 90% less carbon footprint, or only 2.15 kgCO_2eq/kg of H_2. In conclusion, methanol is a powerful tool enabling the H_2 economy.

3.2.2 Oxygen

Oxygen has many medical and industrial uses. Oxygen is usually produced cryogenically, via pressure-swing adsorption, via membrane filtering, or as a chemical byproduct (such as via electrolysis). The global O_2 Generation market size was valued at USD 653.34 million in 2021 and is expected to expand at a CAGR of 2.68% during the forecast period, reaching USD 765.53 million by 2027. In 2021, global production was around 1.7MT/year.

Top Manufactures in O_2 Generation Market are:

- Linde plc
- Sumitomo Seika Chemicals
- Air Products and Chemicals, Inc.
- Praxair
- PCI
- OGSI
- On Site Gas Systems
- Atlas Copco
- Oxymat
- Air Water Inc.
- Novair

The historical price for oxygen is as follows:

Date	Value (USD/ton)
December 31, 2021	383.19
December 31, 2020	313.30
December 31, 2019	309.00
December 31, 2018	291.00
December 31, 2017	280.80
December 31, 2016	261.00
December 31, 2015	251.80
December 31, 2014	255.30
December 31, 2013	254.00
December 31, 2012	244.30
December 31, 2011	240.80
December 31, 2010	229.40
December 31, 2009	238.00
December 31, 2008	235.10
December 31, 2007	222.50
December 31, 2006	214.50
December 31, 2005	194.90
December 31, 2004	185.30
December 31, 2003	167.80
December 31, 2002	164.30
December 31, 2001	171.40
December 31, 2000	169.20
December 31, 1999	168.10
December 31, 1998	167.00
December 31, 1997	171.80
December 31, 1996	179.30
December 31, 1995	167.00

Figure 13: Table of Historical Oxygen Prices

3.2.3 Carbon Credits

CarbonCredit.com list spots prices for carbon credits in various markets around the world. The following is a list of spot prices as of 16 October 2022:

CarbonCredits.com Live Carbon Prices	Last	Change	YTD
Compliance Markets			
European Union	€67.77	-	−15.52 %
California	$26.85	-	−16.15 %
Australia (AUD)	$29.75	-	−41.67 %
New Zealand (NZD)	$81.00	-	+18.33 %
South Korea	$16.44	-	−27.52 %
China	$8.07	-	+6.97 %
Voluntary Markets			
Aviation Industry Offset	$3.75	−0.27 %	−53.13 %
Nature Based Offset	$7.89	-	−43.96 %
Tech Based Offset	$1.86	−1.06 %	−63.39 %

CarbonCredits.com Real-time Pricing (Updates Every 5 Mins)

Figure 14: Current Carbon Credit Spot Prices

Ernst and Young predicts "Prices for carbon could rise to a central estimate of US$80-$150 per tonne by 2035 (in real 2020 dollars). In comparison, prices are currently US$25 per tonne today." The following figure shows Ernst and Young's forecast for carbon credit prices.

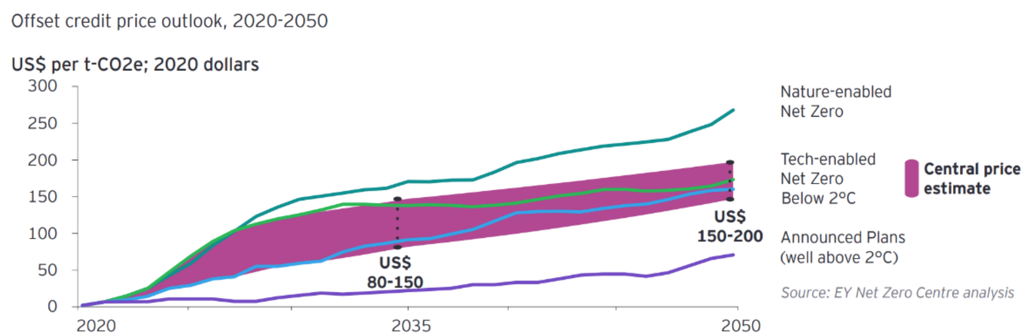


Figure 15: Carbon Credit Forecast Values to 2050

3.3 Preferred Locations for Atmospheric Methanol

Atmospheric Methanol plants are optimally placed in areas of the world where there is an excess of renewable energy, such as solar, wind, hydro, or geothermal. It is preferrable that renewable power source be consistently available 24 hours a day, instead of periodic, to minimized plant capacity costs, but not required. Hence, high hydro or geothermal areas would be better than high solar or wind, because of the periodicity.

These locations should be in an area of the world where water and carbon dioxide are available. Water can be source from surface sources or from the humidity in the air which depends on the air's average temperature and relative humidity. Carbon dioxide can be pulled from the atmosphere or from other high CO2 sources, such as the exhaust of another power plant.

These locations should also be adjacent or close to a market where the methanol and oxygen can be sold.

Such places include the following:

- Brazil: Lots of humidity and renewables.
- Southern USA, Hawaii
- Spain: Lots of sunshine, and rain
- Japan: High rainfall and humidity
- Columbia: Lots of rain, humidity, and renewables
- Chile: Lots of rain and renewables
- Norway, Sweden, Finland: Lots of renewables and water
- Canada: Lots of renewables and water
- India, Malaysia, Indonesia: Lots of renewables and water
- Iceland: Lost of renewables

4 Explore Alternatives

4.1 Power Sourcing

The most important aspect of sourcing electrical power is its cost, comprising the largest expense. The renewable nature of the fuel is critical to getting the resulting carbon credits, but this is a minor revenue.

Since transporting power over a grid incurs an additional expense, it is best if utility companies were not involved, and the power source was local.

The consistency of power is also critical to keep the utilization of the Atmospheric Methanol plant high. Therefore, hydro and geothermal renewable sources should be prioritized above solar or wind. Other sources like nuclear can achieve the cost and reliability requirements.

4.2 Water Sourcing

Water sourcing is a minor cost regarding Atmospheric Methanol.

Water can be sourced from surface water or utility water, usually at about a cost of $3 per thousand gallons, which is about $0.75/ton. This water will still need to be distilled and deionized.

Given that water is becoming increasingly scarce, water can also be pulled from the humidity in the air, which is called atmospheric water generation. Getting water from the air only increases the cost of the water slightly.

4.3 Carbon-Dioxide Sourcing

Carbon dioxide capture is one of the larger costs of the Atmospheric Methanol process after electricity. Carbon dioxide concentrations in the air are currently about 300ppm, but easily exceed 10% in exhaust gases of a combustion process. Direct air capture is the process where carbon dioxide is pulled from the general air supply. Obviously, significant savings would result if a source of high carbon dioxide concentration were found as an alternative source.

4.4 Excess Water Production – Sale of Water

Typically, water produced from AWG is expensive compared to utility water, but there are areas of the world where surface and utility water are contaminated and not potable. In these areas, AWG may be a viable optional market.

Likewise, the excess heat from the methanol generation process can also be used in thermal water distillation processes, where fresh, brackish or sea- water is distilled and/or purified into fresh water. Therefore, if there is a suitable water source, the excess waste heat could be used to generate potable fresh water.

4.5 Excess Carbon Dioxide Production – Sale of Carbon Dioxide

There are small markets for the sale of carbon dioxide, such as for soft drinks. Typically, these markets can only absorb the sale of a few tons per day.

4.6 Excess Hydrogen Production – Sale of Hydrogen

Hydrogen is a booming market. Hydrogen vehicles are refueled from 350 Bar or 700 Bar stations. For the hydrogen produced by the Atmospheric Methanol process to be sellable to the hydrogen market, it would need to be purified and compressed to these levels. In some markets, the hydrogen is liquified to make it more dense for ease of transportation.

4.7 Produced Materials

4.7.1 Sale of the Methanol, Alternative Sale of DME, Formaldehyde, Biodiesel, etc.

Atmospheric Methanol typically generates methanol, but it could just as easily generate many other products, each of which methanol is the key reagent. These include DME, Formaldehyde, biodiesel, acetic acid, etc.

4.7.2 Sale of Oxygen, and Oxygen By-Products

Industrial or medical-grade oxygen is a substantial market. The Atmospheric Methanol process makes high-purity oxygen that can be easily sold into these markets. Since transporting oxygen is difficult, sometimes oxygen needs to be liquified to make it more dense.

4.7.3 Sale of Carbon Credits

Since Atmospheric Methanol creates methanol that can replace the use of gasoline, Atmospheric methanol earns credits not only for that replacement but also for the CO_2 that it pulls from the air.

4.8 Excess Heat Production – Sale of Steam

The Atmospheric Methanol process generates waste heat in the form of steam or hot water. Because this waste heat cannot travel far before its transportation is no longer viable, the market for the waste heat is extremely local.

5 Pro Forma / Plant Calculator

The pro forma is based on the modeled Atmospheric Methanol process. The inputs for that process are the following:

- Plant Capacity (tons/year of Methanol)
- Plant Usage Rate (%)
- Source CO2 concentration (ppm)
- Source Air Humidity (lbm H_2O/lbm Air), Average

Then the plant is modeled economically with the following variables. The capital cost, operations and maintenance of the plant are all automatically calculated.

- Plant Land Cost ($)
- Methanol Value ($/ton)
- Oxygen Value ($/ton)
- Carbon Credit Value ($/ton)
- Electrical Power Cost ($/kWh)
- Contract or Plant Term (years)
- Capital Cost (Annual Interest Rate)

Also, the proforma is configured to be a calculator. All the input variables and output results are all located on the first sheet, with technical and financial details on the following sheets.

6 Patent Questions

6.1 Provide at least a few examples of exemplary operations of the system, such as overall and sub-process temperature and pressure states, material and energy flows, and material compositions.

See the DWSim model of the methanol production system.

6.2 Examples of algorithms used to operate the system

The general chemical reactions are listed in section 2. Detailed catalytic reactions formulas are included in the DWSim model

6.3 List of components used for the system

See the DWSim Model

6.4 Example storage devices used in the system

See the DWSim Model

6.5 Description of any fuel production techniques

See the DWSim Model

6.6 Quantities of amines used.

None

6.7 CO_2 saturation levels

None

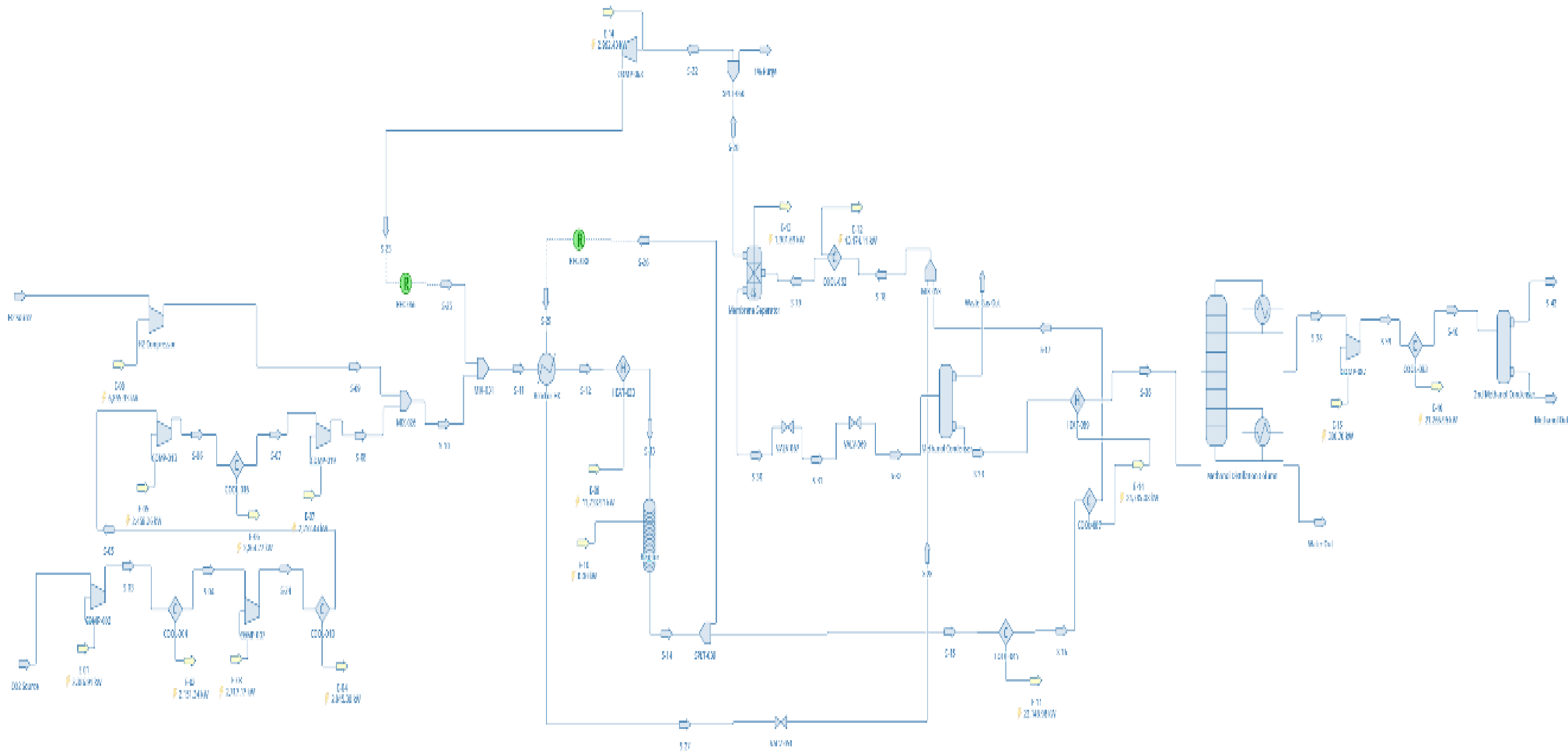
6.8 Quantity of steam produced and its state.

See the DWSim model.

7 Process Description

This section describes the methanol generation process in detail. The remaining parts of the Atmospheric Methanol process, namely AWG, DAC, and electrolysis, are not covered because there are various ways of achieving each of those goals that all achieve the inputs to the methanol generation step.

Below is a DWSim model of the Atmospheric Methanol process, which assumes the production of 59266kg per hour of Methanol.



Master Property Table				
Object	Water Out	S-42	Methanol Out	
Temperature	[illegible]	[illegible]	[illegible]	C
Pressure	1.1	1.2	1.2	bar
Mass Flow	[illegible]	[illegible]	[illegible]	kg/h
Mass Flow (Mixture) / Methanol	[illegible]	[illegible]	[illegible]	kg/h
Mass Flow (Mixture) / Water	[illegible]	[illegible]	[illegible]	kg/h
Mass Flow (Mixture) / Carbon dioxide	[illegible]	[illegible]	[illegible]	kg/h
Mass Flow (Mixture) / Carbon monoxide	[illegible]	[illegible]	[illegible]	kg/h
Mass Flow (Mixture) / Hydrogen	[illegible]	[illegible]	[illegible]	kg/h

Figure 16: Diagram of the Atmospheric Methanol Process

Overall, the process inputs are on the left and the outputs are on the right. In the middle is the generation loop, which is required because the reagents involved need to pass through the reactor multiple times, because the methanol generation process is reversible. The process inputs, hydrogen and carbon dioxide, charge this loop. The methanol separator removes the created methanol and water. Lastly, a waste valve dumps excess gases and controls the overall loop pressure. The loop produces excess waste heat, which is used to preheat the reagents for the reactor, and to heat the methanol/water mix prior to reaching the distillation column. On the right are the multiple stages of distillation that purify the methanol by removing the water and entrained gases.

The process inputs both compress and heat the incoming streams. The 12100kg/hr of hydrogen is assumed to delivered at 25C and 30bar. The 88000kg/hr of carbon dioxide are both assumed to be delivered at 25C and 1bar. Both streams are compressed to 78bar prior to injection into the loop. The compression process creates heat in both those streams. These streams can be pressurized in steps and intercooled to reduce the energy required. The model assumes the hydrogen stream is compressed all at once, requiring 6900kW of electricity and heating the hydrogen to 164C. The model assumes the carbon dioxide is compressed in four stages with intercooling. Each of the four stages requires about 2500kW of electricity. Each of the 3 intercoolers release about 2500kW of waste heat between 135 and 40C. At the end, the CO_2 is injected at 78bar and 155C.

Starting at the injection point, the loop consists of a flow of 314000kg/hr at 59C consisting of 91% H_2, 1.5% CO, 6.9% CO_2, and less than a tenth of a percent of methanol and water, all by mole fraction. This flow is heated to 210C by a regenerative heat exchanger. The flow then passes through the reactor. After the reactor the mole fraction of the stream has changed to 87% H2, 1.7% CO, 4% CO_2, 3.5% H_2O, and 3.5% methanol. The stream has also heated to 271C.

At this point the flow is split, with most of the flow going to the regenerative heater. In this heater the reactor's output at 271C cools to 90C, heating the incoming flow as already described. After reactor output is cooled in the regenerative heater it is sent to the methane condenser.

The other, smaller portion of the flow leaving the reactor is cooled to 156C. This process releases roughly 22150kW of waste heat as the flow cools. This flow then passes through the Methanol Distillation Column heat exchanger, cooling to 79C and producing 22100kW of waste heat, before rejoining the first flow on the way the methane condenser. This is a large source of high temperature waste heat. Typically, this waste heat is directed towards the AWG and DAC steps of the Atmospheric Methane process.

The methane condenser operates at 74bar and 35C. This forces the methane and water to condense and separate. To cause this condensation, 45000kW of thermal energy is released between 85C and 35C. This is large source of low temperature waste heat. The separated liquid, mostly water and methanol, is directed toward a second methanol condenser and consists of 100000kg/hr. At this point the separated liquid is 46% methanol, 46% water, 2.4% CO_2, 5.8% H_2, and 0.2% CO, by mole fraction. The separated gases are a 215000kg/hr flow, consisting of 94% H_2, 1.8% CO, 4.1% CO_2, and <1% methanol and water. A waste valve allows the escape of about 1% of this flow to control the accumulation of waste gases resulting from secondary reactions not modeled. The separated gases are recompressed to 78Bar, which heats them to 42C prior to reaching the injection point and starting the loop again.

The second methane condenser is held at 1.2bar, so the separated liquid has its pressure reduced prior to entry. This pressure reduction causes the methanol and water to flash, reducing the gas entrainment concentrations to near zero. The second methane condenser is at about 35C. The separated gases, another waste gas stream of 6950kg/hr consists of about 58% H_2, 2.3% CO, 24% CO_2, 3% water, and 13% methanol, by mole fraction. The separated liquid is a stream of 92100kg/hr, consisting of 50% methanol and 50% water, with only trace amounts of CO, CO_2, and H_2. This separated liquid, on the way to the methanol distillation column, is heated in a heat exchanger to 80C by the second part of the loop.

The methanol distillation column separates the flow into one that is mostly water and the other that is mostly methanol. The water flow of 33900 kg/hr is almost pure water. The methanol flow has 59300 kg/hr of almost pure methanol. This flow can be further compressed and cooled in additional stages to remove the tiny amount of remaining entrained gases, if required to meet quality standards.