Production



## Bioenergy value chain 1: biomass to liquid

Lab scale

ilot Plant

Figure 1: biomass-to-liquid value chain

#### Feedstock

For gasification, any lignocellulosic material is suitable as feedstock. The term lignocellulosic covers a range of plant molecules/biomass containing cellulose, with varying amounts of lignin, chain length, and degrees of polymerization. This includes wood from forestry, short rotation coppice (SRC), and lignocellulosic energy crops, such as energy grasses and reeds. Biomass from dedicated felling of forestry wood is also lignocellulosic but is not considered sustainable.

**Bench scale** 

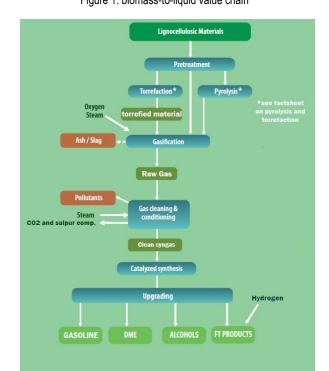
#### Gasification

Gasification is a thermochemical process at 800-1300°C run at under-stoichiometric conditions (typically  $\lambda = 0.2$ -0.5). Under these conditions the biomass is fragmented into raw gas consisting of rather simple molecules such as: hydrogen, carbon monoxide, carbon dioxide, water, methane, etc. Solid by-products are: char, ashes and impurities. The gaseous molecules are then chemically resynthesized to biofuels.

After size reduction of the raw material, it is moved into the gasifier. Typical gasification agents are: oxygen and water/steam. The choice of the gasification agent depends on the desired raw gas composition. The combustible part of the raw gas consists of hydrogen (H<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>) and short chain hydrocarbons; the non-combustible components are inert gases. A higher process temperature or using steam as gasification agent leads to increased H<sub>2</sub> content. High pressure, on the other hand, decreases the H<sub>2</sub> and CO.

Entrained-flow gasifiers operate at high temperatures (1000-1300 °C) and are therefore suitable when a low methane content is preferred. Bubbling and circulating bed gasifiers in contrast are operated at lower temperatures (800-1000 °C).

The process heat can either come from an autothermal partial combustion of the processed material in the gasification stage or allothermally via heat exchangers or heat transferring medium. In the latter case the heat may be generated by the combustion of the processed material (i.e., combustion and gasification are physically separated) or from external sources.



#### **End products**

Biomethanol

Can be blended to gasoline; purely used in race cars

BioDME

Stored in the liquid state under relatively low pressure of 0.5 MPa

Biogasoline

Renewable diesel

Biokerosene (jet fuel)

In contrast to bioethanol or biodiesel (FAME), biogasoline, renewable diesel and biokerosene have the same combustion properties as their fossil based equivalents, gasoline, diesel or kerosene. They can thus be used without adaption or blend-limits in conventional engines.

**By-products** 

Naphta, e.g. from FT synthesis

Impurities of the raw gas depend on the gasification condition and used biomass and can cause corrosion, erosion, deposits and poisoning of catalysts. It is therefore necessary to clean the raw gas. Depending on technology impurities such as dust, ashes, bed material, tars and alkali compounds are removed through various cleaning steps. Components having mainly poisonous effects are sulphur compounds, nitrogen and chloride. The sulphur compounds can be withdrawn by commercially available processes; to get rid of nitrogen and chloride wet washing is required.

The cleaned raw gas will then be upgraded to clean synthesis gas (syngas).

An optimal  $H_2$ /CO ratio of about 1 – 2 is obtained by the Water-gas-shift reaction:

$$\mathsf{CO} + \mathsf{H}_2\mathsf{O} \leftrightarrow \mathsf{CO}_2 \ + \mathsf{H}_2.$$

The gas reforming reaction converts short-chain organic molecules to CO and H2 (for example

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

CO<sub>2</sub> removal can be performed by physical or chemical methods. Other absorption methods are based on pressure or temperature variations.

#### Product formation

#### Fischer-Tropsch-Liquids

In the Fischer-Tropsch (FT) process, the clean syngas is transformed into alkanes using mostly iron and cobalt as catalysts. The Low Temperature Fischer-Tropsch (LTFT) technology ( $200 - 220^{\circ}C$  and less 20 bar) provides outputs for diesel production. The raw product, though, cannot be directly used as fuel, it needs to be upgraded via distillation to split it into fractions; via hydration and isomerization of the C5 – C6 fraction and reforming of the C7 – C10 fraction in order to increase the octane number for gasoline use; and via cracking by application of hydrogen under high pressure in order to convert long-chain fractions into gasoline and diesel fraction.

#### Methanol and dimethyl ether (DME)

The syngas is converted into DME via a two-step synthesis, first to methanol in the presence of catalyst (usually copper-based), and then by

# Example projects on biomass-to-liquid production

#### Pilot

BioDME	producing DME; formerly operated by Chemrec and LTU (Sweden); now idle
Bioliq	producing biogasoline; run by Karlsruhe Institute of Technology (Germany); operational since 2014
Güssing FT	producing renewable diesel on gasifier side stream; run by Vienna University of Technology and BIOENERGY 2020+ (Austria); operational since 2005
BioTfueL	will produce biokerosene; run by a French industrial consortium; planned operation 2020
Demo	
None in Europe	
Edmonton Waste-to- Biofuels	producing ethanol and methanol; run by Enerkem (Canada);

The following reactions occur:  $2H_2 + CO \leftrightarrow CH_3OH$   $2 CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$   $CO+H_2O \leftrightarrow CO_2+H_2$ Alternatively, DME can be produced through direct

Alternatively, DME can be produced through direct synthesis using a dual-catalyst system which permits both methanol synthesis and dehydration in the same process unit, with no intermediate methanol separation.

operational since 2014

#### **Further information**

project

Read up-to-date information about the thermochemical conversion technology at <u>www.biofuelstp.eu.</u>



## Bioenergy value chain 2: biomass to gas

Lab scale

Bench scale

Pilot Plant

Demonstratio

Production

#### Feedstock

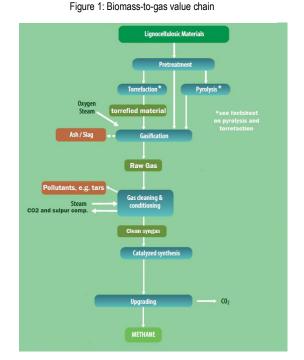
For gasification, any lignocellulosic material is suitable as feedstock. The term lignocellulosic covers a range of plant molecules/biomass containing cellulose, with varying amounts of lignin, chain length, and degrees of polymerization. This includes wood from forestry, short rotation coppice (SRC), and lignocellulosic energy crops, such as energy grasses and reeds. Biomass from dedicated felling of forestry wood is also lignocellulosic but is not considered sustainable.

#### Gasification

Gasification is a thermochemical process at 800-1300°C and under shortage of oxygen (typically  $\lambda$ = 0.2-0.5). Under these conditions the biomass is fragmented into raw gas consisting of rather simple molecules such as: hydrogen, carbon monoxide, carbon dioxide, water, methane, etc. Solid by-products are: char, ashes and impurities. The gaseous molecules are then chemically re-synthesized to biofuels.

After size reduction of the raw material, it is moved into the gasifier. Typical gasification agents are: oxygen and water/steam. The choice of the gasification agent depends on the desired raw gas composition. The combustible part of the raw gas consists of hydrogen ( $H_2$ ), carbon monoxide (CO), methane (CH<sub>4</sub>) and short chain hydrocarbons; the non-combustible components are inert gases. A higher process temperature or using steam as gasification agent leads to increased  $H_2$  content. High pressure, on the other hand, decreases the  $H_2$  and CO.

Entrained-flow gasifiers operate at high temperatures (1000-1300 °C) and are therefore suitable when a low methane content is preferred. Bubbling and circulating bed gasifiers in contrast are operated at lower temperatures (800-1000 °C).



#### **End products**

Synthetic natural gas (SNG)

For application as car fuels, SNG is either compressed at around 200 bar or liquefied at - 161.7°C at atmospheric pressure.

#### **By-products**

Carbon monoxide (CO)

Carbon monoxide is not suitable for the use in vehicle engines.

The process heat can either come from an autothermal partial combustion of the processed material in the gasification stage or allothermally via heat exchangers or heat transferring medium. In the latter case the heat may be generated by the combustion of the processed material (i.e., combustion and gasification are physically separated) or from external sources.

Impurities of the raw gas depend on the gasification condition and used biomass and can cause corrosion, erosion, deposits and poisoning of catalysts. It is therefore necessary to clean the raw gas. Depending on technology impurities such as dust, ashes, bed material, tars and alkali compounds are removed through various cleaning steps. Components having mainly poisonous effects are sulphur compounds, nitrogen and chloride. The sulphur compounds can be withdrawn by commercially available processes; to get rid of nitrogen and chloride wet washing is required.

Components having mainly poisonous effects are sulphur compounds, nitrogen and chloride. The sulphur compounds can be withdrawn by an amine gas treating, a benfield process or similar process; to get rid of nitrogen and chloride wet washing is required.

The cleaned raw gas will then be upgraded to clean synthesis gas (syngas).

- An optimal H<sub>2</sub>/CO ratio of 3,0 is obtained by the Water-gas-shift reaction: CO + H<sub>2</sub>O ↔ CO<sub>2</sub> + H2.
- CO<sub>2</sub> removal can be performed by physical (absorption to water or other solvents) or chemical (absorption to chemical compounds) methods. Other absorption methods are based on pressure or temperature variations.

#### **Product formation**

#### Synthetic natural gas or Bio-SNG

The upgrading to SNG (synthetic natural gas) requires methanation of the cleaned syngas, followed by a final  $CO_2$  removal. In the methanation step (catalyzed by nickel oxide) at 20-30 bar pressure and high temperature carbon monoxide reacts with hydrogen forming methane and water

## Example projects on biomass-to-gas production

Pilot	
ECN	Dutch project producing synthetic natural gas; operational in 2008 ; currently idle
GAYA	producing synthetic natural gas; run by French consortium; start-up planned in 2017
Demo	
GoBiGas I	producing synthetic natural gas; run by Goteborg Energi (Sweden); operational since 2014

The withdrawal of  $CO_2$  can be performed by water scrubbing (a counter-current physical absorption into a packed column) and Pressure Swing Adsorption (an absorption into a column of zeolites or activated carbon molecular sieves followed by a hydrogen sulphide removing step) technologies. Natural gas quality is reached at 98% methane content. The final step is the gas compression (up to 20 bar for injection into the natural gas grid, up to 200 bar for storage or for use as vehicle fuel).

#### Further information

Read up-to-date information about the thermochemical conversion technology at <u>www.biofuelstp.eu</u>





## Bioenergy value chain 3: power and heat via gasification

Lab scale Pilot Plant Demonstration Production

#### Feedstock

For gasification, any lignocellulosic material is suitable as feedstock. The term lignocellulosic covers a range of plant molecules/biomass containing cellulose, with varying amounts of lignin, chain length, and degrees of polymerization. This includes wood from forestry, short rotation coppice (SRC), and lignocellulosic energy crops, such as energy grasses and reeds. Biomass from dedicated felling of forestry wood is also lignocellulosic but is not considered sustainable.

#### Gasification

Gasification is a thermochemical process at 800-1300°C and under shortage of oxygen (typically  $\lambda =$  0.2-0.5). Under these conditions the biomass is fragmented into raw gas consisting of rather simple molecules such as: hydrogen, carbon monoxide, carbon dioxide, water, methane, etc. Solid byproducts are: char, ashes and impurities. The gaseous molecules are then chemically resynthesized to biofuels.

After size reduction of the raw material, it is moved into the gasifier. Typical gasification agents are: oxygen and water/steam. The choice of the gasification agent depends on the desired raw gas composition. The combustible part of the raw gas consists of hydrogen (H<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>) and short chain hydrocarbons; the non-combustible components are inert gases. A higher process temperature or using steam as gasification agent leads to increased H<sub>2</sub> content. High pressure, on the other hand, decreases the H<sub>2</sub> and CO.

Entrained-flow gasifiers operate at high temperatures (1000-1300 °C) and are therefore suitable when a low methane content is preferred. Bubbling and circulating bed gasifiers in contrast are operated at lower temperatures (800-1000 °C).

The process heat can either come from an autothermal partial combustion of the processed material in the gasification stage or allothermally via heat exchangers or heat transferring medium. In the latter case the heat may be generated by the combustion of the processed material (i.e., combustion and gasification are physically separated) or from external sources.

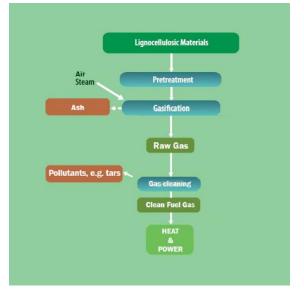


Figure 1: Power-to-heat-via-gasification value chain

#### **End products**

Power

Heat

The excess heat of the power production can be used for district heating, district hot water or industrial process heating.

Cooling

An alternative way to use the excess heat is to produce cooling from heat-driven heat pumps.

Impurities of the raw gas depend on the gasification condition and used biomass and can cause corrosion, erosion, deposits and poisoning of catalysts. It is therefore necessary to clean the raw gas. Depending on technology impurities such as dust, ashes, bed material, tars and alkali compounds are removed through various cleaning steps. Components having mainly poisonous effects are sulphur compounds, nitrogen and chloride. The sulphur compounds can be withdrawn by commercially available processes; to get rid of nitrogen and chloride wet washing is required.

The cleaned raw gas, now a clean fuel gas, must meet the quality requirement of the power (and heat) generating unit which normally would be a gas engine or a gas turbine.

#### Application

#### Use as engine fuel

The fuel gas can be used in spark-ignited (Otto) engines and in compression (Diesel) engines and for gas turbines for power and heat production. Engines are applied for power generation in the range of 500 kW up to 40 MW. Biomass-to-electricity efficiency in practice lies between 25 and 31 %, and the overall performance between 80 and 92 %

As heat is not always a desired output of a CHP plant, some plants use an organic Rankine cycle to further convert heat into electricity, increasing the electric output by 20 to 30 %.

Another point of attention is that the exact composition of the producer gas will vary with each batch of biomass feedstock. This requires advanced automatic engine controls to adapt engine operations to maintain load and avoid excessive amounts of hazardous emissions.

One way to limit too brisk changes in engine operation is to use sufficiently large buffer tanks.

#### Use for co-firing

The idea of co-firing is to use existing large scale power plants and replace part of the fossil fuels (coal, oil, natural gas) by biomass.

Example of gasification CHP plants

Pilot	
Fundacion Cidaut	Spanish project producing 100-150 kWel
Commercial	
Skive plant	Capacity of 6 MWel and 20 MWth; run by city of Skive (Denmark); operational since 2008
Güssing plant	Capacity of 2 MW <sub>el</sub> and 4,5 MW <sub>th;</sub> run by a public-private consortium (Austria); operational since 2002
CFB Geertruidenberg	9600 MW <sub>el</sub> coal power plant, 30 MW <sub>el</sub> of co-firing product gas; run by the Dutch energy company Essent; operational since 2005

The previous gasification of the biomass offers a number of advantages compared to direct cofiring when solid biomass is fed into the boiler:

- Higher fuel flexibility
- No significant impact the • on performance of the boiler
- Less strict requirements in the producer gas quality as compared to other applications
- Possibility of keeping the biomass ash separated from coal ash.

#### Further information

up-to-date information about Read the thermochemical conversion technology is available at www.biofuelstp.eu.





## Bioenergy value chains 4: pyrolysis and torrefaction

Lab scale

Bench scale

Pilot Plant

Production

#### Feedstock

For pyrolysis any lignocellulosic material is suitable as feedstock. The term lignocellulosic covers a range of plant biomass containing cellulose, with varying amounts of lignin, chain length, and degrees of polymerization. This includes wood from forestry, short rotation coppice (SRC), crops residues (such as straw), and lignocellulosic energy crops, such as energy grasses and reeds. Biomass from dedicated felling of forestry wood is also lignocellulosic but is not considered sustainable.

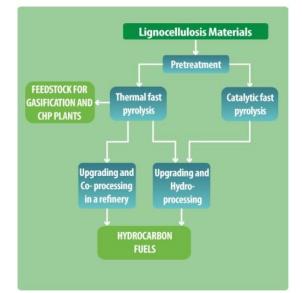
#### Torrefaction

Torrefaction is a thermochemical process typically at 200-350 °C in the absence of oxygen, at atmopsheric pressure with low particle heating rates and a reactor time of one hour. The process causes biomass to partly decompose, creating torrefied biomass or char, also referred to as "bio-coal". Bio-coal has a higher energy content per unit volume, and torrefaction followed by pelletisation at the harvest sites facilitates transport over longer distances. It also avoids problems associated with decomposition of biomass during storage. Hence the benefits of torrefaction may outweigh the additional cost in many cases.

#### **Pyrolysis**

Pyrolysis is the chemical decomposition of organic matter by heating in the absence of oxygen. The biomass decomposes into vapour, aerosols, and char; the proportions of these three states depend on temperature and duration of the pyrolysis. Two alternatives are thermal and catalytic pyrolysis.

The decomposition into a liquid fraction is of particular interest currently as the liquids are transportable and storable. The highest yield of liquid fraction is obtained by thermal fast pyrolysis. Figure 1: Pyrolysis and torrefaction value chain



#### Intermediate products

Char coal (also called bio-coal) Torrefied pellets Bio-oil (also called bio-crude oil)

Fast pyrolysis takes 1 to 2 seconds at around 500°C. In preparation, the biomass needs to be dried to typically less than 10% water and crushed to particles of less than 5 mm. The heating medium is typically sand, but also catalyst has been used. The biomass decomposes into organic vapours, non-condensable gases, pyrolysis water, and char. When the gaseous components cool down and condensate, a dark brown mobile liquid is formed, called bio-oil. Organic bio-oil is obtained in yields of up to 65%wt on dry feed basis. The by-products char and gas are used within the process to provide the process heat requirements so there are no waste streams other than flue gas and ash. Lower yield but a higher quality bio-oil is generated in catalytic fast pyrolysis, where catalyst in-stead of sand is used as a heating media.

Bio-oil has a heating value about half that of conventional fuel oil. It can currently be used to replace natural gas or heating oil. In the future it may be upgraded and co-fed in existing refineries into advanced biofuels that have the same combustion properties as conventional fossil transport fuels.

#### **Further information**

Read up-to-date information about the thermochemical conversion technology at <u>www.biofuelstp.eu</u>.

Example pyrolysis	projects	torrefaction	and
Pilot			
Bioliq	followed producin DME; run by K Technolo	olysis of biomass by gasification; g biogasoline via arlsruhe Institute ogy (Germany); nal since 2014	a
PYTEC		company workin nent of pyrolysis 02.	
		lant started in 20 g bio-oil to a bloo	
UPM/ Metso/ Fortum/ VTT	pilot read deliverin heating p	g bio-oil to a dist	-
Demo			
Topell Energy	offering technolo running	ant constructor torrefaction gy; a demo plant in t uiven since 2010	
First-of-a-k	ind comme	rcial	
Fortum	Finnish d	ng bio-oil in the city of Joensuu; d to heating plan 13	ts
Empyro	run by B (Netherla		
Ensyn		ng bio-oil in Onta since 2008	rio,
-		0	



## Bioenergy value chain 5: sugar to alcohols

Lab scale

Bench scale

Pilot Plant

Production

#### Feedstock

Sugars can be fermented into alcohols. Sugars are obtained from sugar crops, starch crops and lignocellulose.

#### Sugar crops

Among sugar crops, the most extended are sugarcane and sugar beet, and to a lesser extent, sweet sorghum. The sugar is extracted via milling (sugarcane, sweet sorghum) or via heat extraction and vaporisation (sugar beet).

#### Starch crops

Starch crops are mainly maize, wheat, other cereals and potatoes. Starch is a polysaccharide and needs to be hydrolized into monosaccharides (sugars) for fermentation. For this saccharification the technique commonly applied is enzymatic hydrolysis, generally associated to "jet cooking".

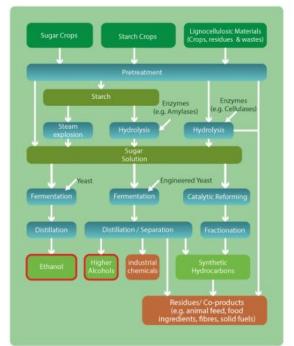
In the enzymatic hydrolysis, the starch crops are crushed and mashed; then enzymes (e.g. amylases) are added to the mash which dissolve the starch into sugar.

#### Lignocellulosics

Lignocellulose is the structural material of biomass. It consists of cellulose (mainly C6 sugar polymers like the sugar extracted from sugar and starch crops), hemicellulose (mainly C5 sugar polymers) and lignin (aromatic alcohol-polymers). The term lignocellulosics includes agricultural and wood residues, wood from forestry, short rotation coppices (SRC), and lignocellulosic energy crops, such as energy grasses and reeds.

A pretreatment is generally first applied on the raw material before saccharification to separate the different elements. The most common one is the steam explosion associated or not with an acid catalyst.

Once the cellulose and the hemi-cellulose are separated from the lignin, saccharification of these polysaccharides can take place, generally speaking through enzymatic hydrolysis (use of cellulases and hemi cellulases). The C6 sugars can be fermented by common yeasts while C5 sugars need specific microorganisms to get fermented. Lignin is for now usually separated and dried to be used as a fuel for the process or for power generation. Figure 1: Biochemical value chains



#### End products

#### Bioethanol

#### Biobutanol

Properties of butanol are closer to gasoline than properties of ethanol as concerns e.g. heating value, vapor pressure, water tolerance, corrosiveness, and polarity.

#### **By-products**

Lignin

Often combusted to produce process heat; also serves as feedstock for a variety of chemical products or materials.

#### Yeast fermentation to ethanol

C6 sugars are fermented by traditional yeasts that are also used for the production of wine, beer or bread. The process is:

#### $C_6H_{12}O_6 \leftrightarrow 2 \ C_2H_5OH + 2 \ CO_2.$

For the fermentation of C5 sugars genetically modified yeasts have been developed in the recent years.

As ethanol is a toxin, there is a limit to the maximum concentration in the brew produced by the yeasts. The upgrading of ethanol from lower concentrations to the required 98.7%m/m for the application as biofuel is performed employing the following known and widely applied technological steps:

- Evaporation of ethanol from beer: in this step the first evaporation of ethanol is performed in order to obtain 'crude' ethanol with concentration ~45%V/V.
- Rectification: in rectification the ethanol concentration is increased to ~96%V/V

Dehydration: by dehydration the remaining azeotropic water is removed in order to obtain the fuel bioethanol with concentration 98.7%m/m and water content below 0.3% m/m.

#### Yeast fermentation to butanol

There is significant interest in the production of butanol as a biofuel because its properties are more adequate to a gasoline blend (e.g. vapor pressure, water entrainment) but the production cost is still more expensive than for ethanol. Some bacterias naturally produce butanol and yeast can be engineered to produce butanol instead of ethanol. Butanol may serve as an alternative fuel, as e.g. 85% Butanol/gasoline blends can be used in unmodified petrol engines.

#### Microbial Fermentation via Acetic Acid

Microbial fermentation of sugars can also use an acetogenic pathway to produce acetic acid without  $CO_2$  as a by-product. This increases the carbon utilization of the process. The acetic acid is converted to an ester which can then be reacted with hydrogen to make ethanol.

The hydrogen required to convert the ester to ethanol could be produced through gasification of the lignin residue. This requires fractionation of the feedstock into a sugar stream and a lignin residue at the beginning of the process.

# Example projects on sugar-to-alcohols production

#### Pilot

Butamax Advanced Biofuels LLC	British facility producing butanol from sugar and starch crops; joint venture of BP and DuPont; currently idle	
Gevo	US-company producing iso- butanol via a biocatalysis/ fermentation; operational since 2012	
Demo		
Inbicon	producing ethanol and lignin by products from mainly wheat straw; run by DONG Energy (Denmark); operational since 2009	
Booregaard	Norwegian facility producing ethanol, lignin and chemicals from various lignocellulosic crops and residues; operational since 2012	
Abengoa	Spanish facility producing ethanol from organic waste; currently idle	
First-of-a-kind commercial		
Beta Renewables	Italian facility producing ethanol from lignocellulosic crops and residues; joint venture of Mossi & Ghisolfi, Chemtex and TPG; operational since 2012	

#### Further information

Read up-to-date information about the biochemical conversion technology on <u>www.biofuelstp.eu</u>.



Production

## Bioenergy value chain 6: sugar to hydrocarbons

Lab scale

Bench scale

Pilot Plant

nstration

# Figure 1: Biochemical value chains

#### Feedstock

Sugars can be fermented into alcohols. Sugars are obtained from sugar crops, starch crops and lignocellulose.

#### Sugar crops

Among sugar crops, the most extended are sugarcane and sugar beet, and to a lesser extent, sweet sorghum. The sugar is extracted via milling (sugarcane, sweet sorghum) or via heat extraction and vaporisation (sugar beet).

#### Starch crops

Starch crops are mainly maize, wheat, other cereals and potatoes. Starch is a polysaccharide and needs to be hydrolized into monosaccharides (sugars) for fermentation. For this saccharification the techniques commonly applied is enzymatic hydrolysis, generally associated to "jet cooking".

In the enzymatic hydrolysis, the starch crops are crushed and mashed; then enzymes (e.g. amylases) are added to the mash which dissolve the starch into sugar.

#### Lignocellulosics

Lignocellulose is the structural material of biomass. It consists of cellulose (mainly C6 sugar polymers like the sugar extracted from sugar and starch crops), hemicellulose (mainly C5 sugar polymers) and lignin (aromatic alcohol-polymers). The term lignocellulosics includes agricultural and wood residues, wood from forestry, short rotation coppices (SRC), and lignocellulosic energy crops, such as energy grasses and reeds.

A pretreatment is generally first applied on the raw material before saccharification to separate the different above elements. The most common one is the steam explosion associated or not with an acid catalyst.

Once the cellulose and the hemi-cellulose are separated from the lignin, saccharification of these polysaccharides can take place, generally speaking through enzymatic hydrolysis (use of cellulases and hemi cellulases).

The C6 sugars can be fermented by common yeasts while C5 sugars need specific microorganisms to get fermented. Lignin is for now usually separated and dried to be used as a fuel for the process or for power generation.

#### Intermediate products

Furanics Blended with diesel and gasoline

Farnesene Feedstock for renewable diesel

#### End products

**Bio-gasoline** 

Renewable diesel

Bio-kerosene (jet fuel)

Bio crude oil

Isobutanol Blended with gasoline and diesel

#### **By-products**

#### Lignin

Often combusted to produce process heat; also serves as feedstock for a variety of chemical products.

#### Farnesene via microbial fermentation

Engineered yeasts can be used to ferment sugar into a class of compounds called isoprenoids which includes pharmaceuticals, nutraceuticals, flavors and fragrances, industrial chemicals and chemical intermediates, as well as fuels. One of these isoprenoids is a 15-carbon hydrocarbon, beta-farnesene.

Beta-farnesenes can be chemically derivatized into a variety of products, including diesel, a surfactant used in soaps and shampoos, a cream used in lotions, a number of lubricants, or a variety of other useful chemicals. This process is applied by Amyris.

#### Catalytic Reforming

Soluble carbohydrate streams can consist of a wide range of molecules such as C5/C6 sugars, polysaccharides, organic acids, furfurals and other degradation products generated from the deconstruction of biomass. These can be processed through aqueous phase reforming (APR). The aqueous phase reforming step utilizes heterogeneous catalysts at moderate temperatures and pressures to reduce the oxygen content of the carbohydrate feedstock. Some of the reactions in the APR step include: (1) reforming to generate hydrogen; (2) dehydrogenation of alcohols/hydrogenation of carbonyls; (3) deoxygenation reactions; (4) hydrogenolysis; and (5) cyclization. Hydrogen is produced in-situ from the carbohydrate feedstock.

The product from the APR step is a mixture of chemical intermediates including alcohols, ketones, acids, furans, paraffins and other oxygenated hydrocarbons. Once these intermediate compounds are formed they can undergo further catalytic processing to generate a cost-effective mixture of nonoxygenated hydrocarbons.

The chemical intermediates from the APR step can be reacted over a zeolite catalyst (ZSM-5) to produce a high-octane gasoline blendstock that has a high aromatic content similar to a petroleum-derived reformate stream.

The chemical intermediates from the APR step can also be converted into distillate range hydrocarbon components through a condensation step followed by conventional hydrotreating.

# Example projects on sugar-to-hydrcarbons production

#### Pilot

Avantium	Dutch company producing furanic building blocks via catalytic dehydration followed by an oxidation process; operational since 2011	
Gevo	US-company producing isobutanol via biocatalysis/ fermentation; operational since 2012	
Neste/ DONG Energy	Finnish/ Danish joint venture to develop sugar-to-oil technology; pilot phase completed in 2014	
Demo		
Virent	US-facility producing renewable diesel from sugar via the patented Aqueous Phase Reforming (APR); operational since 2009	
First-of-its-kind commercial		
Amyris	US-company producing farnesene from sugars facilities in Brazil; first started in 2009	

#### Further information

Read up-to-date information about the biochemical conversion technology on <u>www.biofuelstp.eu</u>.



## Bioenergy value chain 7: aquatic biomass

#### Lab scale

Bench scale

#### Pilot plant

Demonstration Production

#### Aquatic vs. terrestrial biomass

Photosynthetic algae (including macroand micro-algae) and photosynthetic cyanobacteria have the potential to produce considerably greater amounts of biomass per hectare than terrestrial crops; some species directly produce fuel (hydrogen, ethanol or alkanes). Advantages of such aquatic biomass are that non- arable land or even offshore can be used for cultivation; sea or brackish water can be used, as well as industrial carbon dioxide as carbon source or wastewater as nutrient input (nitrogen and phosphorus). Aquatic biomass are energy crops that do not compete with food crops for land or other resources.

There are many parameters that influence aquatic biomass productivity and composition like irradiance levels, dark/light cycles,  $CO_2$  and  $O_2$  concentration, temperature, pH, salinity and nutrients. The maximum theoretical biomass productivity of algae can reach 100 g/m<sup>2</sup>/d, but real productivities in good locations are around 15-20 g/m<sup>2</sup>/d at present. There are intensive R&D activities at lab and pilot scale to improve these results.

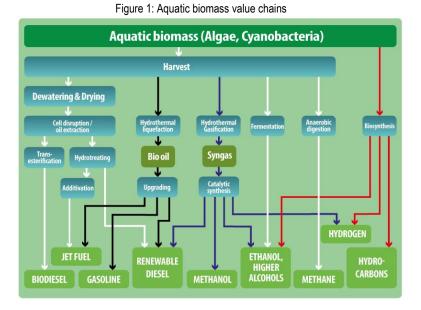
Algae biomass composition consists of carbohydrates, proteins, lipids and other products such as pigments, vitamins, etc., being lipids the most interesting fraction for conversion into biofuels. Oleaginous strains (at least 20% lipid content on Dry Weight (DW) basis) can overproduce lipids (up to 70% lipids on DW basis) under selected severe stress conditions such as N and/or Si starvation.

#### Cultivation

Major distinctions of cultivation methods are between micro- and macroalgae. Macroalgae are mainly cultivated off-shore in open systems, whereas microalgae can be cultivated on-shore in either open or closed systems.

Large scale cultivation of microalgae in on-shore outdoor open pond systems is well established. Cultivation in open systems is only suitable for a few algal species which can tolerate extreme environmental conditions.

Closed cultivation systems for microalgae, usually onshore, utilize photobioreactors made of transparent tubes, plates, bags or domes, which permit culture of single species. Either biomass or lipid productivities in photobioreactors can nearly be twice as high as for open ponds.



#### Final energy products

Biodiesel (FAME) Renewable diesel

- Straight vegetable oil (SVO)
- Biokerosene (jet fuel)
- Gasoline
- Ethanol
- Methanol
- Methane
- Hydrogen
- Syngas

Non-energy co-products

Proteins, special oils (omega-3), vitamins, pigments, nutraceuticals

The scale of photobioreactors is yet limited by the build up of oxygen which would rapidly reach inhibitor levels. Besides, the larger a photobioreactor the more difficult it is to keep the monoculture free of parasites or other species.

Heterotrophic and mixotrophic algae cultivation is done in stirred tank bioreactors or in fermenters.

Macroalgae (seaweed) are usually cultivated in offshore farms but their productivity is much lower than that of microalgae. Their composition is mainly carbohydrates, not lipids.

#### Harvesting and drying

The typical microalgae concentration in cultivation broths is 0.02 - 0.07% of total suspended solids (open ponds), in photobioreactors it ranges from 0.14 - 0.7% dry matter. The recovery of the microalgae from the algae suspension is affected in two steps. A pre-concentration step or bulk harvesting leads to a concentration of 2 - 7%. Methods are flocculation via thickeners, dissolved air flotation (for small microalgae) and sedimentation (for large microalgae). The second concentration step is the thickening or dewatering and brings the concentration of solid matter up to 15 - 25%. Main methods are centrifugation, filtration and ultrasonic aggregation. In a third step the harvested algal paste needs to be dried. To prevent from degradation the moisture level should be kept below 7%. Methods are solar-drying, drumdrying, freeze-drying and spray-drying. Apart from solardrying, drying is very energy intensive and accounts for a large part of total energy consumption.

#### Conversion technologies

Algae and its cellular components have been considered as feedstocks to be processed to create a variety of end-use energy products, which include a wide range of liquid and gaseous transportation fuels.

The most studied and developed bioenergy value chain is the extraction of algal lipids that are either esterified into biodiesel (FAME) or hydrotreated into renewable diesel (HVO or jet fuel). Left unrefined, the algal oil can act as straight vegetable oil. One of the most important R&D challenges in this value chain is to find an effective and noncostly lipid extraction process.

Hydrothermal treatment of aquatic biomass allows for the production of a bio-oil or a syngas, that can be further processed into hydrogen, methanol, ethanol, gasoline, renewable diesel, and jet fuel.

Two other options are fermentation for ethanol production and anaerobic digestion to gain bio-methane. Both ways spare the need of drying the algal culture. Fermentation, hydrothermal liquefaction and anaerobic digestion are also a practical way to treat the residual algal biomass from other conversion routes.

Direct fuel production: In emerging fuel production routes such as microbial biosynthesis, biophotolysis and autofermentation, algae or cyanobacteria are not used as feedstock, but they are the actual producers of the fuels (alkanes, hydrogen or ethanol respectively). These pathways are at pilot scale and huge efforts are being made to improve productivities and recovery technologies.

#### Example projects on algae production

#### Pilot projects in Europe

FP7 Algae Cluster	Three projects - BIOFAT, ALL Gas, and InteSusAI – supported by EU, demonstration at industrial scale of algae and its subsequent use in biofuel production, runs from 2011 – 2015/16	
fuel4me	4-year project funded by the EU, optimisation of lipid production, 2012 - 2017	
Projects in Australia and the USA		
Algae.Tec.	Pilot plant in Australia, since 2007	
Heliae	Pilot plant in Arizona / USA, since 2008	
Sapphire Energy Inc.	First-of-its-kind commercial plant in New Mexico / USA, since 2009	
Algenol	Pilot plant in Florida / USA, since 2011	
Joule Unlimited	Cyanobacteria demo plant in Massachusetts / USA, since 2011	
Biosystems	Demo plant in Florida / USA, since 2013	

# Synergies between biofuels and other industrial sectors

Microalgae provide dissolved oxygen that can be used by bacteria to break down and oxidize organic matter in wastewaters. This leads to the liberation of  $CO_2$ , phosphate, ammonia and other nutrients used by algae. Biofuel production in combination with wastewater treatment and nutrient recycling is thus predicted to be a near-term application.

In any case, the combination of biofuel production with the valorisation of other fractions of the algal biomass (proteins, special oils (omega-3), vitamins, pigments, nutraceuticals) is necessary for the economic sustainability of the process.

#### Further information

Read up-to-date information about the aquatic biomass on <u>www.biofuelstp.eu</u>.