

A. Routes for making methanol from the full range of feedstocks

A.1. Introduction - fuel grade methanol production

Although methanol synthesis using modern catalysts is very reaction specific in producing methanol and water from CO, CO₂ and H₂, the product stream also contains some other chemical species as co-products, ethanol being the most significant. Between them the co-products may constitute as much as 1.5% to 2% of the total product make. For the production of chemical grade methanol, a refining step is required to bring the methanol content of the final product to a specification of 99.9% or 99.98% methanol. This refining step reduces the yield of finished product and costs additional energy.

Plants built specifically to produce fuel grade methanol will be up to 2% more efficient because, when making fuel grade methanol, the only refining step required is to reduce the water content to about 5% by volume. This leaves all the minor compounds in the fuel, but all of them are acceptable ICE fuel components.

A.2. There are many routes to methanol

Methanol, unlike oil or gas, does not occur naturally, but, like hydrogen, it is an energy vector. There are a very large number of routes to make methanol. These range from very large scale processes based on gas, coal or other fossil resources, to a range of processes based on renewable biomass feedstocks, through to advanced processes based on using hydrogen from electrolysis using renewable or nuclear low carbon electricity, combined with CO₂ recovered from flue gases, exhaust gases, industrial processes or even recovered from the atmosphere. Many, but not necessarily all, of the possible routes to methanol are shown in figure A-1 and A-2.

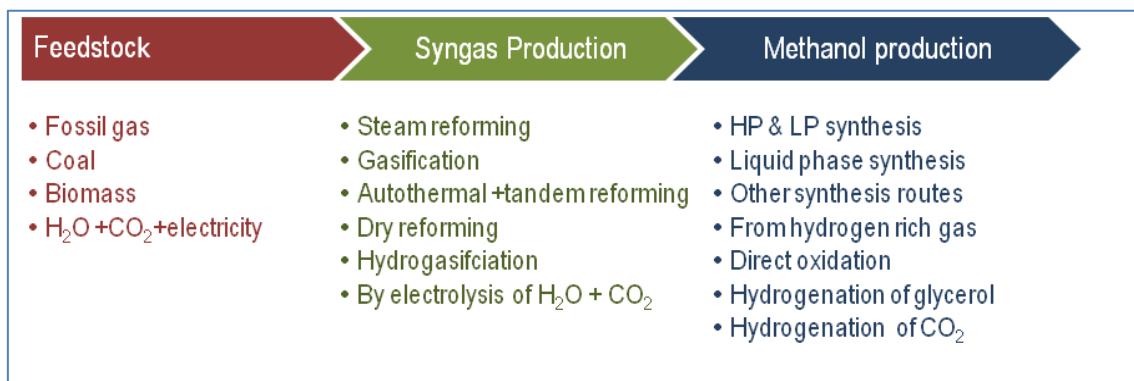


Figure A-1 Simplistic table of routes to methanol

A.3. Overview of the major current production routes

A.3.1. Natural gas steam reforming

Currently, the major large scale production route to methanol is based on first steam reforming natural gas to syngas, which is a mixture of hydrogen (H₂), carbon monoxide (CO) and carbon dioxide (CO₂), and then processing the syngas to methanol. The largest methanol mega-plants based on this process are around 1mtpa¹, but plants have been built up to as large as 1.7mtpa. Such a plant is equivalent to an oil refinery of 23kdb²

¹ mtpa: million tons per annum

² kbd: thousand of barrels oil per day. A refinery of capacity 200kdb (UK average) makes approximately 6.9mtpa of high-value transport fuel. This is equivalent to approximately 14.8mtpa of methanol (Methanol has 47% of the energy content of gasoline / diesel). UK refining capacity of 1,819kdb is, therefore equivalent to ~80 mega methanol plants.

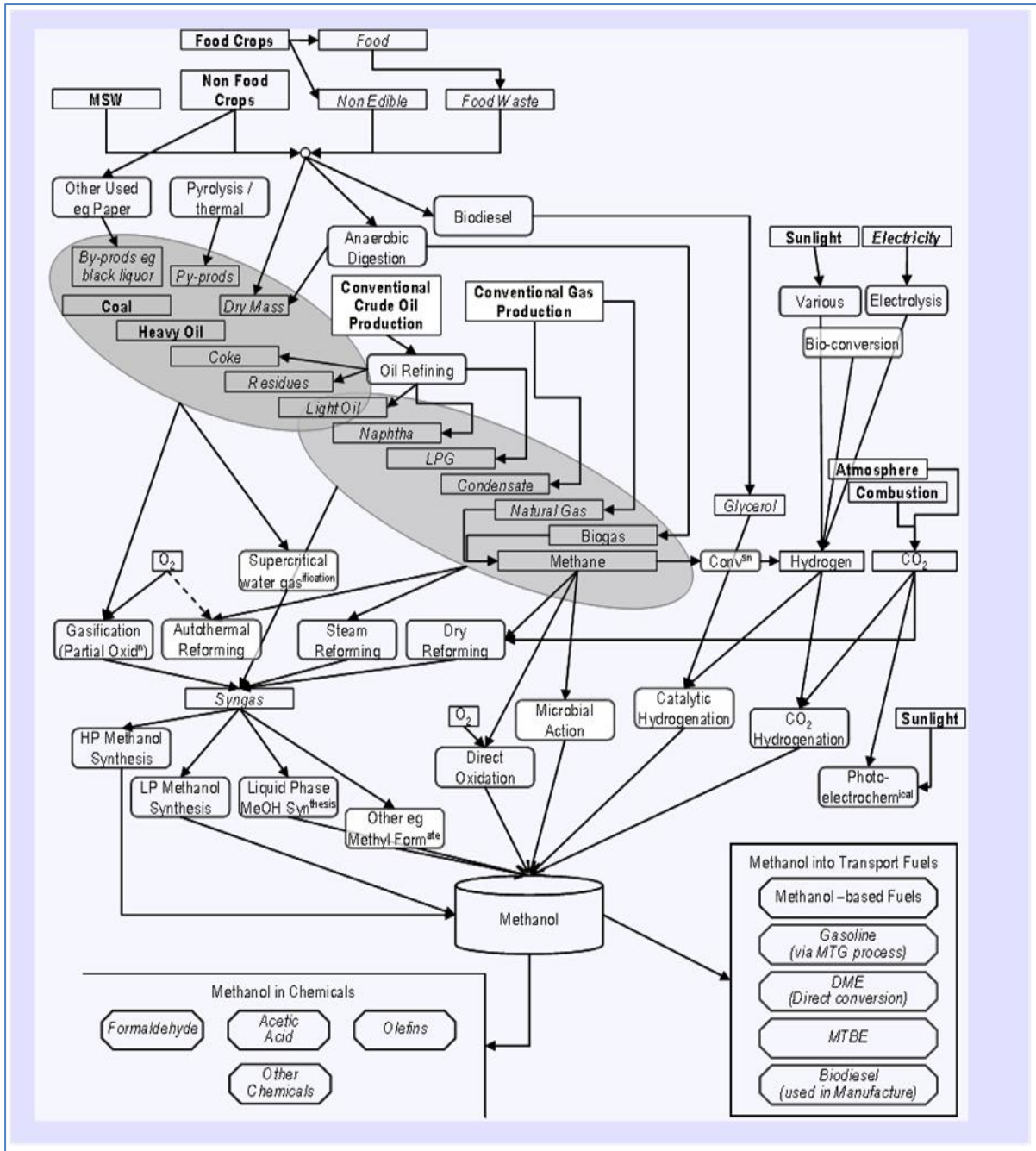


Figure A-2 Production routes for making methanol

In the short to medium-term a lot of effort is going into process improvement and development of large scale natural gas plants. This can be expected to result in better designs with higher efficiencies and lower costs over coming decades. In the near term, until the more advanced technologies are ready for market, it is expected that most methanol will be manufactured from gas in large-scale steam reformer based plants.

A.3.2. Heavy fossil feedstock/biomass gasification

Steam reforming cannot be used satisfactorily for heavy feedstocks such as coal, heavy oil or the residues from conventional oil refining. These feedstocks can however be converted to syngas by gasification (partial oxidation) which uses oxygen to generate the process heat required for the endothermic parts of the chemical reactions. The syngas from heavy feedstocks contains many contaminants that must be removed prior to conversion of the syngas to methanol.

There are many gasification plants in operation worldwide. Most of the syngas production from these plants is presently either burned to make electricity, or used in Fischer Tropsch synthesis, such as at the Sasol plants in South Africa.

Generally partial oxidation gasifiers are more capital intensive than natural gas steam reformers.

Gasification is also a viable route to convert biomass to syngas and several plants are running successfully on a range of feedstocks from wood chips to black liquor (a by-product of paper manufacture). To gain the economies of scale available from larger gasification units they must be run at near full capacity. As biomass generally has a low energy density per hectare of land cultivated and also often has a high water content, the costs of collection and transportation are high, which means there is a maximum catchment area that makes sense commercially for any given size of plant, or conversely, a minimum size plant for any given size of catchment area.

A.3.3. Syngas production processes

Syngas production by all process techniques is favoured by high temperatures and low pressures. The key syngas production routes are described in the table below.

Syngas Production Route	Description
Steam reforming	<p>Steam reforming is best suited for reforming natural gas where the principal component within the natural gas is methane, but it also works for other light hydrocarbons such as ethane, propane and butane.</p> <p>These light hydrocarbons can be reformed at high temperatures (800-1,000°C) and low pressures (typically <25bara³) in the presence steam and a nickel-based catalyst to form a mixture of CO and H₂. This reaction is very endothermic⁴ requiring a significant input of heat that is usually provided either by burning process off-gas, or by combining the process with partial oxidation (see autothermal reforming).</p> <p>Part of the CO formed reacts with steam in the water gas shift (WGS⁵) reaction to yield more hydrogen.</p> <p>Steam reforming results in a syngas with more than the ideal⁶ ratio of hydrogen. In some cases this excess hydrogen can be separated for use elsewhere, or it can be burned to provide the process heat for the endothermic steam reforming reaction.</p>
Gasification (partial oxidation)	<p>Heavier feedstocks, including coal, heavy oil, oil refining residues and biomass, may be converted to syngas by partial oxidation⁷, which is the incomplete combustion of the feedstock in the presence of water. Where the product syngas is to be burned, for example in a gas turbine, the oxidising agent would usually be air as nitrogen dilution is acceptable, but for making methanol, pure oxygen is normally used to avoid the presence of nitrogen in the reaction mixture. This adds expense to the process as an oxygen plant must usually be constructed as part of the project. The amount of oxygen used is</p>

³ bara: pressure measured in bar where 1 bara is atmospheric pressure

⁴ For methane, the reaction $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ requires 49.1 kcal per mol of heat input

⁵ $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ – this reaction is slightly exothermic giving out 9.8 kcal per mol.

⁶ The ratio (or stoichiometry) of components in syngas is given by $S = (\text{conc. H}_2 - \text{conc. CO}_2)/(\text{conc. CO} + \text{conc. CO}_2)$, where concentrations are in moles. For steam reforming this is ~2.8 to 3.0 where the ideal ratio is 2.0. For partial oxidation the ratio falls to nearer 1.0. Dry reforming result in $S = 1.0$.

⁷ The primary reactions are $\text{C}_n\text{H}_m + m\text{H}_2\text{O} \rightarrow m\text{CO} + (n+m/2)\text{H}_2$; $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$; $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ and $\text{CO} + \text{CO}_2 \rightarrow 2\text{CO}$

	<p>minimised so that there is just enough heat to ensure the feedstock conversion takes place and no more.</p> <p>Most heavy feedstocks contain impurities, particularly sulphur and inorganics. These must be removed prior to the methanol synthesis step. Partial oxidation results in a syngas with less than the ideal⁶ ratio of hydrogen.</p> <p>A recent New Scientist article discusses the merits of using gasification as a means of constructively using municipal waste (Ref A.8.7.43).</p>
Autothermal and tandem reforming	<p>When steam reforming and partial oxidation are combined with a natural gas feedstock, the process heat required for the endothermic steam reforming step can be produced from the parallel or tandem exothermic partial oxidation reaction. The result is a syngas with an ideal⁶ ratio of hydrogen. Tandem reforming was developed by GIAP (the Russian Energy Company) and is offered by Linde (Ref A.8.7.17).</p>
Dry Reforming	<p>Methane may be reformed using CO₂ instead of steam - so called dry reforming. The process requires more process heat than steam reforming⁸ and results in a syngas with a less than ideal⁶ ratio of hydrogen. For feedstocks with a high proportion of CO₂ present, such as biogas, combining dry reforming and steam reforming (Ref A.8.7.2), which can be done using the same catalysts, reduces the process heat required and allows approach to the ideal ratio of hydrogen for methanol synthesis.</p>
Hydrogasification	<p>The Hynol process, originating from the Brookhaven National Laboratory (USA), is a process for converting biomass to syngas at high-temperature (1,000°C) and under moderate pressure (~30bara). Gasification is carried out in the presence of hydrogen to produce methane and carbon monoxide that, after a further reforming step, can be processed in a methanol synthesis reactor. The exothermic heat from the methanol synthesis step is sufficient to dry the initial biomass feed. Carbon efficiency of >85% is claimed.</p>
Syngas by co-electrolysis of CO ₂ / H ₂ O	<p>Recent research has shown that electrolysis at high temperatures (700-800°C) of CO₂ / H₂O in the presence of hydrogen can yield a syngas that can then be converted to methanol. This route of electrolysis is more efficient than direct water electrolysis to produce hydrogen. (Ref A.8.7.22)</p>

A.3.4. Making the syngas into methanol

Methanol synthesis from syngas is favoured by high pressures and low temperatures and it produces a significant amount of low level heat⁹. Some of the key synthesis routes are described in the table below:

Syngas conversion Route	Description
Gas-phase (HP & LP) synthesis	Synthesis of methanol from syngas was pioneered by BASF during the 1920s. The process was based on making syngas from coal and industrial off-gases at very high pressures (250 to 350 bara) and moderate temperatures (300-400 °C). ICI (now Syntex) developed a lower pressure

⁸ CO₂ + CH₄ → 2CO + 2H₂ requires 70.7 kcal per mol of heat input compared to 49.1 kcal for steam reforming.

⁹ The main reactions producing methanol are: CO + 2H₂ → CH₃OH (21.7 kcal per mole exotherm) and CO₂ + 3H₂ → CH₃OH + H₂O (9.8 kcal per mole exotherm) – the water gas shift reaction also comes into play converting CO₂ to CO.

	(LP) process (50-100 bara) at lower temperatures (200-300 °C). Lurgi have a similar process. LP methanol synthesis processes now dominate methanol production worldwide. The processes use highly selective copper-based catalysts working in the gas phase.
Liquid phase synthesis	Air Products has developed a liquid phase process for converting syngas to methanol. Catalyst is suspended in an inert oil and the syngas is bubbled through the liquid. This achieves a higher one pass conversion than the LP gas phase synthesis route.
Other synthesis routes	Other syngas to methanol routes are being developed to reduce the pressures and temperatures needed for synthesis and to improve the thermodynamic efficiency. One route is through methyl formate where CO is reacted with methanol to make methyl formate, which is then hydrogenated to make methanol with part of the produced methanol re-cycled back into the process as a reagent.
Methanol from other hydrogen / CO rich gas	Some industrial processes produce gas streams containing large quantities of hydrogen and carbon monoxide. After suitable clean-up these gases may be suitable for methanol synthesis. For example, coke oven gas may be one suitable source (Ref A.8.7.7).
Direct oxidation of methane)	Syngas production from methane requires significant input of high level heat to drive the endothermic reaction. The subsequent synthesis of methanol from the syngas is exothermic and produces a significant amount of low level heat. The direct oxidation of methane to methanol ¹⁰ is therefore a desirable route as it is more energy efficient. The main problem associated with direct oxidation is the higher reactivity of other oxidation reactions which favour formation of CO ₂ and H ₂ O. (Ref A.8.7.10 and Ref A.8.7.14)
Hydrogenation of glycerol	Glycerol is the by-product from biodiesel manufacture (by trans-esterification) and can be hydrogenated directly to methanol. Ref A.8.7.6)
Hydrogenation of carbon dioxide	Many methods of producing methanol by hydrogenation of CO ₂ are known. Depending on the sources of hydrogen and carbon dioxide, this can be an excellent low carbon way of producing methanol. Similar catalysts to those used in methanol production are suitable.
Hydrogenation of carbon dioxide (cont.)	In 1999, using a UK Government SMART feasibility award, Zero-m demonstrated the feasibility of combining photovoltaic electrolytically produced hydrogen with carbon dioxide to make methanol as a way of storing electricity and/or hydrogen Mitsui Chemicals are building a 100tpa pilot plant to make methanol by direct hydrogenation of carbon dioxide as part of the Chemical CO ₂ Immobilisation Project.

A.4. Hydrogen sources as a basis for methanol production

There are a wide variety of sources of hydrogen and considerable research is being undertaken in this area. Wherever hydrogen can be made, so can methanol. Methanol offers a practical method of storing hydrogen as once made from hydrogen methanol can be readily converted back into hydrogen¹¹. It is also much more easily stored and distributed than hydrogen.

Syngas conversion Route	Description
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¹⁰ CH₄ + ½O₂ → CH₃OH with 30.4 kcal per mole exotherm

¹¹ Methanol is very easily decomposed into hydrogen and CO₂. This process occurs at low pressures and relatively low temperatures (200-300°C)

to hydrogen	
From fossil fuel	<p>Some light hydrocarbons are reformed as part of the standard oil refining process to produce high octane fuels. Hydrogen is co-produced and the majority of this hydrogen is used in-refinery for other processes.</p> <p>In general terms this is the only method of making hydrogen on an industrial scale today.</p> <p>Until the bulk of fossil power generation has been replaced with renewable or nuclear power so that surplus renewable power exists for electrolytic hydrogen production, steam reforming fossil fuel feedstocks (including natural gas) will be the only practical production route for hydrogen for transportation fuel use, whether that is in fuel cell vehicles, or in more traditional ICE vehicles.</p> <p>This means that it will be a long time before the transport sector can be decarbonised by adoption of renewable electricity or hydrogen.</p>
From methane	<p>Methane can be decomposed into carbon and hydrogen. This is, potentially, a low carbon route to make hydrogen as the carbon produced by the process is in solid form and can be readily sequestered.</p>
From electricity	<p>Electrolysis of water produces oxygen and hydrogen. Where the electricity is produced with a low carbon footprint then the hydrogen will also have a low carbon footprint. Where renewable electricity is available and where the oxygen produced by the electrolysis can be utilised – for example for the partial oxidation of biomass then the hydrogen can be utilised to further hydrogenate some of the CO₂ produced.</p> <p>As noted above however, from the point of view of maximising the reduction of carbon dioxide emissions it will only make sense to use renewable or nuclear electricity for electrolysis to produce hydrogen for transportation fuel use once all fossil power generation capacity has been replaced by renewable or nuclear electricity plants to the extent that at least off peak electricity is renewable.</p>
From sunlight	<p>In addition to the possibility of making hydrogen from biomass through partial oxidation, there are several more direct routes being researched such as hydrogen producing algae.</p>

A.5. Carbon dioxide sources

Carbon dioxide is a minor natural component of the atmosphere where, despite being essential for all plant growth and therefore for supporting all life on Earth, rising levels since the industrial revolution are attributed to the activities of mankind and now believed to be responsible for harmful climate change.

Carbon dioxide is produced in many industrial processes where fossil fuels or biomass are combusted, from road and air transport and also, naturally, from deforestation and volcanism.

Production Route	Description
Post-combustion CO ₂	<p>Combustion of carbon containing compounds leads to a gas rich in CO₂. This CO₂ may be extracted by one of a series of known acid-gas extraction processes. Where the fuel has been combusted in air, the CO₂ is much diluted by nitrogen and therefore more difficult to extract. For the most effective post-combustion extraction of CO₂ it is desirable that the fuel be combusted in an oxygen rich gas, for example, as produced using pressure swing absorption (PSA).</p>

Pre-combustion CO ₂	Where a process gas has been produced, for example in a partial oxidation reaction prior to combustion in a gas turbine combined cycle plant, the CO ₂ may be extracted more easily before combustion than afterwards because it is then at a higher concentration.
Atmospheric CO ₂	CO ₂ may be extracted from air. In remote locations where renewable hydrogen can be produced, for example using photovoltaic electricity for water electrolysis, CO ₂ extraction directly from the atmosphere for subsequent reaction with hydrogen to produce storable methanol is technically feasible.
Photo-electrochemical reduction of carbon dioxide	Taking hydrogen from water and hydrogenating CO ₂ using a semiconductor photocatalyst on the anode side results in protons diffusing to the cathode side where CO ₂ is converted to methanol ¹² (Ref A.8.7.15)
Recycling CO ₂ and hydrogen via methanol	Where renewable hydrogen from, say, renewable electricity based electrolysis is available, methanol can be used as an efficient means of storing it and delivering it to a vehicle. Using on-board decomposition / reforming of methanol fuel with subsequent recovery of the CO ₂ , means the fuel delivered to the engine is substantially hydrogen (purified as necessary for fuel cell engines).
Recycling CO ₂ and hydrogen via methanol (cont.)	<p>The CO₂ that was recovered on board can then be returned to the fuelling point for conversion with more renewable hydrogen back into methanol. The volume of CO₂ recovered, stored on-board and delivered back to the fuelling station is approximately the same volume as the methanol fuel from which it was produced. This means a “bag-in-a-box” storage system can be used to keep the total on-board fuel storage volume small.</p> <p>Where waste heat is available from an internal combustion engine, this may be used to drive the endothermic decomposition / reforming reaction, thereby uplifting the calorific value of the fuel to be combusted and enhancing fuel efficiency.</p> <p>Zero-m has IP in this area.</p>

A.6. Large scale methanol production from fossil fuel resources

The reserves of natural gas are vast – rivalling the quantity of recoverable conventional oil.

Where the gas would otherwise not be used, for example where gas is associated with more valuable liquid oil production with no viable gas market nearby, or where the associated gas volumes are not large enough to support pipeline or LNG projects, building methanol plants avoids the need to re-inject, flare, or much worse, vent the surplus.

Large modern methanol plants have a thermal efficiency around 70-72% with the most efficient new mega-plant designs approaching 75%. Because steam reforming natural gas results in excess hydrogen, the carbon efficiency of the new mega-plants is well over 90%. With thermal efficiency up to 80%, operation of methanol plants would not lead to the emission of any CO₂. Furthermore because less purification is needed to make fuel grade methanol, methanol fuel plants will be 1-2% more efficient than their chemical grade predecessors.

If, as often happens, associated gas contains moderate amounts of CO₂, methanol manufacturing plants can make methanol from it, whereas the CO₂ would have to be removed and disposed of at an additional carbon or financial cost in the case of a pipeline or LNG project.

¹² The overall reaction for the production of methanol is $2\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2$

In this way large-scale methanol manufacture for fuel use can help reduce, or prevent altogether, greenhouse gas emissions from conventional oil production operations.

As a means of monetising remote gas, methanol manufacture in the largest methanol mega-plants, in the range 1.0 to 1.7 mtpa, rivals LNG¹³ and GTL¹⁴ such that there is a huge, potentially very fast growing, economic opportunity to begin making methanol fuel from these resources now.

In the marketplace there is plenty of capacity to build these plants, for example, in 2007, Lurgi received contracts for methanol mega-plants with capacities ranging from 0.67 to 2.3mtpa (Ref A.8.7.16).

While the resource base for natural gas based methanol is similar in size to the conventional oil resources, coal reserves are much greater than those of conventional oil, as are the reserves of extra heavy oil, unconventional oil and residues¹⁵. This means that the resource base for methanol production by the gasification route is many times larger than that for conventional petrol and diesel.

Large-scale gasification plants result in a syngas that has excess CO₂ that is relatively easy to separate and sequester compared to post (air) combustion flue gas CO₂ sequestration. Although the greenhouse gas emissions from gasification of coal and other similar feedstocks are high relative to conventionally refined oil products, with sequestration, the emissions from gasification can be reduced to less than those from making transport fuels from conventional oil.

Methanol is an excellent solvent for CO₂ and is the reagent basis for the Rectisol® process. Incorporation of CO₂ capture into any fossil or biomass gasification process scheme for methanol manufacture will improve greenhouse gas emissions and reduce their carbon footprint. As methanol is already by definition within the process scheme, Rectisol® can be incorporated at lower capital and operating costs than other stand alone carbon capture systems. (Ref A.8.7.42).

A recent study from the RAND Corporation (Ref A.8.7.21) estimates up to 15% of US fuel demand (3 million barrels per day) could be coming from coal to liquids plants by 2030 and the opportunity for pre-synthesis carbon capture has the potential to make this a low carbon option.

Overall therefore, this analysis supports the conclusion that the resource base available for methanol production from fossil sources is approximately six times larger than the resource base of yet to be produced conventional oil. With pre-synthesis CO₂ capture, this could all be produced with a lower carbon footprint than conventional petrol and diesel fuel.

A.7. Small scale methanol production

Single purpose methanol production plants require good economies of scale to justify their investment. However, designed correctly, small-scale production can also be an efficient and economically sensible route to follow.

¹³ LNG: Liquefied Natural Gas: where the gas is liquefied (-161°C) and transported in large insulated vessels, discharged into and stored at coastal terminals where the LNG is re-gasified to pump into National Natural gas networks.

¹⁴ GTL: Gas to Liquids: usually referring to the manufacture of Fischer Tropsch liquids that are an excellent substitute for diesel. GTL plants include the Sasol Moss gas, the Shell Bintulu and several Qatar plants (currently on-stream or under construction).

¹⁵ Extra Heavy Oil is also called unconventional oil. This covers the bitumens and heavy hydrocarbons found in the tar sands in Canada, Venezuela, USA, Nigeria, Russia and (unknown quantities) Middle East. Shale oil found extensively in N America also makes a suitable feedstock. Also the residues from conventional oil processing such as petroleum coke, vacuum residue, visbreaker residue, hydrocracker residue are a resource and conversion to methanol presents an opportunity to efficiently route these hydrocarbons to transport fuels.

Combined Heat and Power (CHP) is already established as a viable low carbon route to generate power and heat.

Co-production of methanol, electricity and heat is also viable at small-scale as local use of the co-produced heat and embedded electricity generation enhances the economics in just the same way as in conventional CHP.

Zero-m have recognised that there are extensive natural gas pipeline distribution infrastructures in most of the developed markets carrying very large quantities of natural gas to existing power, commercial and heating markets. Methane gas could be drawn from this infrastructure to manufacture methanol transport fuel close to large potential consumer sites, such as trucking depots.

To create an opportunity from this situation, Zero-m has designed a small-scale production plant that co-produces heat, power and methanol fuel and exploits the synergies available from producing all three outputs simultaneously at very high overall system efficiency. The Zero-m unit can be placed near to market on pipeline gas, or it can be used to exploit local production of biogas.

The unit is innovative in terms of its use of low cost, mass produced components, its process flow design and its thermodynamic balance. Output from the unit in LHV¹⁶ terms comprises 55% fuel, 22% electricity and 23% heat and requires 15% less feedstock than would be required to produce the same output from large scale methanol plants, gas CCGT electricity generation, or from gas space heaters.

In addition to pipeline gas, the unit is designed to utilise gaseous feedstocks such as biogas from anaerobic digestion, landfill gas, coal bed methane and small sources of associated remote gas at oilfields.

When the units are positioned close to the consumer it removes the need for long distance transport and distribution of conventional fossil hydrocarbon transport fuels.

A.8. Low carbon and renewable methanol production

As any biomass can be made into renewable methanol via a range of processes potentially production volumes are huge.

There are a large number of ways in which methanol can be manufactured with low greenhouse gas emissions from biomass or fossil feedstocks. The principle ones are:

- Biomass: gasification / syngas
- Biogas: anaerobic digestion (AD) and landfill gas
- Very carbon efficient use of fossil gas or AD gas
- Hydrogenation of CO₂ -where the hydrogen is produced with low carbon emissions e.g. from renewable electricity.
- Supercritical water biomass conversion

A.8.1. Biomass: gasification / syngas

A.8.1.1 Biomass Sources

Almost any type of biomass is suitable for gasification including:

- High cellulose content material such as wood waste from forestry, short rotation energy crops, residual woody bio-matter, wood chips, cereal straw, corn stover, rice husk, water hyacinth, seaweed etc.
- Whole plant matter from energy crops such as miscanthus, corn, red canary grass

¹⁶ LHV: lower heating value or net calorific value: compared to HHV (higher heating value or gross calorific value) excludes the heat from condensing water vapour in the products.

- Waste such as food waste or MSW¹⁷
- Industrial agricultural waste such as bagasse from sugar cane processing, black liquor from paper processing, or solid residues from edible oil crushing
- Residues from Anaerobic Digestion

A.8.1.2 Biomass pre-gasification Processing

The chemical composition of biomass varies greatly as does the level of co-collected non-biomass material.

Faster growing plants tend to contain more ash and hetero-atoms (atoms that are not hydrogen, carbon or oxygen), in particular nitrogen, potassium and chlorine. Straw contains up to 10% ash while wood is a relatively “clean” feedstock.

Biomass has a low bulk energy density and transport costs become very significant where feedstocks have to be collected from a large area to supply a central large scale biomass gasifier.

If the moisture content is too high additional energy will be required for drying, or in severe cases incomplete processing may occur because optimum operating temperatures may not be reached throughout the feedstock charge.

Mechanical processing and some drying may be required close to the biomass source to both make the feedstock more suitable for processing and to increase bulk energy density to enhance transport economics.

In some cases it may also be helpful to use heat processes, such as fast pyrolysis, to produce an intermediate pyrolysis liquid or char, which have bulk energy densities many times greater than unprocessed straw to concentrate the biomass prior to transporting it to a central large plant (Ref A.8.7.34).

A.8.1.3 Gasification

Almost any solid or liquid biomass can be processed by partial oxidation (gasification) to make syngas. Gasification involves a complex series of reactions involving the exothermic¹⁸ oxidation of the carbon in the biomass to CO and CO₂, oxidation of the hydrogen to H₂O, and the endothermic¹⁸ reactions between water, carbon and carbon dioxide to make CO and H₂. The objective of the gasification process is to convert as much of the feedstock as possible into a gas rich in CO and H₂ with the minimum concentrations possible of methane or higher hydrocarbons and tars and chars – all without using too much excess oxygen.

The syngas compositions from a number of biomass gasification processes are (Ref A.8.7.13):

% volume	Atmospheric air-blown CFB	Atmospheric oxygen-blown CFB	Nitrogen Pressurised Oxygen-blown CFB	CO ₂ pressurised oxygen-blown CFB	Atmospheric steam-blown indirect gasifier	Pressurised oxygen-blown direct EFG	10MW Gasifier (Ref A.8.7.18)
CO	19.3	26.9	16.1	16.1	42.5	46.1	15.8
H ₂	15.6	33.1	18.3	18.3	23.1	26.6	37.3
CO ₂	15.0	29.9	35.4	46.9	12.3	26.9	34.7

¹⁷ Municipal Solid Waste

¹⁸ Exothermic reactions generate heat while endothermic reactions absorb heat.

N ₂ / CH ₄	4.2	7.0	13.5	13.5	16.6	0.0	11.4
N ₂ / Ar	44.5	0.7	12.3	0.8	0	0.4	0.3
C ₂	1.4	2.4	4.4	4.4	5.5	0.0	0.0
NCV ¹⁹	5.76	8.85	8.44	8.05	13.64	7.43	
H ₂ / CO ratio	0.81	1.23	1.14	1.14	0.54	0.58	2.36
CFB: circulating fluidised bed gasifier; EFG entrained flow gasifier							

Oxygen-blown circulating fluidised bed gasifiers or char indirect gasifiers are better for making syngas suitable for methanol production than pressurised gasifiers. However, pressurised units have the advantage that they output pressurised syngas thus avoiding some of the energy cost of pressurising the syngas to methanol synthesis pressures.

Pressurised oxygen-blown direct entrained flow gasifiers (Ref A.8.7.32) operating at elevated pressures (10 to 60 bara) and higher temperatures (1,200-1,500°C) have the advantage of a short residence time provided the feedstock is finely divided. This keeps process plant sizes and capital costs lower.

Biomass gasification in the presence of hydrogen, such as in the Hynol process (Ref A.8.7.40), with an additional reforming step to produce syngas, is potentially a very efficient route to making methanol from biomass. The process flow conditions and catalyst system are all well known and the yield of methanol is very high because little purification (mainly to remove surplus water) is needed prior to use as a fuel.

A.8.1.4 Large scale bio-methanol production

Almost any biomass, from purpose grown energy crops to MSW, is a potential resource for methanol manufacture.

However, the nature of the biomass resource base means that “large scale” for bio-methanol production is much smaller than “large scale” fossil fuel based plants. The widespread low density nature of biomass may prohibit construction of just a few large scale process units utilising primary sourced biomass without the need for additional smaller “satellite” processing plants to help feed them. Perhaps the smaller plants would use, for example, thermal decomposition, to first make outlying biomass crops, too distant from the main plant for economic transportation in their own right, into high energy-density bio-oils and other thermal decomposition products that may be readily stored and efficiently transported to a central large plant.

Producing methanol via syngas from biomass (or other gasification feedstocks) encounters the inherent problem of a less than ideal stoichiometric ratio⁶. One way to ameliorate this and simultaneously provide some or all of the oxygen requirement for gasification, is to include an electrolysis unit to electrolyse water to produce hydrogen and oxygen in the process design. (Ref A.8.7.10).

Several types of industrial scale biomass gasification plant are emerging or already available:

- One technology that is already proven at pilot scale is for the gasification of black-liquor²⁰ (ref A.8.7.17).

¹⁹ NCV: net calorific value – also called lower heating value (LHV) – the heat released on combustion excluding the heat of condensation of the water content of the products.

- Other routes are discussed in the ECN report (ref A.8.7.18).
- Lurgi, sponsored by the German Federal Ministry for Nutrition, Agriculture and Consumer Protection, is to build a 2nd generation biofuel plant (commissioning 2011) at Karlsruhe making syngas from straw.
- Syntec Biofuel Inc have developed a process (Ref A.8.7.9) to produce methanol from waste cellulosic material such as woodchips, corn stover, sugar bagasse and straw in their B2A process.

Current pilot activities related to biomass and gasification include the Choren Industries high temperature oxygen-blown slagging entrained flow gasifier (Freiburg, Germany); Chemrec A.B. black liquor air-blown gasification (Sweden); ECN (& Shell Global Solutions) pressurised oxygen-blown entrained flow gasifier (Netherlands); Varnamo IGCC plant (Sweden); Gussing CHP Plant (Austria).

A.8.1.5 Biomass gasification and electrolysis hydrogen

Oxygen is required for biomass gasification as air-blown gasification leads to synthesis gas with a very high nitrogen content unsuitable for methanol synthesis. Additionally, the synthesis gas produced by gasification has a lower hydrogen content than the stoichiometric ideal.

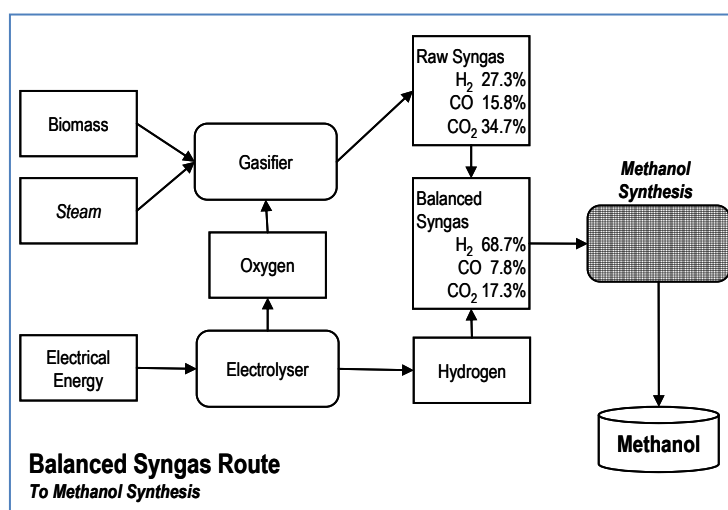


Figure A-3 Balanced syngas methanol production route

Electrolysis of water produces both oxygen and hydrogen that can be utilised to provide the oxygen for the gasifier and to optimise the stoichiometric ratio of the syngas for methanol production. (ref. A.8.7.19)

A.8.1.6 Biomass gasification developments

In addition to the processes and sources of biomass described in A.8.1.5 the following biomass conversion systems are also under development.

Location and choice of feedstock for biomethanol plants has been studied for various situations, geography and agronomy. A study in Austria indicated significant potential (Ref A.8.7.11) as does a study in Japan (Ref A.8.7.12). A European study also identifies prospects (Ref A.8.7.13).

A recent study by Eindhoven University of technology concluded that mass conversion yields of methanol from bio-waste via gasification were high with good exergetic efficiency approximately 30% better than those for heat and power production (Ref A.8.7.46).

²⁰ Black liquor is a by-product of the paper processing industry. Large quantities of this liquor are produced as part of the process and the black liquor contains inorganic chemicals that need to be recovered to make green liquor which is used in the paper making process.

A.8.2. Biogas – anaerobic digestion (AD) and landfill gas

Production route	Description
Anaerobic digestion	Anaerobic digestion of biomass is a well known process by which a variety of biological materials are digested by bacteria in the absence of oxygen to produce a gas that largely consists of methane and carbon dioxide. Land-fill gas is the result of anaerobic digestion of waste materials that have been accumulated in landfill waste disposal sites. Purpose built anaerobic digesters utilise materials such as farm waste, food waste or other biological material
Anaerobic digestion (AD) gas production Anaerobic digestion (AD) gas production (cont.)	<p>Some anaerobic digesters are designed to operate at temperatures of around 35°C (mesophilic) while others operate at higher temperature around 55°C (thermophilic). Thermophilic digestion can lead to higher yields of biogas in shorter periods of time.</p> <p>The processes take place in two stages – hydrolysis and acetogenesis which converts bio-degradable material to intermediate products for methanogenesis where the methane-rich gas is evolved. The reactions can take place in a two stage reaction system or in a single reaction system, but there is a trade-off between biogas yield and capital and operating costs. Clean-up of the gas is required to remove contaminating compounds²¹ before feeding to the methanol synthesis system.</p> <p>The methane content of the biogas can vary from below 40% to above 60%, in some case even as high as 80% depending on a variety of factors.</p> <p>A review of many processes was prepared for Renewables East (Ref A.8.7.38). The University of Natural Resources and Applied Life Science (Vienna) has reviewed the use of sustainable energy crops as AD feedstocks (Ref A.8.7.39).</p>
Landfill gas	<p>Many landfill sites are fitted with gas reticulation systems that collect the gas generated inside the sealed landfill and pipe it to a central point. Often this gas is flared or, at best, used in a gas engine to generate electricity.</p> <p>The quality of the gas is generally poorer than gas produced from a purpose designed anaerobic digester and must go through a more intensive clean-up process before it can be used to make methanol.</p>
Methanol synthesis from AD biogas	<p>Biogas is primarily a mixture of methane (CH₄) and carbon dioxide (CO₂). CH₄ may be reformed using CO₂, a process known as dry reforming²² and results in a syngas with less than the ideal stoichiometric ratio of hydrogen to other components. Generally there is insufficient CO₂ in biogas to get a high conversion of the CH₄ into CO and H₂.</p> <p>By mixing the biogas with steam, a combination of dry reforming and steam reforming²³ reactions can be employed, which use the same catalysts used commercially for steam reforming. This also reduces the process heat required and allows approach to the ideal ratio of hydrogen (Ref A.8.7.2).</p> <p>The syngas produced is readily converted to methanol using conventional technology.</p>
Combined AD gas and	Production of AD gas from biomass proceeds very rapidly in the first few hours of digestion

²¹ AD gas contains sulphurous gases such as H₂S and SO₂ as well as some acidic gases (HCl and HF) that are deleterious to the methanol synthesis system.

²² CO₂ + CH₄ → 2CO + 2H₂ requires 70.7 kcal per mol of heat input compared to 49.1 kcal for steam reforming.

²³ For methane, the steam reforming reaction CH₄ + H₂O → CO + 3H₂ requires 49.1 kcal per mol of heat input

<p>gasification</p> <p>Combined AD gas and gasification (cont.)</p>	<p>as the more accessible molecular types are consumed by the AD bacteria. Although prolonged exposure can convert more of the biomass to biogas, it is possible to take the digestate from the relatively quick early stage and feed this to an oxygen-blown gasifier. Reforming the AD gas and combining the reformat with the gasifier product stream to feed a methanol synthesis reactor (with re-cycle) coupled with further gasification of part of the methanol reactor effluent stream, leads to a very efficient methanol synthesis system.</p> <p>A moderate scale combined plant situated close to suitable sources of biomass will produce a high yield of fuel methanol that can easily be stored and transported to market. The design of a combined plant has been studied and the performance considered. (Ref A.8.7.41)</p>
<p>Small scale methanol production from AD gas or landfill gas</p>	<p>Zero-m has designed a small scale combined fuel, heat and power unit (CFHP) that is innovative in the use of low cost mass produced components, process flow and thermodynamic balance. Output from the unit in LHV²⁴ terms comprises 55% fuel, 22% electricity and 23% heat and requires 15% less feedstock than would be required to produce the same output in large scale methanol plants, gas CCGT electricity generation or gas space heaters.</p> <p>The unit is designed to utilise gaseous feedstocks such as natural gas from the pipeline system, but it can equally well be designed to use biogas from anaerobic digestion or from landfill. The positioning of these units close to the consumer cuts out the need for the long-distance transport and distribution of fuel normally associated with conventional fossil hydrocarbon transport fuels</p>

A.8.3. Very efficient use of fossil gas

The bulk of the world's supply of methanol is manufactured from natural gas in locations where the gas cannot be readily piped to mature markets. By a process of steam reforming or autothermal reforming²⁵ at high temperatures, followed by methanol synthesis at moderately high pressures, there is highly efficient conversion of methane to methanol. The most efficient new mega-plants have thermal efficiencies approaching 75% and because steam reforming natural gas results in excess hydrogen, the carbon efficiency of the new mega-plants is well over 90%.

Because of the location and size of the mega plants, there is no market for the waste heat produced as a result of the processing and often little opportunity for efficient co-production of electricity.

However a Zero-m purpose built unit produces fuel close to where it is required and cuts out the road transport normally required for fuel distribution. At small scale in units located near to a national electricity grid and near to users of space of hot water heating it is possible to very efficiently co-produce methanol, heat and power. Zero-m has designed a unit to process between 0.5MW and 5MW of feedstock.

In the Zero-m design, in contrast to the methanol mega-plants, very high overall system efficiencies are possible because of the thermodynamic linkage between the different elements and also because there is no need for the very high methanol specific conversion and high purification process steps necessary in the large plants. As a result the Zero-m plant needs 20% less carbon, power and heat than a mega-plant.

²⁴ LHV: lower heating value or net calorific value: compared to HHV (higher heating value or gross calorific value) excludes the heat from condensing water vapour in the products.

²⁵ Autothermal reforming combines steam reforming with partial oxidation to produce a syngas with an ideal stoichiometric ratio.

The unit can process natural gas from the gas main and as explained above is also ideal for processing AD or landfill gas.

A.8.4. Hydrogenation of CO₂

In nature, CO₂ is re-cycled through photosynthesis in green plants, which capture CO₂ and convert it with water using the sun's energy and chlorophyll as the catalyst. No pathway has yet been developed to reproduce this process of nature at an industrial scale to make fuel. A photo-catalyst where sunlight is captured to reduce CO₂ directly to methanol is under development (Ref A.8.7.15). This takes hydrogen from water and hydrogenates CO₂ directly using a semiconductor photo-catalyst on the anode side giving protons that diffuse to the cathode side where CO₂ is converted to methanol.

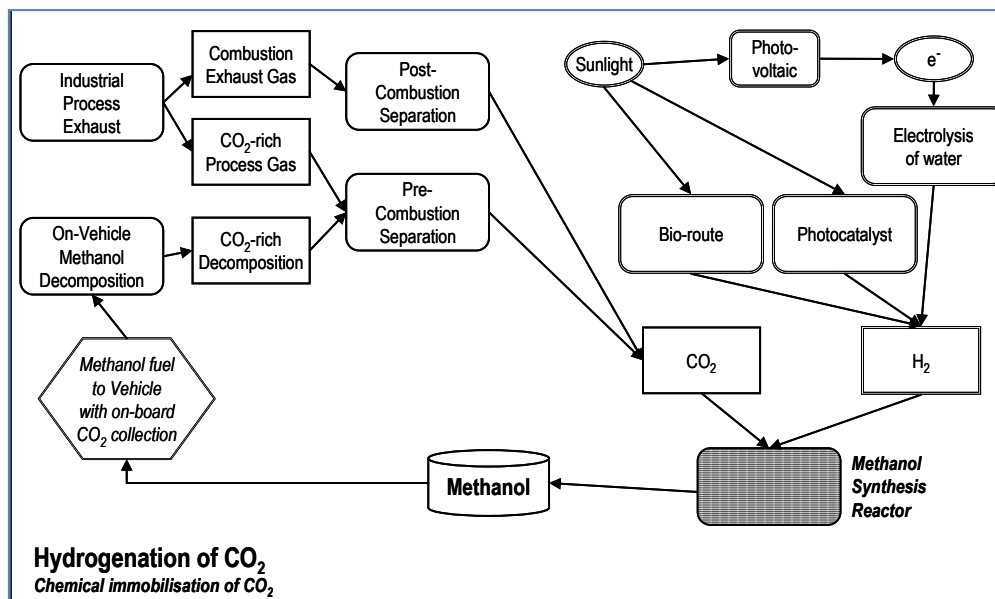
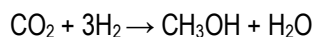


Figure A-4 Hydrogenation of CO₂

Chemists have known for over 80 years that methanol can be made from CO₂ and some early methanol plants used this process. Where hydrogen can be produced renewably, or with a low carbon footprint, then advantage can be taken of the simple conversion of carbon dioxide into methanol by hydrogenation by the following reaction:



Mitsui Chemicals are building a 100tpa pilot plant to make methanol from CO₂ as part of the Chemical CO₂ Immobilisation Project (Ref A.8.7.25).

A.8.5. A carbon dioxide hydrogenation process cycle for road transport vehicles.

Zero-m gained a UK SMART award in 1999 to demonstrate the feasibility of storing photo-voltaic electrolytic hydrogen as methanol essentially by hydrogenating captured CO₂.

Zero-m has also investigated the feasibility of collecting CO₂ on board a vehicle when methanol is used as a fuel as feedstock for this process.

Methanol is readily decomposed into hydrogen and CO₂ at low pressures and temperatures (200 – 300°C). For the simple de-composition reaction, the net calorific value of the products is a little more than 19% greater than the net calorific value of the base liquid fuel and results in a gaseous mixture of CO and H₂ that is suitable for use in an internal combustion engine (ICE). The exhaust heat from such an engine can be used to drive the

decomposition and effectively uplifts the efficiency of the engine²⁶.

After combustion of the hydrogen and carbon monoxide in the engine the exhaust contains only water, nitrogen and carbon dioxide. The carbon dioxide can be removed from this mixture, liquefied and stored on board to be returned to base for subsequent hydrogenation with more hydrogen converting it back into methanol fuel again.

In this way the carbon dioxide can be used as a hydrogen/energy carrier making the hydrogen/energy into a simple easily manageable liquid fuel via a simple process cycle.

A.8.6. Supercritical water gasification

Water, under supercritical conditions²⁷, rapidly decomposes biomass to produce syngas while suppressing the formation of tar and char. This route is very promising as a means to produce high quality syngas with a good stoichiometric ratio, particularly where the original feedstock is wet – as is the case with much biomass (Ref A.8.7.4).

²⁶ All other factors being equal, the use of exhaust heat to decompose all of the methanol would turn an engine operating at 40% efficiency to one operating at 47.7% efficiency. Clearly, 100% conversion efficiency cannot be obtained in practice. However, preliminary consideration of the system indicates a potential to achieve a 15% uplift, which, all other factors being equal, would potentially increase a 40% efficient engine to 46% efficiency very close to the likely efficiency of a fuel cell vehicle.

²⁷ Water at above 374°C and pressures greater than 223bara becomes supercritical and exhibits very different characteristics. Under these harsh conditions, biomass is rapidly decomposed and leads to syngas formation.

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