BACKGROUND INFORMATION

Workshop

Advanced Biofuels

Towards Renewable Energy Transition in Europe

Background Information to the Workshop "Advanced Biofuels: Towards Renewable Energy Transition in Europe"

in Brussels, 5th September 2019

CONTENT

Introduction

To place the subject of the workshop in the right frame and to structure the information needed as much as possible, first a simplified overview of fuels for combustion engines is provided, classified according to feedstock, conversion method and product(s):

Raw materials		Conversion process	Product examples	
Fossil	crude oil natural gas black coal	**Chemical** syngas (Fischer-Tropsch) thermochemical …	**Liquid**	ethanol butanol gasoline kerosene rape oil diesel OME XtL
Organic	**Biomass** sugar(s) starch (hemi)cellulose oils & fats proteins lignin	**Biotechnological** microorganisms enzymes	**Gaseous**	natural gas biogas DME methane hydrogen
Inorganic	CO_2 H_2O	**Physical** pyrolysis electrolysis …		

Figure 1: *Overview of fuels classified according to feedstocks, conversion methods and products.*
OME = Poly-oxy-methylene-dimethyl ether ($H_3C\text{-}O\text{-}(CH_2O)_n\text{-}CH_3$, $n \geq 2$), XtL = X-to-Liquid, DME = Dimethyl ether

XtL fuels (X-to-Liquid) includes GtL (Gas-to-Liquid), CtL (Coal-to-Liquid) and BtL (Biomass-to-Liquid).

GtL describes a process converting fossil natural gas into synthesis gas by addition of oxygen and water vapor. Subsequently, Fischer-Tropsch reaction is applied for the transformation of synthesis gas to liquid hydrocarbons.

CtL processes are chemical processes converting solid black coal to liquid hydrocarbons.

In **BtL** processes, biomass is converted to synthesis gas, followed by the application of the Fischer-Tropsch reaction or the methanol-to-gasoline (MtG) process resulting in biofuels. Although these fuels differ chemically from conventional ones, they can still be used in petrol or diesel engines. BtL fuels are so-called second-generation biofuels.

Regarding biomass, one has to distinguish between such that may be used as food or feed and such, which may be not. This discrimination has its origin in the “food or fuel” debate. Hence, a more specific split of biomass for the production of fuels in general is depicted here:

Raw materials		
Fossil	crude oil natural gas black coal	
Organic	**Biomass**	food/feed
		non-food/ feed: e.g. residues waste energy crops
Inorganic	CO_2 H_2O	

Conversion process
Chemical syngas (Fischer-Tropsch) thermochemical …
Biotechnological microorganisms enzymes
Physical pyrolysis electrolysis …

Product examples	
Liquid	ethanol butanol gasoline kerosene rape oil diesel OME XtL
Gaseous	natural gas biogas DME methane hydrogen

Figure 2: *Overview of fuels with a more specific split of the biomass compared to figure 1.*
OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, $n \geq 2$), XtL = X-to-Liquid, DME = Dimethyl ether

Advanced Biofuels: The European Commission describes advanced biofuels in the RED II (Renewable Energy Directive II) as fuels produced from feedstock that does not compete directly with food and feed crops, such as waste (i.e. municipal waste, animal manure), agricultural residues (i.e. wheat straw, husks, nut shells), non-food crops (i.e. miscanthus, switchgrass) and algae. (Clarification: Algae [“3G biofuels” producer] are not feedstock: Algae are rather a “conversion factory”! The feedstock here is CO_2.)

The transition from **fuels** in general to **advanced biofuels** leads to the following eliminations or conditionalities:

On the side of the raw materials:

- Exclude: fossil raw materials and food/feed biomass

... and on the side of the products:

- Exclude: 1G (first-generation) alcohols; rape (plant) oil, (bio)diesel (FAME/RME[1])
- OME is ok, only if the primary raw material to produce it was renewable methanol
- XtL: exclude GtL, CtL
- Exclude: natural gas
- DME is ok, as long as it is produced from non-food/feed biomass

1 *Fatty acid methyl ester (FAME) is produced from vegetable oils. In Germany the basic material is mostly rapeseed oil, therefore biodiesel is often called RME (rapeseed oil methyl ester).*

Results in:

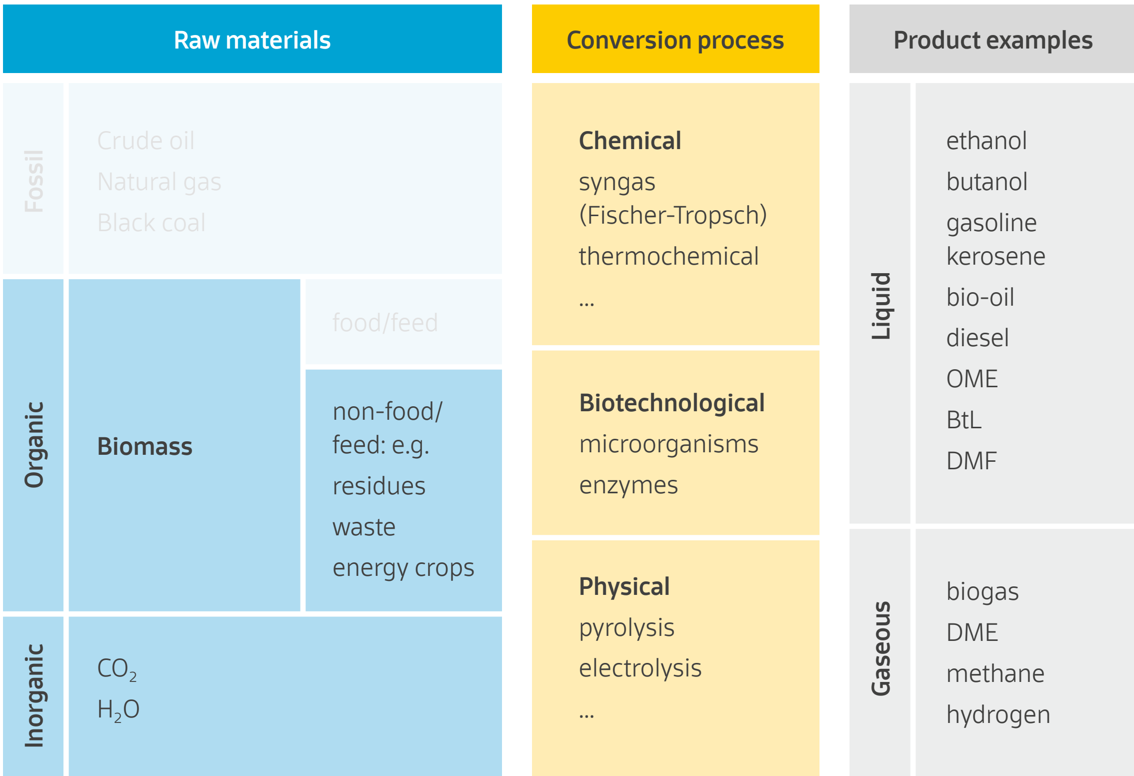


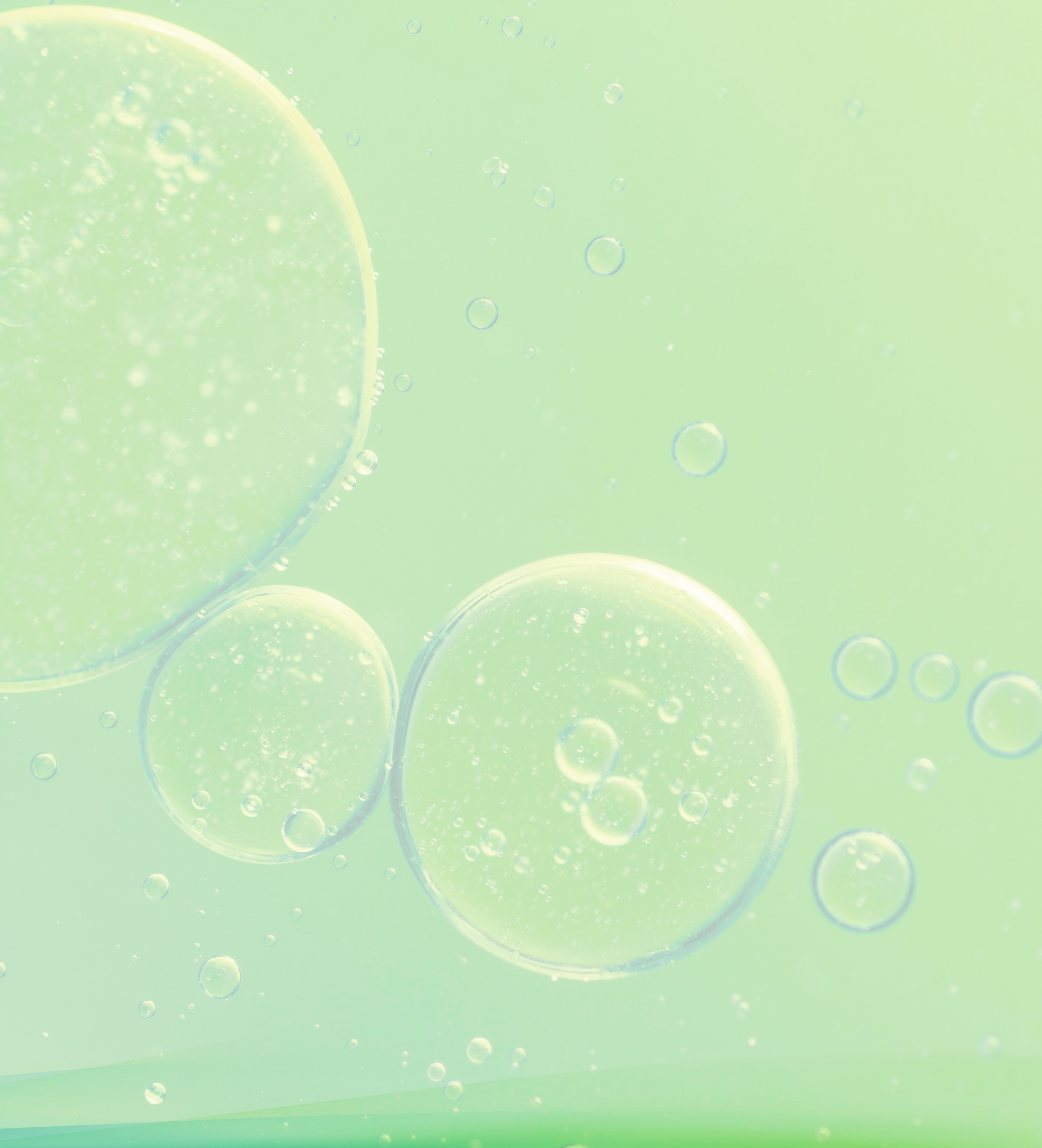
Figure 3: *Overview of* ***advanced (bio)fuels*** *classified according to feedstocks, conversion methods and products. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, n ≥ 2), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Second-generation (2G) ethanol differs from 1G ethanol mainly in terms of feedstock used for its production. The renewable non-food/feed raw materials utilized include agricultural and forestry residues like wheat straw, corn stover, bagasse, lignocellulosic spruce chips as well as waste materials. Subsequently, production processes are adjusted to the respective feedstock.

Third-generation (3G) ethanol refers to ethanol produced by algae as well as cyanobacteria utilizing carbon dioxide as their feedstock.

In the following, some examples of advanced liquid and gaseous (bio)fuels are described. The list is not exhaustive, yet representative for the many different European approaches in this area.

Examples of liquid (bio)fuels



1. Production of cellulosic ethanol using microorganisms

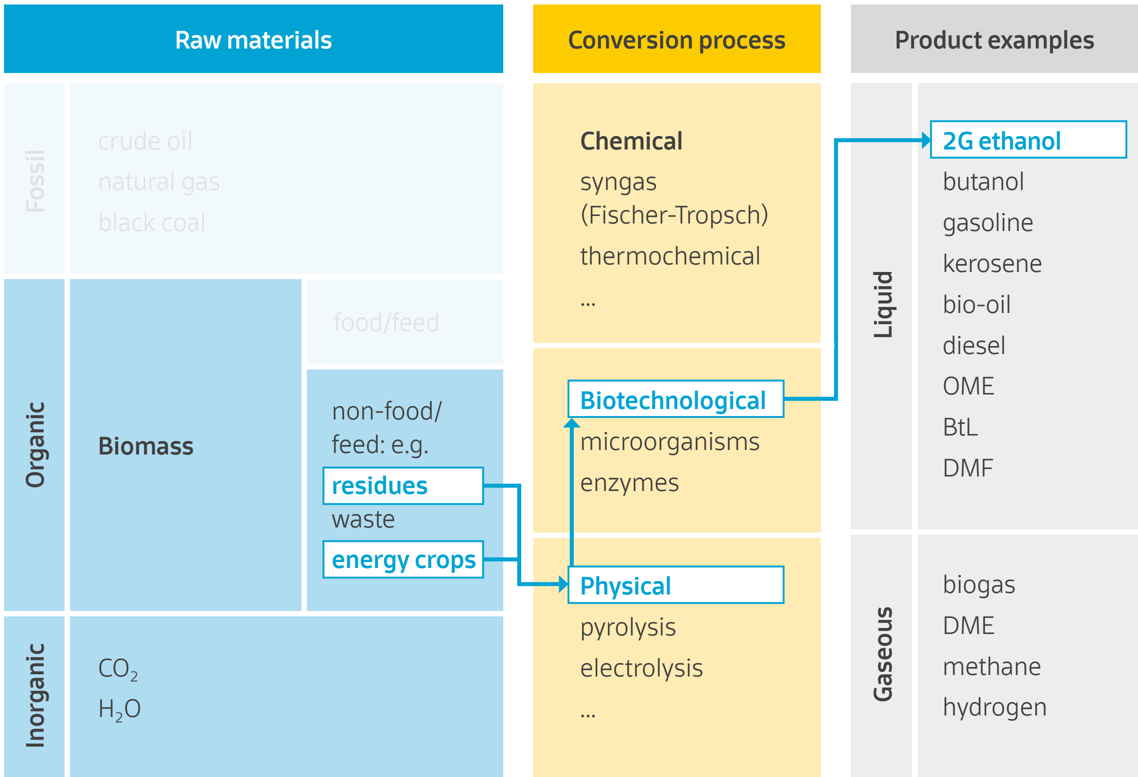


Figure 4: *Flow diagram of the process of producing cellulosic ethanol from residues or energy crops using microorganisms. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, n ≥ 2), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Clariant, sunliquid®

Clariant's sunliquid® technology produces cellulosic ethanol, an advanced and sustainable biofuel, which is almost carbon dioxide neutral. It is produced from agricultural residues or energy crops, e.g. wheat straw, corn stover or miscanthus. The feedstock is converted into cellulosic sugars, which are then fermented with the help of specially designed yeast strains to produce cellulosic ethanol. Innovative features like chemical free pre-treatment, the integrated production of feedstock- and process-specific enzymes as well as simultaneous C5 and C6 sugar fermentation ensure a commercially viable process.[2]

After seven years of successful operations of its pre-commercial plant in Straubing, Germany, Clariant broke ground on its greenfield first-of-its-kind full-scale commercial cellulosic ethanol plant in Podari, in the southwestern region of Romania, in the fall of 2018. The new plant will be a flagship site with an annual production capacity of 50,000 tons.[3]

2 https://www.clariant.com/en/Solutions/Products/2014/10/16/16/16/sunliquid
3 https://www.clariant.com/en/Corporate/News/2018/09/Groundbreaking-for-Clariantrsquos-sunliquidreg-cellulosic-ethanol-plant-in-Romanianbsp

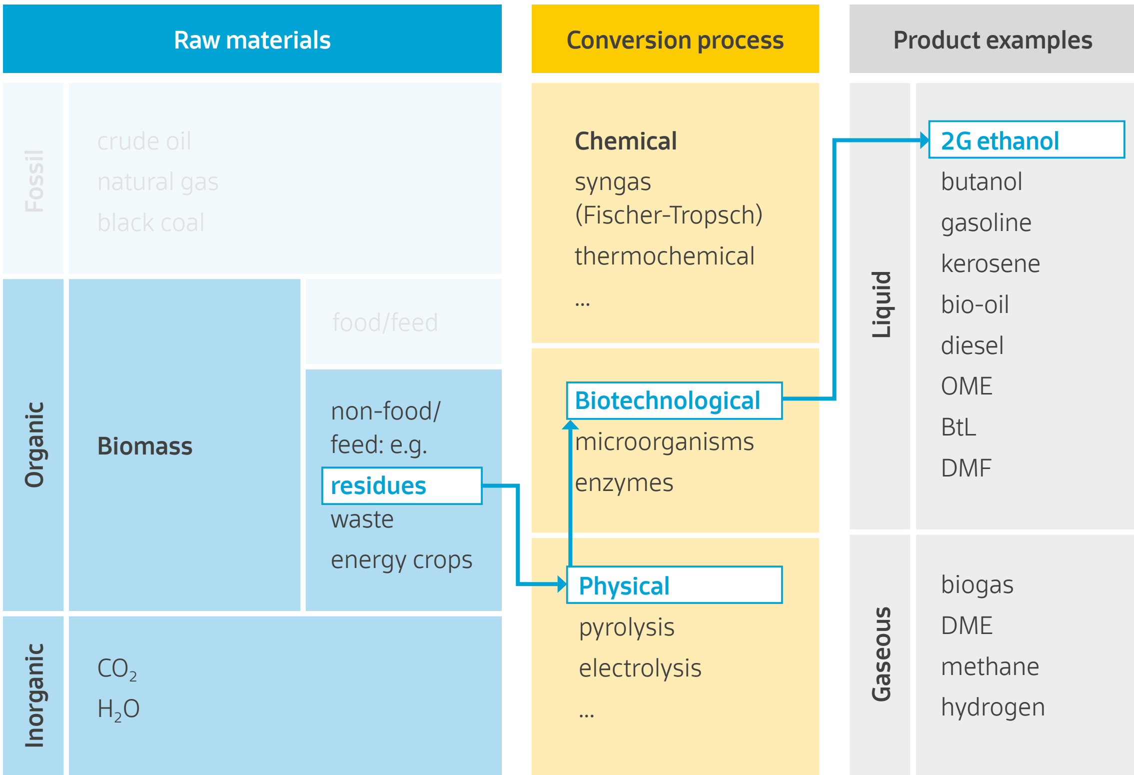


Figure 5: *Flow diagram of the process of producing cellulosic ethanol from forest residues or lignocellulosic spruce using microorganisms. OME = Poly-oxy-methylene-dimethyl ether ($H_3C\text{-}O\text{-}(CH_2O)_n\text{-}CH_3$, $n \geq 2$), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

SEKAB, CelluApp[4]

The technology developed by SEKAB uses lignocellulosic materials from forestry and agricultural residues – mainly wood – to produce second generation ethanol. An acidic and thermal pre-treatment of the raw material is necessary in the so-called CelluApp Process, before the cellulose is hydrolysed using special enzymes. Resulting sugars from the cellulose and the hemicellulose are fermented by yeasts capable of fermenting both hexoses and pentoses. Via distillation of the complete slurry, the ethanol is accessed and cleaned.

SEKAB's technology is established at the ethanol DEMO plant in Örnsköldsvik, Sweden. Further, the special yeast strains are verified to function on an industrial scale in a full-scale process in Örnsköldsvik.

Borregaard, ChemCell Ethanol[5]

The Norwegian company Borregaard uses an approach similar to that of Clariant and SEKAB. The main difference is that Borregaard mainly focuses on lignin-based products, generating ethanol as one of

4 http://www.sekab.com/biorefinery/e-tech-process/
5 http://www.etipbioenergy.eu/images/Factsheet_Borregaard_final.pdf

several products, not their main product. Nevertheless, they produce second generation bioethanol from wood since 1938.

In their sulfite mill in Sarpsborg, Norway, lignocellulosic spruce chips are digested with the help of acidic calcium bisulfite cooking liquor, whereas various sugars are hydrolyzed from the contained hemicellulos fibres. Hereafter, only the resulting C6 sugars are fermented with non-GMO yeast strains in order to generate ethanol, which can be procured by distillation. In this commercial plant, 15,800 tons p.a. of bioethanol are produced. Further, Borregaard runs a second bioethanol refinery, which is called BALI demonstration plant in Sarpsborg as well. In contrast to the commercial plant, this demo refinery uses all lignocellulosic fibres, not just the hemicellulosic ones, for the production of sugars and bioethanol.

In Crescentino, Italy, the industrial group Mossi & Ghisolfi S.p.A. has also been developing cellulosic ethanol by a similar technology, called PROESA™. Cellulosic ethanol has been produced in industrial scale since October 2013 with a capacity of 40,000 tons p.a. The investment amounted to 150 million € and the project has been supported by the 7th FP of the EC. However, on 30 October 2017, it was reported that the Crescentino cellulosic refinery is to be shut down as a part of a restructuring effort for the debt-laden parent company[6]. Last news on this subject on 10 October 2018: Versalis (Eni) has won the bidding process for the cellulosic refinery. Consequently, an integrated technological platform of chemicals from biomass can be developed, in line with Versalis' strategy undertaken in recent years.[7]

6 *https://www.biofuelsdigest.com/bdigest/2017/10/30/beta-renewables-in-cellulosic-ethanol-crisis-as-grupo-mg-parent-files-for-restructuring/*
7 *http://news.bio-based.eu/versalis-acquisition-of-bio-run-companies-of-the-mossi-ghisolfi-group/*

2. Chemical conversion of crude tall oil to renewable diesel

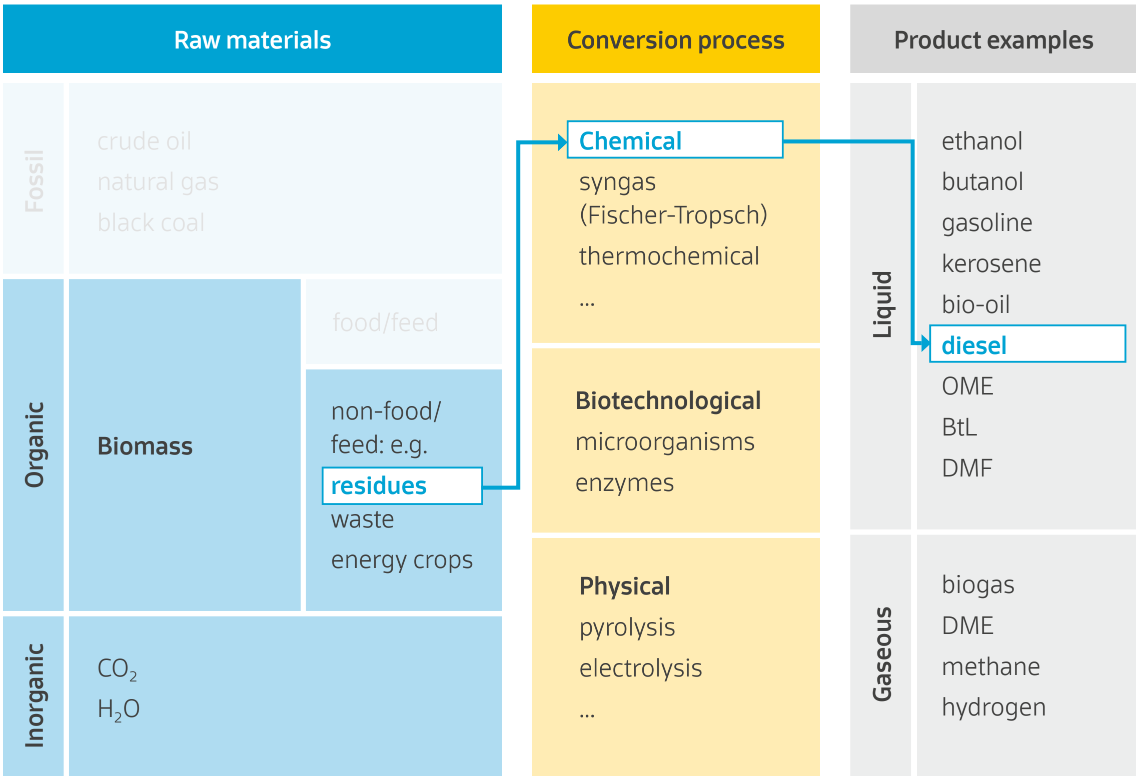


Figure 6: *Flow diagram of the process of producing renewable diesel by the chemical conversion of crude tall oil. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-($CH_2O)_n$-CH_3, n ≥ 2), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

UPM, BioVerno[8,9,10]

UPM's Lappeenranta biorefinery operates since 2015 and produces annually over 100,000 tons of renewable diesel (brand name: "UPM BioVerno") and renewable naphtha from crude tall oil[11]. UPM BioVerno reduces GHG emissions by over 80% and, as drop-in fuel, can be used in high blends as the chemical properties are identical to fossil fuel. The technology used at the biorefinery in order to procure renewable diesel comprises four steps: The pre-treatment of crude tall oil, hydro-treatment of processed tall oil, purification of recycled gas and fractionation of remaining liquid.

The biorefinery feedstock, crude tall oil, is a residue of (coniferous) wood pulp production. Consequently, UPM can apply this residue from its pulp mills and therefore uses already harvested wood from sustainably managed forests more efficiently.

8 https://www.upmbiofuels.com/traffic-fuels/upm-bioverno-diesel-for-fuels/
9 https://www.chemicals-technology.com/projects/upm-lappeenranta-biorefinery-biodiesel-biofuels-finland/
10 http://www.etipbioenergy.eu/fact-sheets/upm-biofuels-fact-sheet
11 https://www.upm.com/about-us/for-media/releases/2012/02/upm-to-build-the-worlds-first-biorefinery-producing-wood-based-biodiesel2/

3. Fast pyrolysis technology to produce bio-oil from renewable raw materials

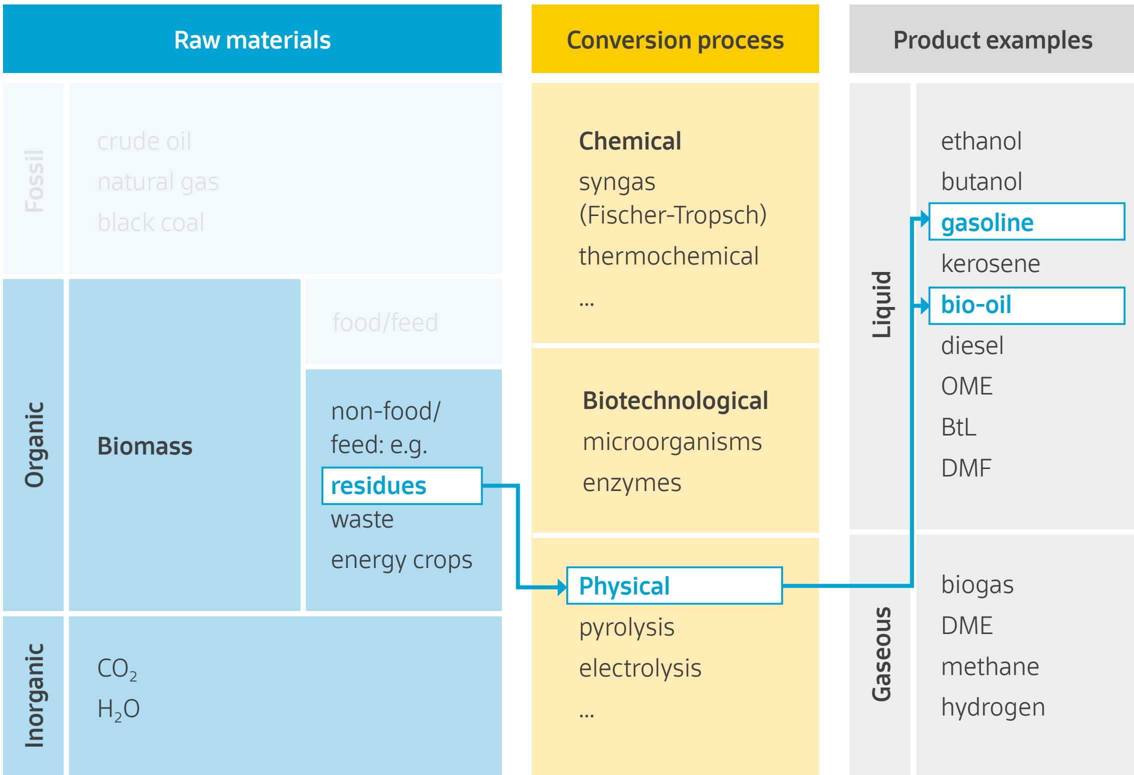


Figure 7: *Flow diagram of the process of bio-oil production from renewable raw materials by using fast pyrolysis technology. OME = Poly-oxy-methylene-dimethyl ether ($H_3C\text{-}O\text{-}(CH_2O)_n\text{-}CH_3$, $n \geq 2$), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Karlsruhe Institute of Technology (KIT), bioliq®[12,13]

KIT developed a technology named bioliq®, converting residual biomass, e.g. straw and other biogenic residues, into synthetic fuels, like high-quality petrol. The stages of the process include: Fast pyrolysis, high-pressure entrained flow gasification, hot gas purification and synthesis. bioliq® is environmentally friendly and fully compatible with conventional petrol. In principle, the bioliq® concept can also be used to produce fuels for diesel engines and aircraft. KIT successfully runs a pilot plant since 2014, producing one ton of fuel per day.

Fortum, Otso bio-oil[14]

Fortum Otso bio-oil is produced from renewable wood-based raw materials by using fast pyrolysis technology, i.e. rapid heating or super-heated water to convert organic matter to oil. The commercial plant (112 million gallons p.a. capacity) located in Joensuu, Finland, shows the feasibility of this approach since 2013. Fortum's Otso bio-oil is so far used for heat and steam production only and not yet as advanced biofuel.

12 https://www.bioliq.de/english/55.php
13 http://www.kit.edu/kit/english/pi_2014_15980.php
14 https://www.fortum.com/products-and-services/power-plant-services/fortum-otso-bio-oil

Fraunhofer Institute UMSICHT, BioMates[15]

Generally, fuels with a biogenic component are produced almost exclusively by blending fuels from conventional refineries with finished biofuels at the end of both processes. In contrast, the Horizon 2020-funded project BioMates, launched in October 2016, aspires in the cost-effective production of defined intermediates out of 2nd generation biomass, which can be fed directly and risk-free into an existing refinery towards the production of hybrid fuels (= based on fossil and up to 30% renewable feedstock). Therefore, non-food/feed plant biomass is first converted into bio-oil by ablative fast pyrolysis. The bio-oil can then be further treated by mild catalytic hydro-processing to yield intermediates with the required material properties. Recently, a pilot plant was developed that can turn up to five kilograms of straw and non-food plants into bio-oil[16].

15 http://www.biomates.eu/
16 https://www.umsicht.fraunhofer.de/en/press-media/press-releases/2018/biomates.html

4. Production of gasoline from sewage sludge using the TCR process

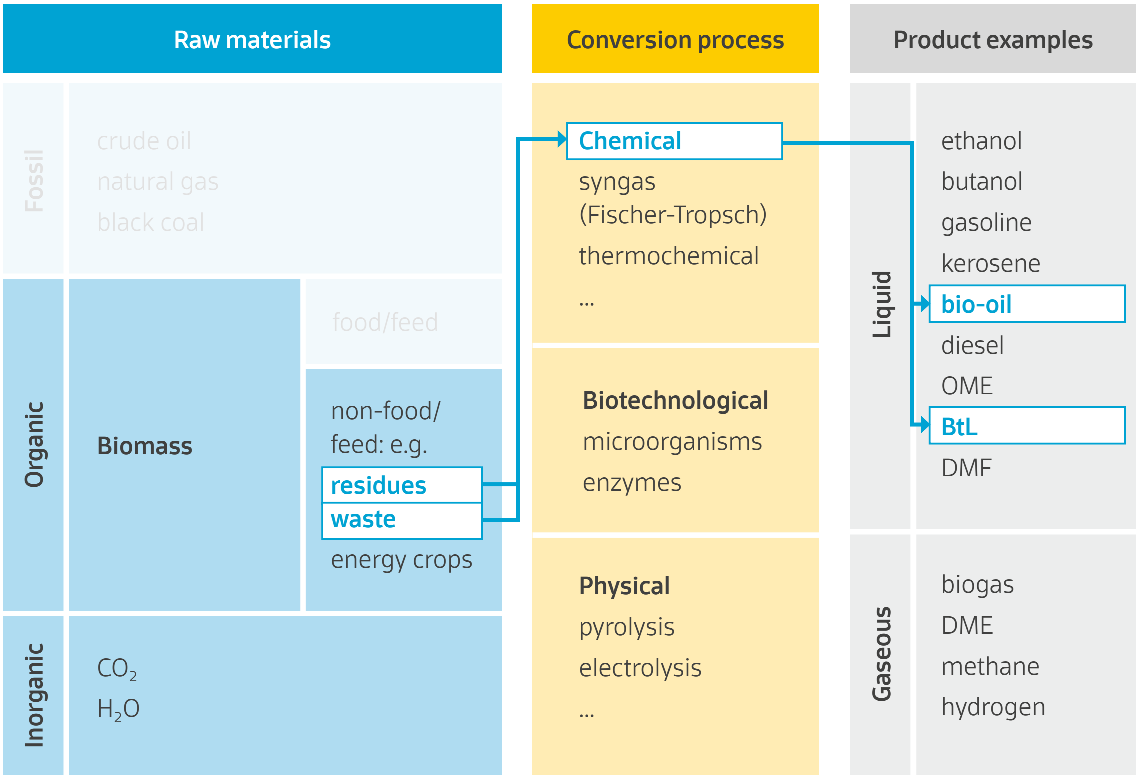


Figure 8: *Flow diagram of the process of gasolinel production from sewage sludge using TCR. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-($CH_2O)_n$-CH_3, n ≥ 2), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Fraunhofer-Institute UMSICHT Sulzbach-Rosenberg, Thermo-Catalytic reforming[17]

The TCR approach (thermo-catalytic reforming) converts 65 different types of organic waste and residues into high quality syngas, bio-oil – straight suitable for refining –, biochar and water. Dried feedstock is slowly heated by external flue gas to carbonize the material. Subsequently, it is thermally cracked into a vapor containing gas, oil and water. After catalytic reforming using biochar, the four products of the process can be easily segregated by their aggregate state and phase separation. The steam reforming of water and carbon increases the yield of a hydrogen-rich syngas for a subsequent Fischer-Tropsch process.

Since 2015, Fraunhofer UMSICHT has been operating a test facility in Sulzbach-Rosenberg that has a throughput of 300 kg biomass per hour producing ~30 L of green fuel per hour.[18] The first industrial pilot plant with a throughput of 80 kg biomass per hour was shipped in a standard container to England in 2017.[19] The ground-breaking ceremony for a large-scale demonstration plant (throughput 500 kg biomass per hour) took place in 2018 in Hohenburg in the Upper Palatinate. Commissioning is planned for 2020.[20]

17 https://www.susteen-tech.com/en/technology
18 https://www.umsicht-suro.fraunhofer.de/en/Our_Solution/BiobasedFuel.html
19 https://www.umsicht-suro.fraunhofer.de/en/press-and-media/press-releases/2017/tcr-technology-in-the-UK.html
20 https://www.umsicht-suro.fraunhofer.de/en/press-and-media/press-releases/2018/Groundbreaking_demonstration_plant.html

5. Fuel synthesis by using biotechnologically derived isobutene

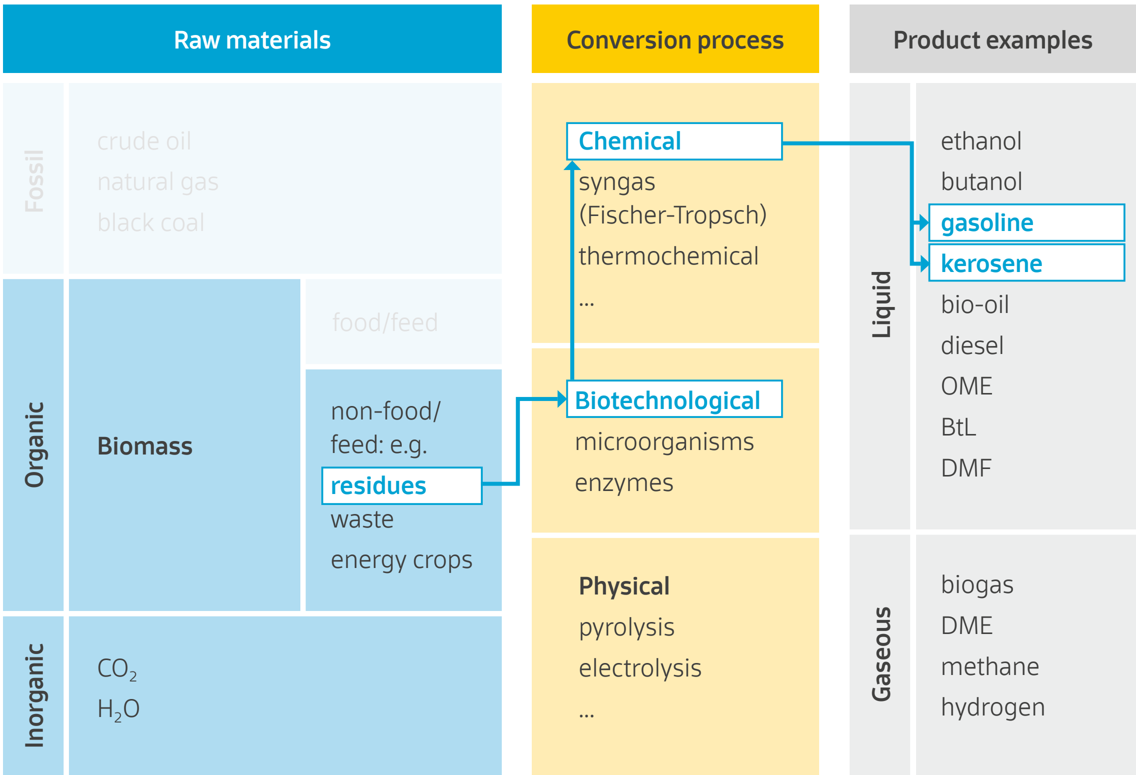


Figure 9: *Flow diagram of the process of gasoline production by bio-isobutene conversion. OME = Poly-oxy-methylene-dimethyl ether ($H_3C\text{-}O\text{-}(CH_2O)_n\text{-}CH_3$, $n \geq 2$), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Global Bioenergies, isobutene and derivates[21]

The technology developed by Global Bioenergies uses a genetically modified microorganism to convert forestry and agricultural residues into isobutene. As the special fermentation results directly into a gas, purification of the product can be achieved easily. The final product, bio-isobutene, is one of the major building blocks of the petrochemical industry. In 2017, a demo plant for the production of bio-isobutene, based on this technology, was inaugurated at Fraunhofer CBP in Leuna, Germany[22]. Moreover, derivates of isobutene can be applied as gasoline additive or as potential drop-in fuel, as was shown by operating an Audi car with a blend containing 34% isobutene-derived compounds[23,24].

A future plant for the production of isobutene and derivatives thereof, named IBN-One, is pursued in a joint venture with Cristal Union[25]. To this end, Global Bioenergies and an industry consortium are receiving EU funding for a three-year project called REWOFUEL, to demonstrate the production of isobutene-based gasoline and kerosene from wood in the cubic meter range.[26,27]

21 https://www.global-bioenergies.com/group/isobutene-process/?lang=en
22 https://www.cbp.fraunhofer.de/en/press-media/Press-media1/2017/Pressreleases.html
23 https://www.ibbnetzwerk-gmbh.com/en/nachrichten/nachricht/datum/2018/04/05/erstes-auto-faehrt-mit-dem-erneuerbaren-benzin-von-global-bioenergies/
24 https://www.audi-mediacenter.com/en/press-releases/audi-advances-e-fuels-technology-new-e-benzin-fuel-being-tested-9912
25 https://www.global-bioenergies.com/cristal-union-and-global-bioenergies-have-formed-a-joint-venture/?lang=en
26 https://www.global-bioenergies.com/global-bioenergies-and-an-industrial-consortium-including-sekab-neste-engineering-solutions-repsol-and-skynrg-receive-major-eu-funding-to-demonstrate-the-production-of-isobutene-derived-gasoline-and/?lang=en
27 https://www.ibbnetzwerk-gmbh.com/de/nachrichten/nachricht/datum/2018/07/13/global-bioenergies-and-audi-renew-their-partnership-in-renewable-gasoline/

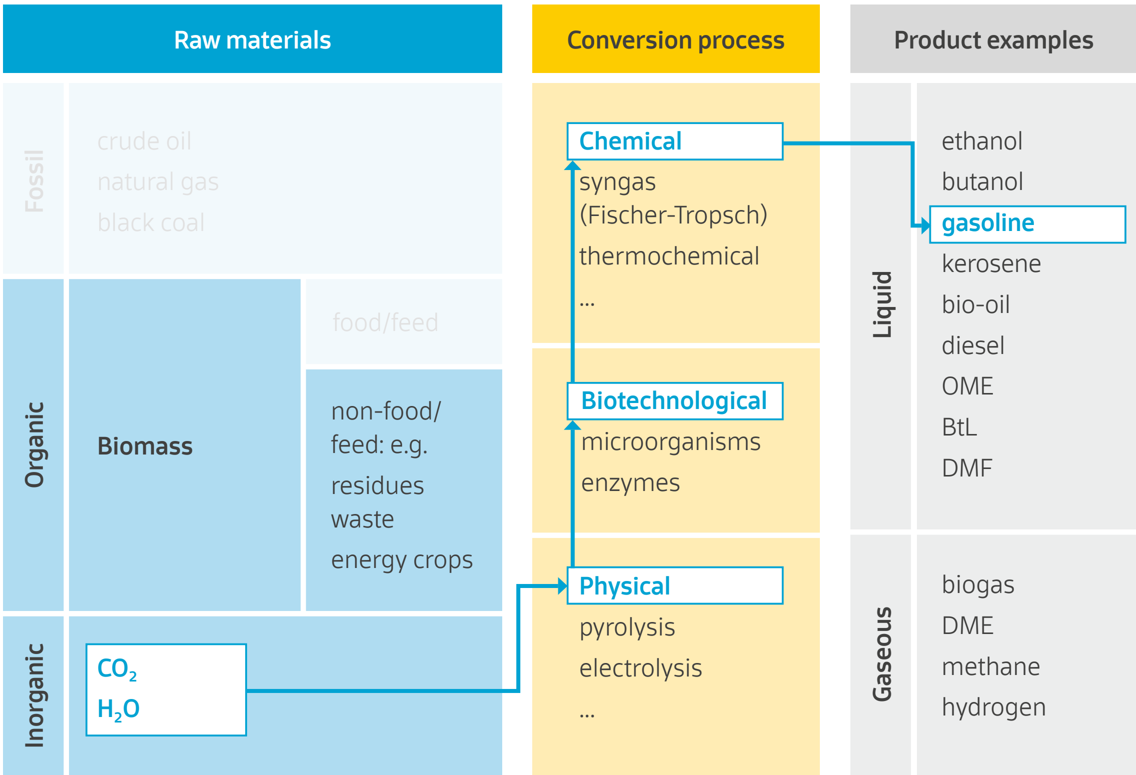


Figure 10: *Flow diagram of the process of the biologically propane and isobutene production from carbon dioxide. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, $n \geq 2$), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ethen*

Institute for Energy and Environmental Research Heidelberg, eForFuel

In the Horizon 2020-supported eForFuel[28] project, launched in 2018, carbon dioxide in water is first converted (reduced) via electrolysis to formic acid. Formic acid is, unlike hydrogen and carbon monoxide, fully soluble, easily stored and safe to handle. Genetically modified, formatotrophic microbes metabolize then formic acid (formate) to propane and isobutene, which – since gaseous – can be easily separated from the microbial culture, reducing production cost and increasing energy efficiency. These products can be integrated into existing fuel facilities: propane as component of LPG (Liquefied Petroleum Gas), and isobutene for production of the fuel substitute isooctane.

28 http://news.bio-based.eu/eforfuel-fuels-from-co2-and-electricity/

6. “3G” biofuels produced by photosynthetic microorganisms

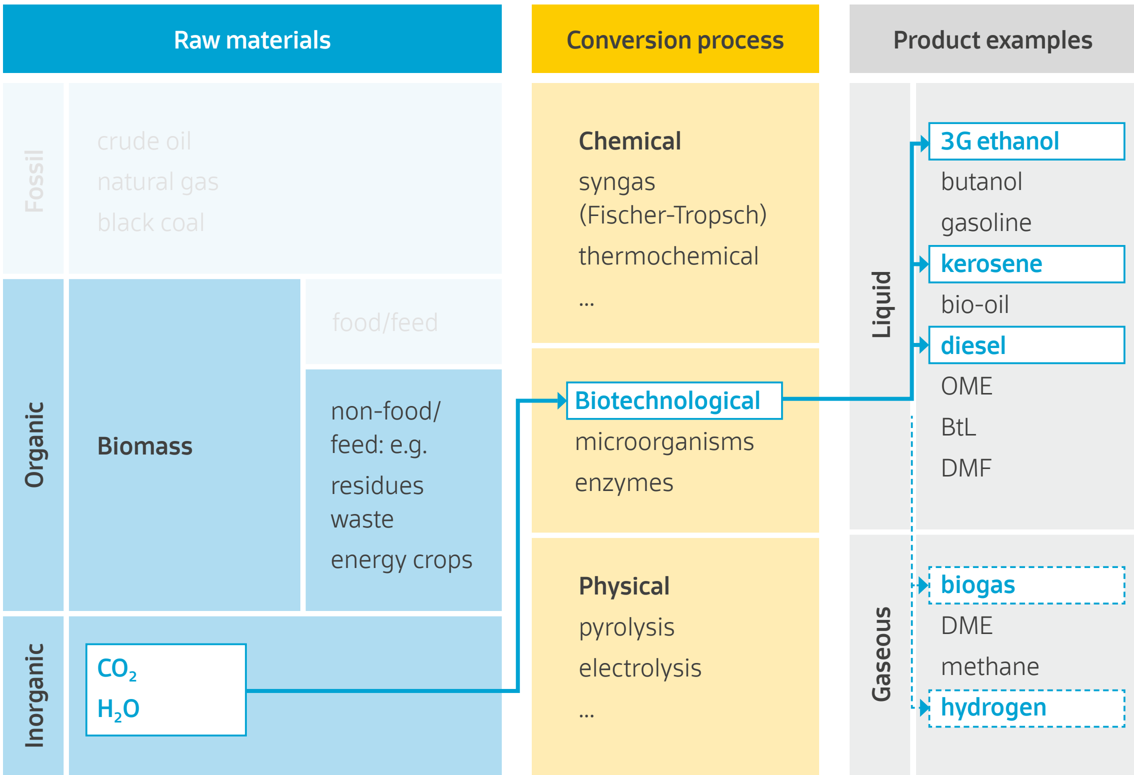


Figure 11: *Flow diagram of the process of algae-produced biofuels e.g. kerosene. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, n ≥ 2), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Algae fuel is a fuel obtained using photosynthetic microalgae as conversion factories or as biomass. These phylogenetically diverse microorganisms can generate many different compounds that can be used as so-called “3G” biofuels. Different fuels like biodiesel[29], biokerosene[30,31] and bioethanol[32] (and gaseous fuels like hydrogen[33] or biogas[34]) can be produced from or by algae. E. g. algal oil can be converted by transesterification into a fuel whose properties are comparable to diesel fuel. Algal carbohydrates can be fermented to ethanol or methane.

Similar to algae, also cyanobacteria are able to generate “3G” biofuels. Researchers of the Lindblad group at Uppsala University demonstrated the efficient photosynthetic production of 1-butanol directly from carbon dioxide with modular engineered cyanobacteria[35].

29 *Chisti, Y. (2007). Biodiesel from microalgae. Biotechnology advances, 25(3), 294-306.*
30 *https://www.department.ch.tum.de/en/wssb/research/abv/*
31 *https://www.fz-juelich.de/ibg/ibg-2/DE/Projekte/_bund/AUFWIND/_node.html*
32 *https://www.cleanthinking.de/biothenaol-cyano-biofuels-algen/*
33 *http://news.rub.de/wissenschaft/2017-07-11-biologie-evolution-eines-bakteriellen-enzyms-gruenalgen*
34 *Salerno, M., Nurdogan, Y., & Lundquist, T. J. (2009). Biogas production from algae biomass harvested at wastewater treatment ponds. American Society of Agricultural and Biological Engineers.*
35 *Liu, X., Miao, R., Lindberg, P., & Lindblad, P. (2019). Modular engineering for efficient photosynthetic biosynthesis of 1-butanol from CO_2 in cyanobacteria. Energy & Environmental Science.*

Exxon Mobile and Synthetic Genomics, Algae Biofuels[36]

These companies invest heavily in their joint algae biofuels research program. In 2018, the companies planned an outdoor testing for different algae strains in California as a critical step towards commercial production. By 2025, a production volume of 10,000 barrels of algae biofuels per day is supposed to be achieved.

36 *https://news.exxonmobil.com/press-release/exxonmobil-and-synthetic-genomics-algae-biofuels-program-targets-10000-barrels-day-202*

7. "e-Fuels" produced from carbon dioxide and water

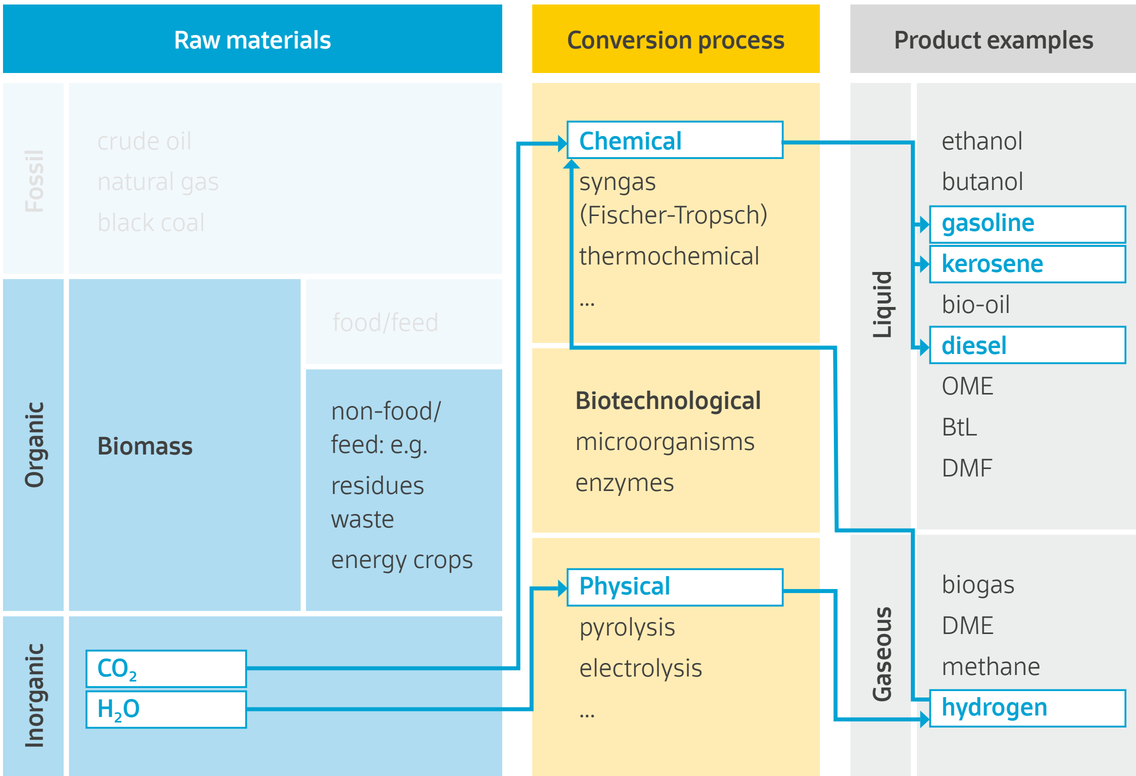


Figure 12: *Flow diagram of the process of "e-Fuel" production using CO_2 and H_2. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, $n \geq 2$), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Sunfire, Blue Crude[37]

Sunfire develops and manufactures substitutes for mineral oil and natural gas, known as e-Naphtha, e-Fuel, e-Diesel, e-Gas and e-Chemicals (e.g. e-waxes), which may replace fossil fuels in existing infrastructures. Of particular interest in this technology is the steam electrolysis process (SOEC), which splits water vapor efficiently into hydrogen and oxygen. Subsequently, carbon dioxide is transformed to carbon monoxide before Blue Crude is generated. A breakthrough for the technology is the recently developed co-electrolysis combining the dissociation of hydrogen from water and the production of carbon monoxide in a single process step.[38]

The first commercial plant for the industrial production of the synthetic crude oil substitute Blue Crude is planned in Heroya, Norway. Commissioning of the plant shall start in 2020. The annual production volume of Blue Crude will be 8,000 tons.[39]

37 https://www.sunfire.de/en/products-and-technology
38 https://www.sunfire.de/de/unternehmen/news/detail/breakthrough-for-power-to-x-sunfire-puts-first-co-electrolysis-into-operation-and-starts-scaling
39 https://www.sunfire.de/de/unternehmen/news/detail/first-commercial-plant-for-the-production-of-blue-crude-planned-in-norway

Power-to-Liquid “PtL”[40]

The processes employed e.g. by Sunfire, belong to the family of the so-called Power-to-Liquid methods. Other PtL approaches are described below.

- **Fuel production using synthesis gas (special case of GtL):** With the starting materials water, carbon dioxide and electrical energy, synthesis gas (carbon monoxide and hydrogen) is produced in a first step. Subsequently, this gas is converted via Fischer-Tropsch synthesis to long-chain, hydrocarbons (e.g. benzine, kerosene and diesel), suitable for biofuels.
- **Biotechnological Process:** The term Power-to-Liquid can also involve an integrated electro-microbial bioreactor yielding various liquid butanols suitable as fuel with the help of genetically modified soil bacteria *(Cupriavidus necator)*. To this end, electric current transforms CO_2 in water to formate, which is the feedstock for these bacteria.[41]
- **Liquefaction of Renewable Energy Gas (RE-Gas):** Additional energy is required for the liquefication of combustible hydrocarbon gas (= methane) obtained from power-to-gas process (see page x). The advantage of this liquefied gas is that it can be transported more easily (depending on the type of transport route) than in gaseous form.

Notes about further liquid advanced biofuels, which are not considered here in detail:

OME (poly-oxy-methylene-dimethyl ether ($H_3C\text{-}O\text{-}(CH_2O)_n\text{-}CH_3$, $n \geq 2$) are a class of chemical compounds used as diesel fuel additives or as an eco-friendly alternative fuel[42,43]. Compared to the production costs of conventional diesel fuels, OME production is competitive[44]. The primary raw material for the production of OME is methanol, which can be produced both from conventional natural gas and regeneratively from CO_2 and hydrogen. For advantages of OME, see Deutz et al. (2018)[45].

DMF (2,5-dimethylfuran) can be obtained from fructose using a catalytic biomass-to-liquid process[46]. Fructose, in turn, can be produced from glucose, a building block in cellulose. Dimethylfuran is seen as a potential biofuel that could replace ethanol. Having an energy density 40% higher than ethanol, DMF is comparable to petrol, as verified in a single-cylinder gasoline engine.[47]

Agency of Renewable Resources (FNR – Fachagentur Nachwachsende Rohstoffe), ADVANCEFUEL[48]

The Horizon 2020 supported ADVANCEFUEL project investigates liquid advanced biofuels produced from lignocellulosic feedstocks as well as other liquid fuels, produced from renewable hydrogen and CO_2 streams. ADVANCEFUEL aims to facilitate the commercialization of renewable transport fuels by providing market stakeholders with new knowledge, tools, standards and recommendations to help remove barriers to their uptake. Therefore, a framework to monitor the current status and future perspectives of renewable fuels in Europe is developed. Further, the availability of biomass for second-generation biofuels is examined as well as innovative conversion technologies. ADVANCEFUEL supports the development of new transport fuel value chains to achieve the EU’s renewable energy targets.

40 *https://de.wikipedia.org/wiki/Power-to-Liquid*
41 *https://www.scientificamerican.com/article/microbe-uses-solar-electricity-to-build-liquid-fuel/*
42 *Lumpp, B., Rothe, D., Pastötter, C., Lämmermann, R., & Jacob, E. (2011). Oxymethylene ethers as diesel fuel additives of the future. MTZ worldwide eMagazine, 72(3), 34-38.*
43 *Liebl, J., & Beidl, C. (Eds.). (2015). Internationaler Motorenkongress 2015: Mit Nutzfahrzeugmotoren-Spezial. Springer-Verlag. [Article in German]*
44 *Schmitz, N., Burger, J., Ströfer, E., & Hasse, H. (2016). From methanol to the oxygenated diesel fuel poly (oxymethylene) dimethyl ether: An assessment of the production costs. Fuel, 185, 67-72.*
45 *Deutz, S., Bongartz, D., Heuser, B., Kätelhön, A., Langenhorst, L. S., Omari, A., ... & Pischinger, S. (2018). Cleaner production of cleaner fuels: wind-to-wheel–environmental assessment of CO 2-based oxymethylene ether as a drop-in fuel. Energy & Environmental Science, 11(2), 331-343.*
46 *Román-Leshkov, Y., Barrett, C. J., Liu, Z. Y., & Dumesic, J. A. (2007). Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. Nature, 447(7147), 982.*
47 *Zhong, S., Daniel, R., Xu, H., Zhang, J., Turner, D., Wyszynski, M. L., & Richards, P. (2010). Combustion and emissions of 2, 5-dimethylfuran in a direct-injection spark-ignition engine. Energy & Fuels, 24(5), 2891-2899.*
48 *http://www.advancefuel.eu/contents/mediakit/1807-advancefuel-press-release-kick-off-final.pdf*

Examples of gaseous (bio)fuels

8. Chemical "e-gas" production from carbon dioxide and water

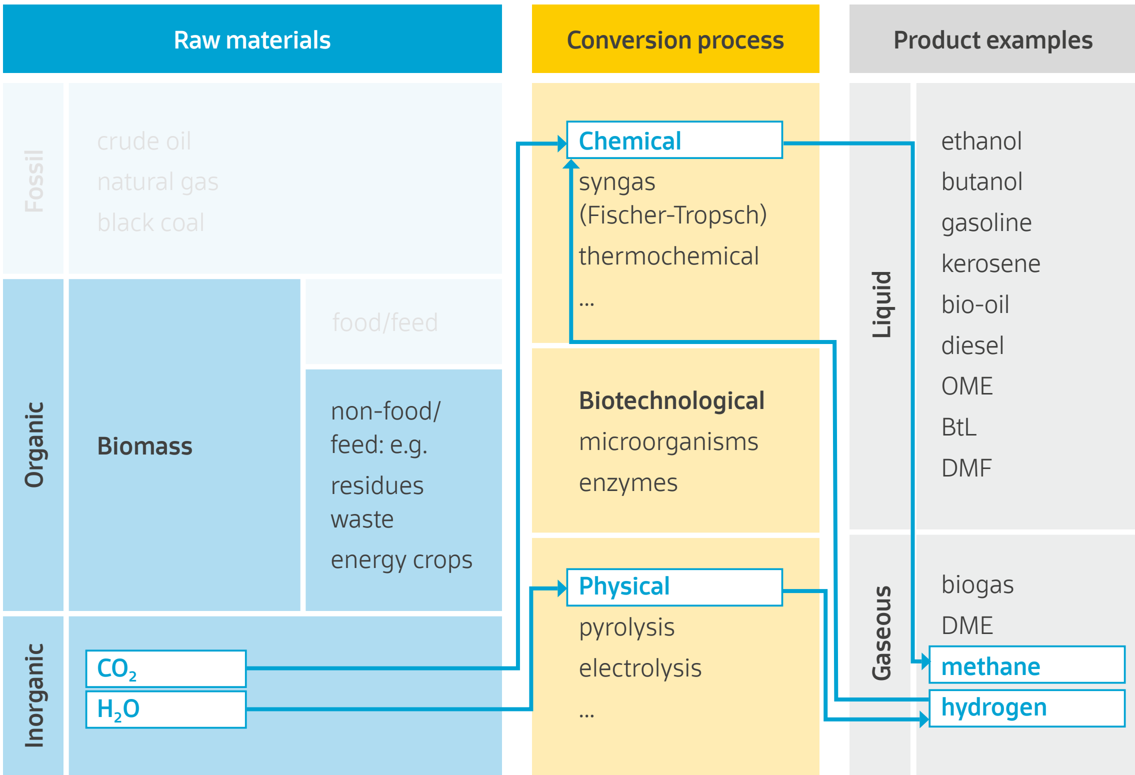


Figure 13: *Flow diagram of the process of "e-gas" production using CO_2 and H_2. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, $n \geq 2$), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

AUDI, "e-gas"[49,50]

To produce "e-gas" (methane), AUDI requires electricity, water and carbon dioxide. Using "green power", i.e. from renewable energy sources, hydrogen is procured by the electrolysis of water. Carbon dioxide reacts in a second step with hydrogen via chemical coupling to methane. This synthetic natural gas can be used as a fuel in a standard gas engine. In this process solely climate-neutral oxygen and water are generated as by-products.

Since 2013, AUDI operates an industrial plant for the production of ~1,000 tons of "e-gas" per year in Werlte, Germany. During this process ~2,800 tons of carbon dioxide, provided by a nearby waste biogas plant, are utilized, which equals to the amount of carbon dioxide bound per year by a forest consisting of 220,000 beech trees. The produced synthetic methane can be fed into the existing natural gas grid. This annual production volume is sufficient to run 1,500 cars CO_2-neutrally for 15,000 km[51].

49 https://www.audi.com/en/experience-audi/models-and-technology/alternative-drive-systems/energy-revolution.html
50 https://www.audi-mediacenter.com/en/press-releases/new-audi-e-gas-offer-as-standard-80-percent-lower-co2-emissions-7353
51 https://www.audi-technology-portal.de/en/mobility-for-the-future/audi-future-lab-mobility_en/audi-future-energies_en/audi-e-gas_en

9. Biotechnological methane production from carbon dioxide and water

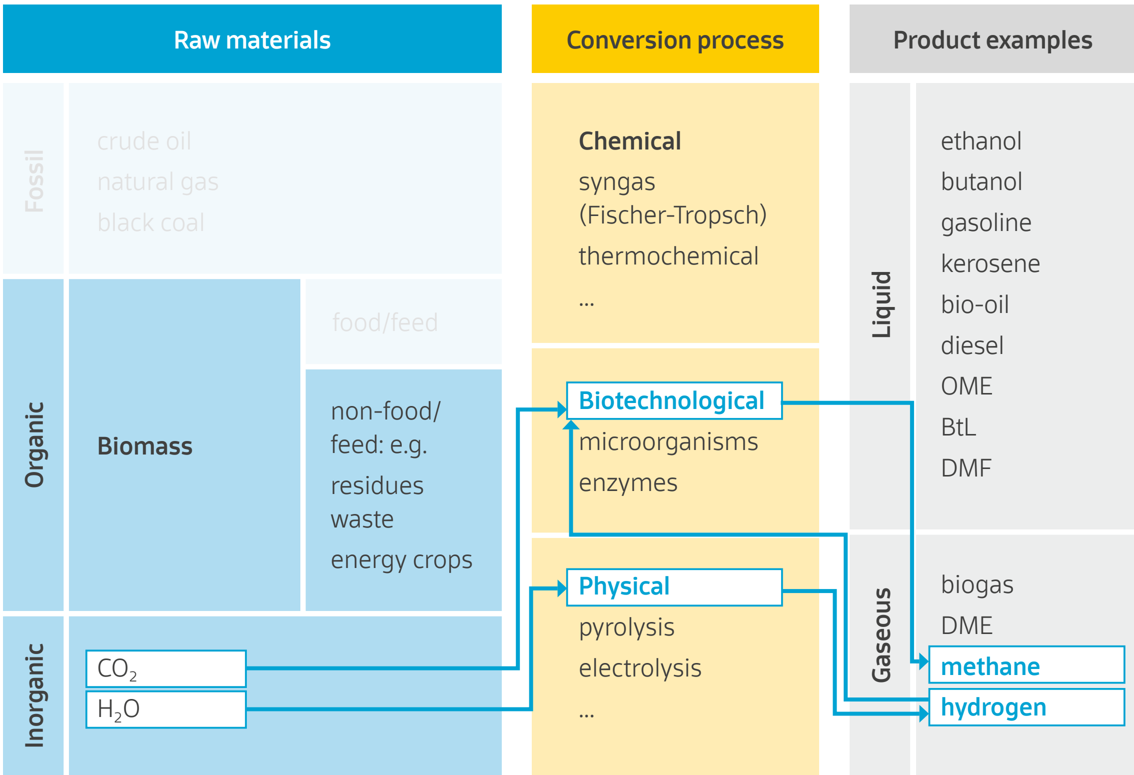


Figure 14: *Flow diagram of the process of biomethanation using CO_2 and H_2. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH3, n ≥ 2), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

Electrochaea, Biomethanation[52]

Electrochaea's technology relies on a special, selectively evolved methanogenic microorganism, a patented archaea strain, with an exceptionally high methane production capacity. More specifically, water is hydrolysed to hydrogen (and oxygen) using electricity from renewable energy sources. Hereafter, the microorganism is able to convert hydrogen and carbon dioxide under moderate conditions (1-10 bar, 62 °C) to pipeline-grade biomethane. The process has been dubbed "biomethanation".

Electrochaea operates three industrial scale plants for biomethanation. As part of the "BioCat" project, a facility for an 1 MW commercial-scale field trial was constructed in Avedøre, Denmark, in 2016[53]. From the plant in Solothurn, Switzerland, biomethane is injected into the gas grid since June 2019. Merely in the first four days, 370 kg of high-quality methane were generated biotechnologically. This amount corresponds to the amount of gas needed to drive a small gas-powered car for 10,000 km[54]. Also, in 2019 a biomethanation reactor system was commissioned in Colorado, USA[55]. The biomethanation technology of Electrochaea is ready for market entry.

52 *http://www.electrochaea.com/technology/*
53 *http://biocat-project.com/news/the-biocat-project-reaches-important-milestones-and-has-started-commissioning-for-the-plant/*
54 *http://www.electrochaea.com/wp-content/uploads/2019/03/PM-Electrochaea_STOREGO_Grid-Injection_EN.pdf*
55 *https://sempra.mediaroom.com/index.php?s=19080&item=137672*

Viessmann Group, BiON© process[56,57,58]

Viessmann Group, respectively its daughter MicrobEnergy GmbH, employs a similar process of biological methanation. The main difference to Electrochaea's approach consists in that MicrobEnergy uses a non-patented mixed archea culture. Nevertheless, this technology generates as well pure methane (purity >98%) under similar conditions, which can be injected directly into the gas grid, too. Since 2015, MicrobEnergy runs a demonstration plant in Allendorf, Germany. It was the first power-to-gas plant using biological methanation across Germany.

Power-to-Gas, "PtG"[59]

As described above, several companies, e.g. AUDI, Electrochaea and Viessmann, employ the PtG technology to produce methane as natural gas substitute.

The term power-to-gas stands for a concept applying electrical power to produce gaseous fuel. Using excess electricity, hydrogen is produced by water electrolysis. Subsequently, as needed, hydrogen can be converted into synthetic methane utilizing carbon dioxide.

Although this technology has lower efficiencies and higher costs than the use of surpluses in the heat sector or transportation (Power-to-Heat, Vehicle-to-Grid), it serves as a seasonal long-term storage facility. Therefore, only the use of surplus electricity from renewable energies makes this technology energetically and economically viable.

56 *https://www.sccer-biosweet.ch/wp-content/uploads/Heller-Biomass-for-Swiss-Energy-Future.pdf*
57 *https://www.microbenergy.de/microb/dienstleistungen/power-to-gas*
58 *https://www.audi-mediacenter.com/en/press-releases/new-method-for-producing-the-synthetic-fuel-audi-e-gas-5722*
59 *https://de.wikipedia.org/wiki/Power-to-Gas*

10. “One-pot” approach for hydrogen production from renewable resources

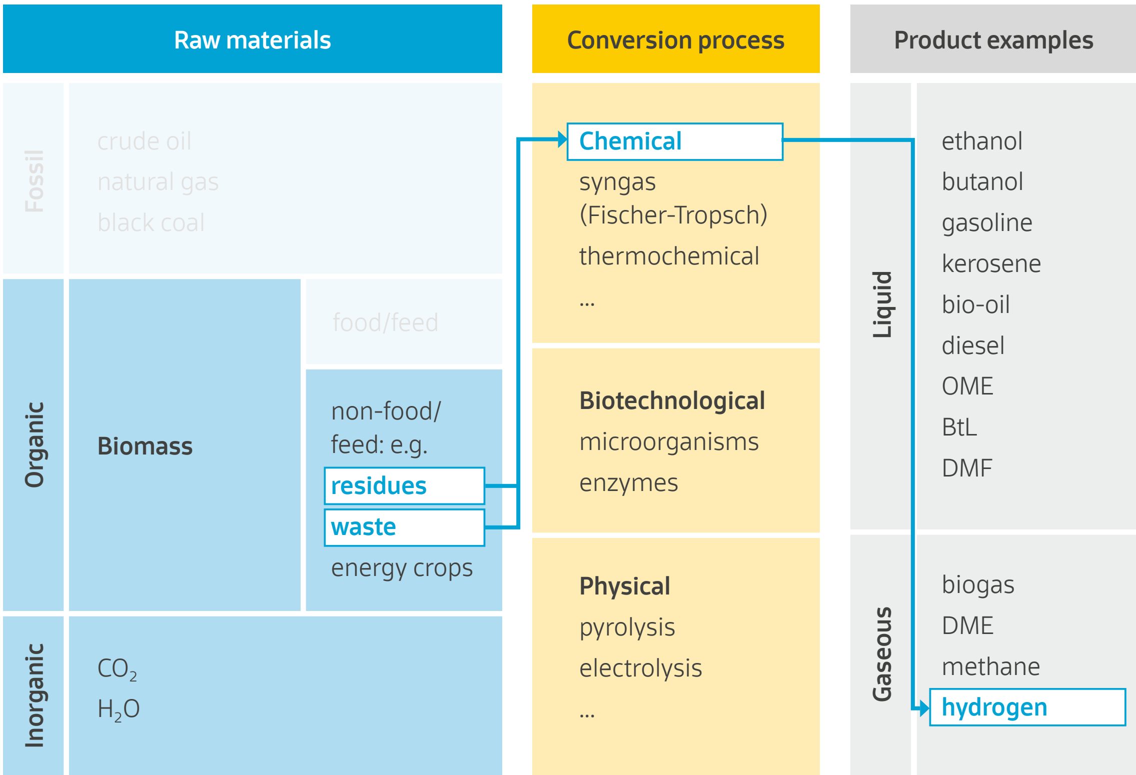


Figure 15: *Flow diagram of the process of H_2 production from renewable resources. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, n ≥ 2), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

So far, only H_2 from electrolysis has been considered. However, researchers from LIKAT and two Chinese universities described a chemical laboratory route for the production of hydrogen from various kinds of non-food-related biomass and daily waste. The authors achieved a hydrogen yield of 95% by using a two-step/one-pot reaction. Applying a special catalyst, formic acid could be obtained from straw in a first step, followed by the generation of hydrogen in a second one. Formation of unwanted side products like carbon monoxide and methane was marginal.[60] Of course, this very recent route has no industrial application yet, but it opens the chance to easily and economically obtain hydrogen from non-food biomass with formic acid as intermediate.

60 *Zhang, P., Guo, Y. J., Chen, J., Zhao, Y. R., Chang, J., Junge, H., ... & Li, Y. (2018). Streamlined hydrogen production from biomass. Nature Catalysis, 1(5), 332.*

11. Production of hydrogen using microorganisms

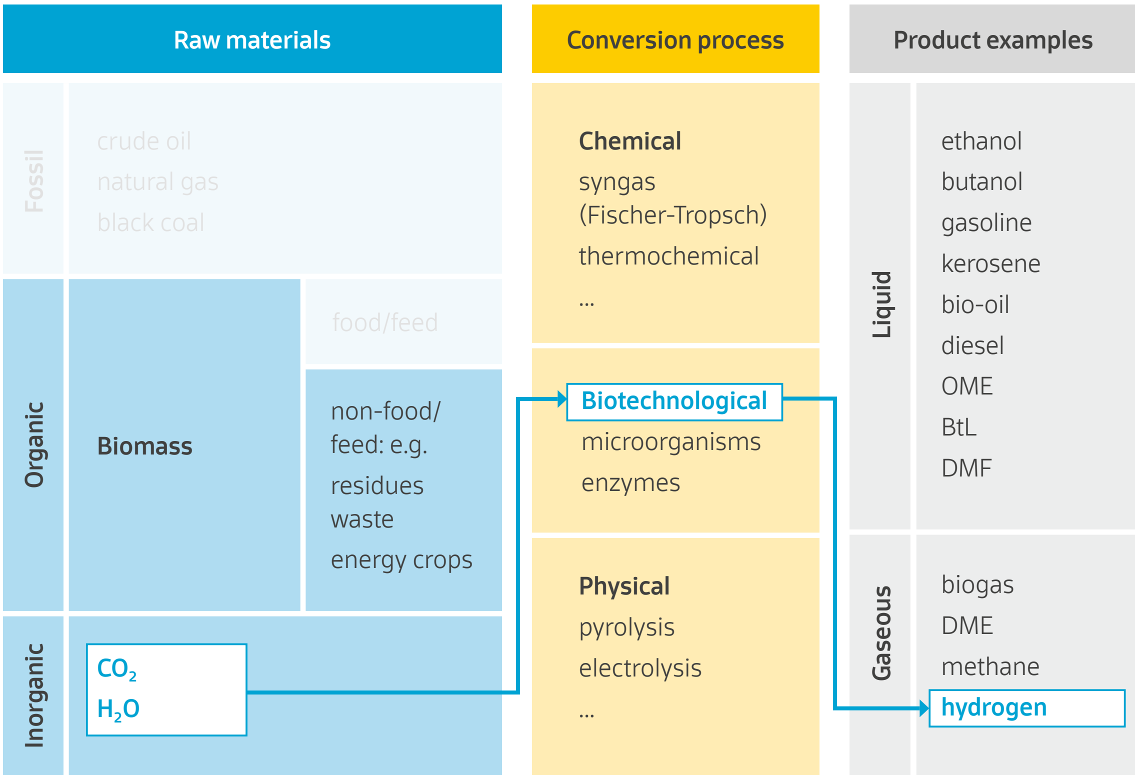


Figure 16: *Flow diagram of the process of the biologically hydrogen production from carbon dioxide and water. OME = Poly-oxy-methylene-dimethyl ether (H_3C-O-$(CH_2O)_n$-CH_3, $n \geq 2$), BtL = Biomass to Liquid, DMF: Dimethylfuran, DME = Dimethyl ether*

In the methods compiled above, hydrogen has been reported to be obtained by electrolysis of water or by chemical conversion of formate, which in turn may be produced from biomass.

Since several microorganisms can produce hydrogen, microbial fermentation appears to be, in principle, a suitable alternative for hydrogen production. However, biological hydrogen production methods are faced with multiple barriers including substrate cost, low production rates and low yields. Moreover, most of the hydrogen-producing microbes need an oxygen-free environment. Attempts to overcome these barriers do exist. For example, in 2010 a marine cyanobacterium was found to produce hydrogen at a rate at least ten times higher than that of other known microbes and without the need of oxygen exclusion[61]. In 2015, the complete cell-free conversion of glucose and xylose with the maximum possible yield of hydrogen (and carbon dioxide) and with reasonable kinetics was reported[62]. In this method, more than ten purified enzymes were combined into artificial enzymatic pathways.

61 Bandyopadhyay, A., Stöckel, J., Min, H., Sherman, L. A., & Pakrasi, H. B. (2010). High rates of photobiological H 2 production by a cyanobacterium under aerobic conditions. Nature communications, 1, 139.

62 Rollin, J. A., del Campo, J. M., Myung, S., Sun, F., You, C., Bakovic, A., ... & Senger, R. S. (2015). High-yield hydrogen production from biomass by in vitro metabolic engineering: mixed sugars coutilization and kinetic modeling. Proceedings of the National Academy of Sciences, 112(16), 4964-4969.

A completely new method enabling the production of hydrogen gas from solar energy has been developed recently at Uppsala University. Researchers of the Lindblad group generated an artificial enzyme functioning in and connecting to the metabolism in living cyanobacterial cells producing hydrogen at high rates[63].

In contrast to hydrogen, the storage of formate requires neither enormous volume, nor cooling or high pressure. Unsurprisingly, due to its favorable storage properties, formate plays a role in biological hydrogen production as well. Formate itself can be produced from various sources. Müller and co-workers[64] established a formate-based hydrogen production method utilizing the acetogenic bacterium *Acetobacterium woodii* (different from the formatotrophic microbes in eForFuel, which metabolize formate to propane and isobutene). *A. woodii* reached one of the highest formate-dependent specific hydrogen productivity rates at ambient temperatures reported so far for an organism without genetic modification. Consequently, this organism is a very promising candidate for sustainable formate-based hydrogen production and, because of the reversibility of the reaction, vice versa.

To our knowledge, however, all these results have been demonstrated in laboratory scale only. More approaches for the biological generation of biomass based and photosynthetic hydrogen are described in the reviews of Mudhoo et al. (2018)[65] and Khetkorn et al. (2017)[66], respectively.

Notes about the gaseous advanced biofuel DME, which is not considered here in detail:

DME (Dimethyl ether, "bioethers"): DME can serve as a diesel substitute in diesel engines, after slight modifications. After the gasification of lignocellulosic biomass to generate synthesis gas, it can be converted to DME. According to the European Commission, DME produced in this way is considered a biofuel and can replace liquid gas in the long term.[67] Since 2012, the feasibility of this technology is demonstrated at the Chemrec pilot plant in Piteå, Sweden. Here, black liquor from the paper and pulp industry is converted to BioDME[68].

63 Wegelius, A., Khanna, N., Esmieu, C., Barone, G. D., Pinto, F., Tamagnini, P., ... & Lindblad, P. (2018). Generation of a functional, semisynthetic [FeFe]-hydrogenase in a photosynthetic microorganism. Energy & environmental science, 11(11), 3163-3167.

64 Kottenhahn, P., Schuchmann, K., & Müller, V. (2018). Efficient whole cell biocatalyst for formate-based hydrogen production. Biotechnology for biofuels, 11(1), 93.

65 Mudhoo, A., Torres-Mayanga, P. C., Forster-Carneiro, T., Sivagurunathan, P., Kumar, G., Komilis, D., & Sánchez, A. (2018). A review of research trends in the enhancement of biomass-to-hydrogen conversion. Waste management, 79, 580-594.

66 Khetkorn, W., Rastogi, R. P., Incharoensakdi, A., Lindblad, P., Madamwar, D., Pandey, A., & Larroche, C. (2017). Microalgal hydrogen production – A review. Bioresource technology, 243, 1194-1206.

67 http://ec.europa.eu/research/energy/pdf/draft_vision_report_en.pdf

68 http://www.etipbioenergy.eu/index.php?option=com_content&view=article&id=279

Some critical remarks on advanced biofuels

The main criterion for any biofuel to be designated “advanced” is that it is made from sustainable feedstock. However, one must be very cautious with the statement that a certain feedstock and accordingly the production process as well as the resulting biofuel are renewable, sustainable and environmentally friendly. A renewable feedstock is not automatically sustainable. E.g. a crop that might be clearly renewable but is not available in “a large enough quantity to meet a reasonable proportion of our energy demands”[69]; which implies major direct or indirect land use changes; or its cultivation, harvest and/or processing does have a large impact on greenhouse gas emissions, cannot be considered sustainable[70].

In fact, second-generation (energy) crops, e.g. Jatropha, have often led to disappointment, as they require a great deal of water and fertilizer to grow and therefore indirectly actually lead to an increased impact on greenhouse gas emission. Similarly, biofuels produced by algae, have not met the criteria to be called truly sustainable yet. Their heavy demand for water, nitrogen and phosphorus means “that the production of fertilizer to meet the needs of algae, used to produce biofuel, would produce more greenhouse gas emissions than were saved by using algae-based biofuel”[71].

Furthermore, users of the term sustainability sometimes also fail to recall clearly and to consider additional important aspects, e.g. what impact the extended use of a particular feedstock could have on biodiversity. Henceforth, biofuels, even from non-food/feed biomass, must be carefully assessed to meet at least all these requirements in order to be truly sustainable.

In addition, for industrial purposes advanced biofuels must prove their economic viability and competitiveness to fossil-based or first-generation (bio)fuels, in order to be worth considering or at least to be deemed promising developments.

69 *http://biofuel.org.uk/advanced-biofuels.html*
70 *http://biofuel.org.uk/advanced-biofuels.html*
71 *http://biofuel.org.uk/third-generation-biofuels.html*

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