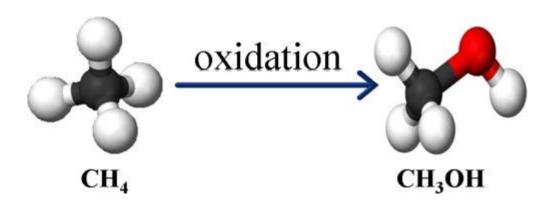
The Methane Story – Part 2 Methane (CH₄) vs. Methanol (CH3OH)

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Methane vs. Methanol

Recently someone asked me why there was so much talk about using methanol both as a carrier of green hydrogen and as a fuel for maritime and other transportation when we know that it is a much worse greenhouse gas than CO₂. After a few minutes of discussion, I realized that he was confusing *methanol* with *methane*. Which generated the idea for this article.

Last week I posted The Methane Story Part 1 – which was focused on methane, how it differed from carbon dioxide, and what was being done to reduce methane emissions. But despite the similar names, methane is definitely **not** the same as methanol.

Methane (CH₄) and methanol (CH₃OH) are both chemical compounds, but they differ completely in terms of their molecular structures, properties - and uses.

While methane is a simple hydrocarbon gas used primarily as a fuel (as the major component of natural gas), methanol is a liquid alcohol with diverse applications - and associated toxicity.

Some key differences are outlined in the table below:

	Methane	Methanol
Chemical Structure	Simple hydrocarbon consisting of a single carbon atom bonded to four hydrogen atoms.	Also known as methyl alcohol and sometimes wood spirit or wood alcohol, methanol consists of a single carbon atom bonded to three hydrogen atoms and one hydroxyl (-OH) group.
Physical State	Colorless, odorless gas at room temperature and atmospheric pressure.	<i>Liquid</i> at room temperature and atmospheric pressure.
Sources	Naturally occurring gas - and the primary component of natural gas. It is also produced during the decay of organic matter and is a significant greenhouse gas.	Can be produced synthetically from natural gas or obtained from the destructive distillation of wood. It is also produced naturally in small quantities by using anaerobic bacteria.
Uses	In the form of natural gas - is commonly used as a fuel for heating, cooking, and electricity generation. It is also used as a feedstock for the production of various chemicals.	Wide range of uses, including as a solvent, antifreeze, and as a feedstock for the production of chemicals such as formaldehyde and acetic acid. It is also used in the production of biodiesel and is becoming more widely used in maritime transportation.
Flammability	Highly flammable and can form explosive mixtures with air in certain concentrations.	Flammable, but less so than methane. Its vapors can ignite when exposed to an open flame.
Toxicity	Not toxic; however, it can displace oxygen in enclosed spaces, leading to asphyxiation.	Toxic to humans and can cause blindness or death if ingested. It is important therefore to handle methanol with care.

Bottom line: methanol is a more versatile carbon source than methane and is a readily transportable liquid. It can be used to make a large number of products. Most significantly; while methane is an extra powerful greenhouse gas, methanol can be used as a clean fuel, as will be discussed.

BTW, the other compound that *methanol* often gets confused with is *ethanol*. (CH₃CH₂OH). While methanol and ethanol are both alcohols, they are very different types. Ethanol, also known as ethyl alcohol, is formed by combining an *ethyl* group with a hydroxyl group, while methanol is created by combining a *methyl* group with a hydroxyl group. Ethanol has two carbon atoms, while methanol has only one.

Ethanol is the primary ingredient in alcoholic beverages. Since methanol is highly poisonous it is not appropriate for that type of use at all. More than 98% of U.S. gasoline contains ethanol (@10%) to oxygenate the fuel. Ethanol is typically prepared by the fermentation of food crops from factories. Methanol is manufactured mainly by synthetic processes.

Let's focus next on how methanol is currently used.

Uses of Methanol

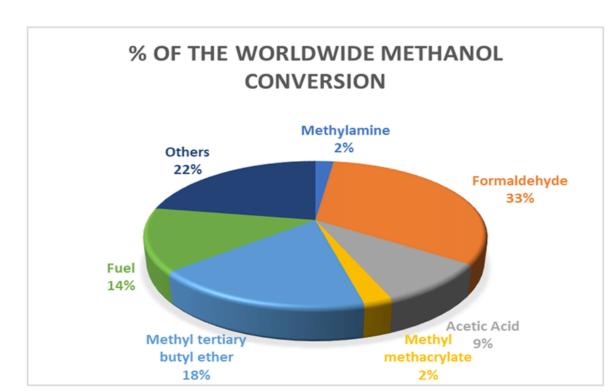
Methanol and its derivative products - such as ascetic acid and formaldehyde created via chemical reactions - are used as base materials in acrylic plastics, synthetic fabrics and fibers used to make clothing, adhesives, paint, and plywood, and as a chemical agent in pharmaceuticals and agrichemicals.

Some specific major uses include:

1. Formaldehyde: Methanol readily transforms into formaldehyde which is a heavily used commercial product in the production of fertilizer, paper, plywood, and some resins. It is also used as a food preservative and in household products, such as antiseptics, medicines, and cosmetics.

2. Biofuel: Methanol can be used as a renewable fuel source. It is cheaper, has a reduced flammability risk, and is more easily acquired than gasoline, although it is not generally used as a replacement. It has a lower energy density than gasoline but has still been used as a fuel in racecars. It can be a substitute for diesel fuel when combined with potassium hydroxide. More on the use of methanol as a transportation fuel to come.

3. Fuel Cells: Methanol can be used as the fuel in fuel cells as it can store a large amount of energy while taking up only a small amount of space. These cells often exist in small devices like laptops and phones.



4. Windshield Washer Fluid: Methanol is effective for deicing windows because alcohols have a much lower freezing point than water.

Source: Research Gate

5. Wastewater Denitrification: Methanol can be used to prevent the formation of harmful, toxic algal blooms in water. Algal blooms are generated by bacteria that proliferate in the presence of nitrate. By adding methanol to a wastewater system, anaerobic bacteria activity is increased. That bacteria can break down the nitrate in the water and allow it to be released into the air as nitrogen.

6. Dimethyl Ether: Methanol can be converted to dimethyl ether, which is commonly used as an aerosol propellant.

7. Acetyl Resin: Methanol can be used to create heat resistant and durable thermoplastic used in high intensity mechanical operations in industries including automotive, technology, and healthcare.

8. Camping Fuel: Methanol is often used to fuel camping stoves because only a small volume is required to fuel the stove.

9. Acetic Acid: Methanol is a component of acetic acid which is used for pickling in the food industry, household cleaners, and as an antiseptic in medical procedures.

10. Laboratory Solvent: Methanol is used as a solvent for liquid chromatography (HPLC - a broad analytical chemistry technique used to separate compounds in a chemical mixture) analysis or ultraviolet/visible spectroscopy (UV-vis). It is also used as drying agent and solvent for laboratory instrument analysis.

As will be described below, there are a variety of new uses for methanol – particularly green methanol. And new ways to create it.

Using Methanol as a Carrier for Green Hydrogen

As I discussed in an article a few months ago on the difficulties of transporting Green Hydrogen, a lower cost alternative being developed is *materials-based storage*, where solids and liquids that are chemically able to absorb or react with hydrogen are used to bind it and then carry it for transport. The substances currently most identified as potential hydrogen carriers are liquid ammonia and methanol.

Given its high energy density, methanol can potentially be an efficient hydrogen carrier, packing a large amount of hydrogen in one simple methanol molecule and enabling the storage of a large amount of energy in a small volume. Since it is a liquid at ambient conditions, methanol can be easily handled, stored, and transported, leveraging the existing infrastructure that supports the transport of methanol. That also makes it safer to transport than gaseous hydrogen. And, since it is less flammable than hydrogen, the risk of accidents during transportation and storage are also lower than that of gaseous hydrogen.

Methanol reformers are able to generate on-demand hydrogen at the point of use to avoid the complexity and high cost associated with converting liquid hydrogen back to a gas – a major advantage over converting hydrogen to a liquid for transport.

A very complex image of methanol as a hydrogen carrier published by the Methanol Institute is copied below.



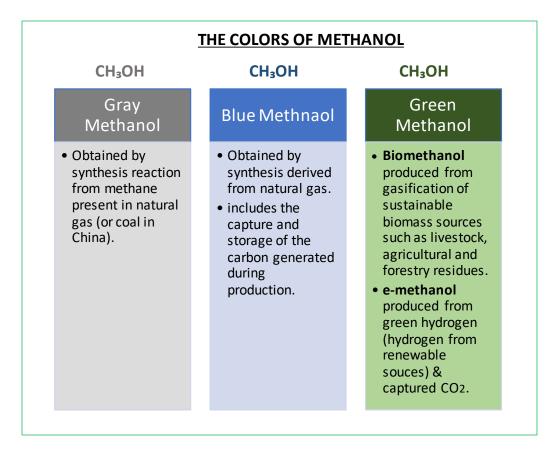
Green Methanol

To date, the vast majority of methanol produced is generated from natural gas, which links it directly to greenhouse gas emissions. However, green methanol is becoming much more common

Very much like the case with hydrogen, methanol is being classified according to the degree of sustainability of its production process – which makes it a more or less environmentally friendly raw material. As with hydrogen, different "colors" are attributed to methanol based on that process, as described below.

Green hydrogen is generated through a chemical process known as electrolysis, which uses electric current generated by renewable sources to separate hydrogen from the oxygen in water. When the hydrogen is synthesized together with captured/recycled carbon dioxide – say from a biomass power plant after the pyrolysis process – the form of Green Methanol known as *e-methanol* can be distilled.

Green methanol can be used as a low-carbon liquid fuel and is a promising alternative to fossil fuels in areas where de-carbonization is a major challenge, such as maritime transport. Green Methanol as a maritime fuel is more bully discussed below.



There are multiple companies that are producing green methanol. One example is *Carbon Recycling International,* an Icelandic company which has developed a technology designed to produce renewable methanol from carbon dioxide and hydrogen, using water electrolysis or, alternatively, hydrogen captured from industrial waste gases.

Methanol as a Transportation Fuel

A variety of advantages of methanol make it a leading alternative maritime fuel choice for today and the future, offering the shipping industry a clear pathway to decarbonization. Because it is a liquid at room temperature, it is much less costly to store and transport than gaseous fuels and has the lowest carbon footprint of all liquid fuels. It can also be used in both internal propulsion engines **and** to power fuel cells, providing flexibility depending on individual needs. In the short term, conventional methanol reduces greenhouse gas emissions from combustion, while in the medium to longer term as its availability grows, Green Methanol can enable the industry to meet the International Maritime Organization's decarbonization goals. Since Green Methanol is chemically identical to conventional methanol, there are no compatibility issues or further engine investments required of shipping companies, allowing a seamless, gradual transition from conventional to Green Methane. Green Methanol is also compatible with current methanol dual-fuel engine technology.

Even non-Green Methanol can reduce SOx and PM emissions by more than 95%, and NOx by up to 80% compared to conventional marine fuels.

Methanol also has a higher volumetric energy content than alternative clean maritime fuels like ammonia or hydrogen, making it a better choice for a wide range of vessel types and longer voyages, as it requires less frequent bunkering.

As a result of the above, the cost of converting diesel engines to methanol dual-fuel vessels - and landbased infrastructure to store and supply methanol - is significantly lower than other alternative fuels that require pressurization or cryogenics – like hydrogen.

Although ammonia can also be made from green hydrogen for use as a maritime fuel (or skip hydrogen entirely as is done by an Israeli company called NitroFix which has developed a process to generating ammonia from nitrogen and water only), it is highly toxic and requires special storage. In contrast, methanol is biodegradable and therefore can be handled and stored much like gasoline, requiring fewer retrofits or infrastructure changes and making it much safer if it spills.

Back in 2022, the maritime company Cosco – based in Shanghai - reported that it had ordered a dozen methanol-burning ships. The major shipping line Maersk has committed to introducing 19 container ships by 2025 that run on e-methanol (they may also be able to run on biodiesel). Maersk has also agreed to buy half a million tons of hydrogen-based and biogenic Green Methanol per year (with an undisclosed split between the 2) from Chinese wind farm Goldwind.



One Green Methanol hurdle is cost – it can be 3-4 times as expensive as diesel-based marine fuels. The expected drop in the cost of Green Hydrogen will clearly help. And, although methanol has had a headstart over ammonia in the shipping industry over the past year, the International Energy Agency (IEA) warns in a recent report, entitled <u>The Role of E-fuels in Decarbonizing Transport</u>, that methanol could be 25-100% more expensive than ammonia, This is largely because of the need to provide captured CO_2 — from biogenic sources or direct air capture — to ensure that the Green Methanol produced is carbon-neutral over its lifetime. The IEA calculates that equivalently optimized plants, located on sites with high-quality renewable resources and low-cost biogenic CO_2 , would produce low-emission e-methanol today at a cost of \$47/GJ, compared to eammonia at \$40/GJ, with these costs respectively falling to \$35/GJ and \$30/GJ by 2030.

So why are shipping companies opting for more vessels capable of running on methanol rather than ammonia in the short term?

One reason is the increased cost of managing safety. While both ammonia and methanol are hazardous chemicals, ammonia is toxic at much lower concentrations, necessitating extra costs for corrosion-resistant tanks and on-board safety measures such as spacing out storage, double piping, leak detectors and dedicated ventilation systems. So, while methanol is more expensive to produce, ammonia is more expensive to handle

Furthermore, methanol is currently covered in the International Maritime Organization's *Interim Guidelines for the Safety of Ships Using Methyl/Ethyl Alcohol as Fuel*, and engines capable of running on the fuel are already commercially available. However the UN agency is yet to update its guidance for ships using low-flash-point fuels or those carrying liquefied gases in bulk to allow for ammonia to be used as a fuel.



Source: Vessel Finder

Methanol is currently available at more than 125 of the world's largest ports. Industry interest in methanol as a marine fuel is rapidly growing, leading to commitments from some of the world's largest shipping companies to companies that offer methanol as a maritime fuel – such as <u>Methanex</u>, which is the world's largest producer and distributor of methanol.

The bottom line is that methanol appears to be ready to take off as a meaningful clean fuel for the maritime industry.

Converting Methane to Methanol

While the theme of this article is the differences between methane and methanol, there has in fact long been interest in finding an economical and efficient way to *convert* methane into methanol. This would not only help reduce methane emissions, but it would also provide an economic incentive to do so while at the same time greatly increasing the availability of methanol – hopefully dropping its cost in the process.

Researchers have been interested in ways to convert methane to methanol at ambient temperatures to sidestep all the heat and pressure that has traditionally been required in industrial processes to perform this conversion.

A primary challenge of converting methane to methanol has been the difficulty of weakening or breaking the carbon-hydrogen (C-H) chemical bond in order to insert an oxygen (O) atom to form a C-OH bond. Conventional methane conversion methods typically involve two stages; steam reforming followed by syngas oxidation, which are energy intensive, costly and inefficient as they require high temperatures and pressures.

A team of researchers from Stanford University and the University of Leuven in Belgium proposed an approach to convert methane into methanol back in 2021. The process uses common crystals known as iron zeolites to convert natural gas to methanol at room temperature.

When methane is infused into porous iron zeolites, methanol is rapidly produced at room temperature with no additional heat or energy required. By comparison, the conventional industrial process for making methanol from methane requires temperatures of 1,000°C (,1832°F) and extreme high pressure.

Stanford has acknowledged that their approach is challenging to achieve since methane is chemically inert and most iron zeolites deactivate quickly. Therefore, there are still significant barriers to scaling this process up to industrial levels.

Also in 2021, scientists from the University of Illinois, Chicago (UIC) <u>reported a new method</u> for the conversion of methane in natural gas into liquid methanol at room temperature.

Huge amounts of pressure and heat have been needed to disintegrate the hydrocarbon bonds present in methane gas, which is the initial step to be performed to produce methanol. The UIC team reported that it had discovered a catalyst material that helps reduce the energy required to break such bonds so that the reaction can occur at room temperature. The catalyst, which includes copper and titanium. along with a small amount of electricity, enables the disintegration of methane's hydrocarbon bonds and the synthesis of methanol. The process consumes much less energy compared to conventional techniques,

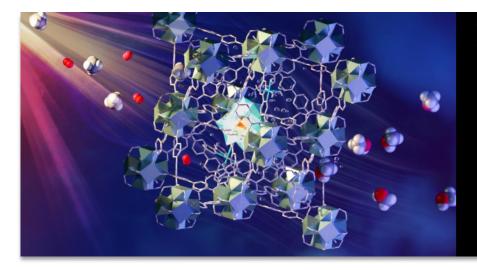
and since there is no need for machinery to produce high heat and pressure, it can be set up rapidly and cost-efficiently.

In what appears to be the most significant development towards a more effective conversion method, in 2022 an international team of researchers led by scientists at the University of Manchester (in England), developed a fast and economical method of converting methane into liquid methanol at ambient temperature and pressure.

The method involves a continuous flow of methane along with oxygen-saturated water over a metalorganic framework (MOF) catalyst while exposed to light. The MOF is porous and contains different components that each have a role in absorbing light, transferring electrons, and activating and bringing together methane and oxygen. The MOF contains different designed components that are located and held in fixed positions within the porous superstructure. They work together to absorb light to generate electrons which are passed to oxygen and methane within the pores to form methanol.

Liquid methanol is then easily extracted from the water. This type of process has been an area of focus for research supported by the U.S. Department of Energy. The team's findings are published in an article in Nature Materials titled "Direct photo-oxidation of methane to methanol over a mono-iron hydroxyl site".

Oak Ridge National Laboratory has referred to this development as "the 'holy grail of catalysis' — turning methane into methanol under ambient conditions using light".



University of Manchester scientists have developed the "holy grail of catalysis," a fast and economical method of converting methane, or natural gas, into liquid methanol at ambient temperature and pressure. Credit: ORNL/Jill Hemman

Source: Oak Ridge National Laboratory

By eliminating the need for high temperatures or pressures and using the energy from sunlight to drive the photo-oxidation process, the new conversion method could substantially lower equipment and operating costs. The higher speed of the process and its ability to convert methane to methanol with no undesirable byproducts should facilitate the development of processing procedures that minimize costs......and when rolled out results in a significantly increased amount of methanol – combined with a reduced amount of methane

Bottom Line

Methane is not the same as methanol.

That being said, it appears that there is going to be a push very soon to *convert* significantly more methane into methanol. Which will be an effective way to achieve the desired goal of reducing the amount of methane in the atmosphere.

At the same time, there is a major movement to expand the role of methane as a clean fuel – starting with Green Methane used in maritime transportation.

So, methane vs. methanol: *vive la difference*.

As they say.