

ADVANCEFUEL

Biomass conversion technologies - Definitions

D3.1 Report on definition of parameters for defining biomass conversion technologies

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Executive Summary

The project ADVANCEFUEL focuses on accelerating the market uptake of RESFuels in the European transport sector. RESfuels refer to liquid advanced biofuels produced from lignocellulosic biomass and other liquid renewable fuels from non-biological origin. This document contains information in the form of general descriptions and definitions of the conversion technologies in the scope of the ADVANCEFUEL project (i.e., technologies with TRL 5 or higher) starting from the pre-treatment of lignocellulosic biomass, the thermochemical methods of gasification and pyrolysis for production of syngas and pyrolysis oil respectively, the fermentation of sugars to alcohols (mainly ethanol and butanol production technologies), and downstream chemical synthesis and refining. After a general description of each conversion technology, the information is summarized in the most important input (i.e., feed), process and output (i.e., product) parameters. The information mainly stems from recent literature reviewing a wide range of conversion technologies for lignocellulosic biomass to fuels and chemicals.

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Introduction

The project ADVANCEFUEL focuses on accelerating the market uptake of liquid advanced biofuels and other liquid renewable fuels in the European transport sector. Liquid advanced biofuels are defined as all liquid biofuels produced from lignocellulosic biomass, while other liquid renewable fuels refer mainly to renewable fuels from CO₂ and renewable hydrogen sources. The ADVANCEFUEL project focuses on conversion technologies at the demonstration stage and near to commercialization, namely with technology readiness levels (TRL) of 5-9. The scope and boundaries of the ADVANCEFUEL project in terms of feedstocks, conversion technologies and target fuels are described in deliverables D1.1 and D1.3 and summarized in Figure 1. The rationale for selecting these boundaries and the respective technologies is described in these deliverables. Moreover, in Chapter 4 of D1.3 the main definitions with respect to feedstock supply, infrastructure and specifications, conversion technology parameters and efficiencies, sustainability performance, and end use specifications and infrastructure are provided.

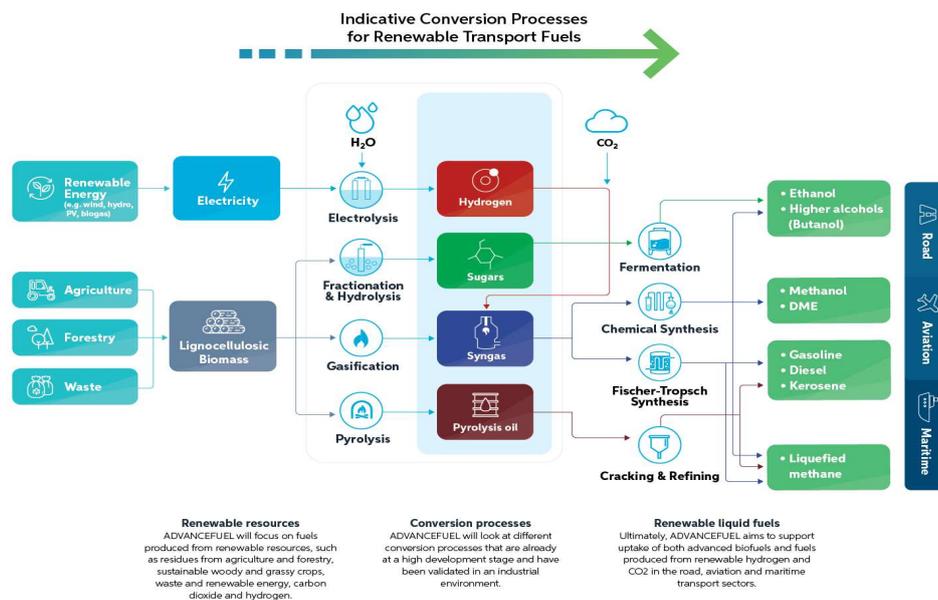


Figure 1 ADVANCEFUEL project main focus (feedstock-to-renewable fuels pathways)

For the conversion technologies in particular, the generic terminology, relevant for all technologies, was provided in D1.3, including terms such as Technology Readiness Level (TRL), process complexity, material and energy flow analysis, process investment and operating cost, maximum allowable payback period, synergistic or added value potential, on and off-site infrastructure and fuel specifications. In this context, the generic parameters and data for characterizing a technology were also listed, including:

- TRL and level of commercial application
- Detailed description of the operating principle
- Detailed description of the input specifications
- Material efficiencies and closed mass balance (e.g., less than 5% error)
- Energy efficiencies and requirements on when energy balances can be considered (e.g., less than 5% error in balance)
- Operating costs
- Lifetime of the equipment and investment costs
- Number of typical full load hours per year
- Labour requirements of typical installation (expressed in full-time equivalent (FTE))

In addition to this generic terminology and parameters, specific parameters for the biomass conversion technologies of the ADVANCEFUEL project are presented in this document. These technologies are divided to:

- Pre-treatment technologies (i.e., after mechanical size reduction of the biomass and potential pelletisation), categorised in physical, chemical, physicochemical (including thermal), and biological methods, such as drying, steam explosion, torrefaction, fractionation and hydrolysis of lignocellulosic biomass
- Thermochemical technologies, including gasification (direct and indirect), and pyrolysis
- Biochemical technologies, including fermentation
- Downstream technologies, including Fischer-Tropsch (FT) synthesis of liquid fuels, methanol and dimethyl ether synthesis, cracking and refining technologies of pyrolysis oil, toward gasoline, diesel, kerosene and liquefied methane (bio-LNG).

Electrolysis technologies for production of renewable hydrogen and subsequent conversion to syngas, either using additional CO₂ sources or as drop-in for upgrading syngas composition (e.g., from gasification technologies), are not included in this document, as they are considered auxiliary technologies of different nature compared to biomass conversion technologies. The reference technologies for electrolysis will be presented in detail together with the relevant biomass reference technologies with respect to TRL levels and their performance indicators in deliverable D3.2.

The specific parameters for the biomass conversion technologies are divided into three categories:

- Input (or feed) specifications,
- Process operation,
- Output (or product) characterisation



The input related parameters define the specifications required by a technology to process the provided feed (capacity, composition, etc.). The process related parameters define the operating principle, the operating parameters and ranges thereof, and the type of equipment. The output related parameters define the type of products, composition, and potential application or suitability for further downstream processing.

These parameters are defined for each category of technologies, complemented with exemplary data where relevant, in chapter 3. These defined parameters will be used for a complete characterisation of biomass reference conversion technologies in deliverable 3.2.

1. Definitions of Conversion Technologies and Parameters

1.1. Pre-treatment

General description and options: There are various options for pre-treatment of lignocellulosic biomass and the most appropriate one or the most appropriate combination mainly depends on the subsequent utilisation of that biomass (i.e., for thermochemical or biochemical conversion technologies). There are some common pre-treatment steps for all conversion technologies, mainly related with removing the moisture by drying and decreasing the size of biomass particle, typically through grinding and milling. These steps may also influence the efficiency of the subsequent biomass utilisation; the impact of these steps on the conversion technologies are mentioned, where important, in the respective conversion technology paragraphs of this document.

After these first common pre-treatment steps, the mode of action, reaction conditions and outcome can vary even within the same type of subsequent conversion technology. For instance, the general concept of pre-treatment methods for lignocellulosic ethanol production should consider criteria such as release of cellulose and hemicellulose from the lignocellulosic complex, minimum damage of hemicellulose and cellulose with efficient recovery of these polysaccharides, minimisation of sugars derived inhibitors or toxic compounds, reasonable size reduction, batch sizes, cost of reactors and energy requirements, high yield of pre-treated biomass compatible to fermentation technologies, and high yield and quality of lignin (Zabed et al., 2016).

Cl_a

Classification of pre-treatment technologies: There are physical, chemical, physicochemical and biological pre-treatment methods (E4tech et al., 2015). The physical pre-treatment methods aim to increase the accessible surface area and pore volume and decrease the degree of polymerisation of cellulose and its crystallinity. In most cases, when physical pre-treatment is the only option, the required energy is higher than the theoretical energy content of biomass, making this expensive and impractical, at least for large scale biochemical processes. The chemical pre-treatment methods typically include alkalis and acids for delignification of the biomass and decrease the polymerisation and crystallinity of cellulose. The most commonly used acid is H₂SO₄ (Morales et al., 2017) and the most common alkali NaOH. The two are applied to solubilise the hemicellulosic fraction of biomass and make cellulose accessible to enzymes. Organic acids can also be used to enhance cellulose hydrolysis and reduce production of inhibitors. Other chemical solvents (e.g., H₂O₂, organosolv, ethylene glycol) have also been reported to disrupt cellulose and promote hydrolysis. Physicochemical pre-treatments affect both physical

and chemical properties of the biomass and include, for instance, steam explosion, ammonia fiber explosion (AFEX), wet explosion, CO₂ explosion, etc. Biological pre-treatment is carried out using microorganisms, such as white rot fungi (Sarkar et al., 2012). This alters the structure of lignin and cellulose, separating them from the lignocellulosic matrix. Although biological pre-treatment is typically carried out under mild conditions, the rates of hydrolysis are low and current efforts focus on combining this technology with other pre-treatment methods and developing new microorganisms for rapid hydrolysis.

Among the pre-treatment methods AFEX, wet oxidation and liquid hot water treatments seem to be more successful for agricultural residues. Woody biomass such as softwood is more difficult to hydrolyse and so acidic pre-treatment is typically used. Depending on the further utilisation of pre-treated biomass, detoxification based on physical, chemical, and biological methods may be necessary to remove lignocellulosic-derived inhibitors (e.g., sugar acids, acetic acid, formic acid, levulinic acid, furfural) for enzymes and fermenting microorganisms.

Physical, physicochemical, chemical and biological pre-treatment is also important for thermochemical conversion technologies. Pelletisation is a technology that consists of multiple steps, including preparation of feedstock suitable for this process, its filtration, storage and protection. Raw materials used are sawdust, wood shavings, wood wastes, agricultural residues like straw, switchgrass etc. Filtration is done to remove unwanted materials like stone, metal, etc. The feedstock should be stored in such a manner that it is away from impurities and moisture. The moisture content should be reduced to 10 to 15%, typically in rotary drum dryers, while superheated steam dryers, flash dryers, spouted bed dryers and belt dryers can also be used. It should be noted that the feedstock should not be over dried, as a small amount of moisture helps in binding the biomass particles. The drying process is the most energy intensive process and accounts for about 70% of the total energy used in the pelletisation process. Before feeding biomass to pellet mills, the biomass should be reduced to small particles of the order of not more than 3mm. Size reduction is done by chipping (for large feedstock) and grinding using a hammer mill equipped with a screen of size 3.2 to 6.4 mm. Then, during pelletisation, biomass is compressed in high pressures which causes through friction high temperature, and in turn this causes the lignin and resins present in biomass to soften which acts as a binding agent between the biomass fibers. This way the biomass particles fuse to form pellets. Binders or lubricants may be added in some cases to produce higher quality pellets. Binders increase the pellet density and durability. Wood contains natural resins which act as a binder. Similarly, sawdust contains lignin which holds the pellet together. However, agricultural residues do not contain much resins or lignin, and so a stabilizing agent needs to be added in this case. Distillers dry grains or potato starch is some commonly used binders, their use depending on biomass composition.

When physical pre-treatment is conducted at temperatures between 200 °C and 300 °C (torrefaction), the water content is completely removed and the oxygen content is partially reduced (Uslu et al., 2008). Torrefied biomass has a higher energy density, improved grindability, lower

hygroscopicity when stored in open air, lower risk of biological degradation and self-ignition, and an improved capability of being fed to the reactors. A higher quality and lower yield of bio-oils from pyrolysis of torrefied biomass are also reported (Zheng et al., 2013). Pre-treated biomass with steam explosion leads to bio-oils with lower acid values and viscosity and higher water content. Similar effects are observed with liquid hot water pre-treatment (Carpenter et al., 2014). Chemical pre-treatment for biomass to be pyrolysed typically includes acid washing to reduce the ash content. This can increase the subsequently produced bio-oils and decrease char formation. Biological pre-treatment of lignocellulosic biomass prior to pyrolysis can lower the pyrolysis temperature, decrease the emission of SO_x through reduction of the sulphuric content, and increase the product yields of valuable aromatics. In general, the TRLs of the pre-treatment options mentioned above can vary from 2-8. Pre-treatment technologies with TRLs higher than 5 are those related with size reduction (chipping, grinding, milling, palletisation), torrefaction, steam explosion, dilute acid treatment, concentrated acid hydrolysis, organosolv treatment, alkaline treatment, and AFEX. In Table 1, the various pre-treatment technologies (Liu et al., 2017) are categorised with respect to their use in thermochemical and biochemical conversion technologies. The important parameters of the pre-treatment technologies are summarized in Table 2.

Table 1: Overview of pre-treatment technologies for thermochemical and biochemical conversion technologies

Pre-treatment Technology	Thermochemical Conversion	Biochemical Conversion
Chipping, grinding, milling	√	√
Pelletisation	√	
Torrefaction	√	
Acid hydrolysis		√
Organosolv		√
Alkaline		√
Steam explosion	√	√
Liquid hot water		√
AFEX		√
Biological		√

Table 2: Definitions for pre-treatment technology: input, process and output parameters

Input Parameters	Definition
Capacity with respect to feed	It expresses the size of the technology as the maximum rate of biomass that can be pre-treated
Biomass feedstock	A well characterised feedstock according to Chapter 4 in D1.3.
Process Parameters	Definition
Type of pre-treatment	Physical, Chemical, Physicochemical, Biological
Physical methods	Mechanical chipping (10-30 mm particle size), grinding or milling (0.2 – 2mm particle size): increase of surface area,

	<p>reduction of cellulose crystallinity, no lignin removal, poor sugar yields, high energy consumption, important that is integrated with mild chemical treatments</p> <p>Pelletisation, after drying (i.e., to 15 wt% moisture content) chipping and grinding: binding of biomass fibers due to softening of lignin and resins in high pressure and resulting high temperatures due to friction, facilitating consistent feedstock to thermochemical treatment, mainly pyrolysis (Yang et al., 2014)</p> <p>Torrefaction: lower temperatures compared to pyrolysis (200-300 °C)¹, complete removal of water, partial removal of oxygen, improved grindability, lower risk of degradation, biomass with higher energy density, higher quality bio-oils when pyrolysis follows</p>
Chemical methods	<p>Dilute acid pre-treatment (acids < 4 wt%): high temperature (180 °C)/short period of time or low temperature (120 °C) for longer retention time (30-90 min), high reaction rate, increased accessible surface area, good removal of hemicelluloses, alteration of lignin structure but low lignin removal, improved digestibility, degradation byproducts and inhibitors, requirement for neutralisation and removal of the resulting salts, requirement for microorganisms more tolerant to inhibitors, suited for low lignin feedstocks</p> <p>Concentrated acid hydrolysis (acids 70-80 wt%): complete removal of cellulose crystalline structure, high reaction rate, increased accessible surface area, good removal of hemicelluloses, high use of chemicals and capital investment, corrosion and toxic hazards, degradation byproducts and inhibitors, requirement for recovery and reuse of chemicals, new catalysts and more tolerant microorganisms, suitable for a wide variety of feedstocks</p> <p>Organosolv: lignin and hemicellulose hydrolysis, solvent (methanol, ethanol, acetone, ethylene glycol) can be combined with acids to break hemicellulose bonds, recovery of relatively pure lignin as byproduct, minimum cellulose loss (< 2%), low sugar degradation, solvent may inhibit cell growth, requirement for solvent removal/recovery from the system, formation of inhibitors, high capital and operating costs</p>

¹ Torrefaction is sometimes referred to as "mild pyrolysis" which is categorized in thermochemical conversion technologies. This shows that the classification of technologies between pre-treatment and conversion technologies is not always straightforward.

	<p>Alkaline pre-treatment: room temperature, low pressure, increased surface area, removal of hemicellulose and lignin, alteration in lignin structure, low degradation of sugars, reaction time ranges from seconds to days, low capital costs, low inhibitor formation, formation of irrecoverable salts, requirement for pH adjustment for subsequent processes, high glucose yields, residue formation, need to recycle chemicals and adjust enzymes (new enzyme development required), suitable for smaller scale plants</p>
Physicochemical methods	<p>Steam explosion: high temperature (160-260 °C) and pressures (7-50 bar), reaction time of seconds to minutes, reduction of particle size and improved enzyme accessibility, high glucose yields, cost effective, hemicelluloses removal, lignin removal may be low if not catalysed by acids, low environmental impact, formation of inhibitors and toxic compounds, requirement for catalyst to optimise pre-treatment, requirement for microorganisms more tolerant to inhibitors, suitable for a variety of herbaceous and woody feedstocks, already at commercial plant scale</p> <p>Liquid hot water: hydrothermal treatment of biomass with rapid decompression, high temperature (160-260 °C) and pressure to keep water in the liquid phase, pH range 4-7, reaction time of a few minutes, no catalyst or chemicals, increased accessible surface area, removal of hemicellulose, structural and chemical alteration of lignin, low inhibitor formation, low reactor costs, high water demand and energy requirement, hemicellulose degradation</p> <p>AFEX: treatment with anhydrous liquid ammonia at 60-120 °C, and above 30 bar for 30-60 minutes, followed by rapid decompression, no need for small particles, increased surface area, reduction in cellulose crystallinity, removal of hemicellulose and lignin, alteration of lignin structure, low inhibitor formation, high cost due to solvent, a requirement for recovery and reuse of chemicals, environmental concerns, less efficient for softwood based biomass, not effective for biomass with high % of lignin, suitable for smaller decentralised plants</p>
Biological methods	<p>Microbial treatment: use of microbes (brown, white and soft rot fungi), low energy requirement, mild environmental conditions, low inhibitor formation, no corrosion, lignin and hemicellulose removal, lignin degradation and depolymerisation of cellulose and hemicellulose, time consuming (10-15 days residence time), saccharide losses, need for development of more robust microorganisms</p>

Type of equipment	Reactor vessels, (e.g., 50-400 m ³ are typical sizes)
Output Parameters	Definition
Capacity with respect to pre-treated biomass	The size of the pre-treatment technology as the maximum rate of pre-treated biomass (e.g., dry tonnes of biomass/day)
Type of product	<p>Acid pre-treatment: xylose removal 85%, solid yield 50%, downstream glucose yield 15-45%, lignin removal 12%, hemicellulose removal 75%</p> <p>Organosolv: downstream digestibility 50-60%, downstream sugar yield 75-85%</p> <p>Steam explosion: Lignin removal 2-50%, hemicellulose removal 40%, downstream sugar yield 30-80%</p> <p>Liquid hot water: downstream glucose yield 20%</p> <p>AFEX: downstream glucose yield 50%</p> <p>Microbial treatment: lignin removal 40-50%, 7 fold increase in hydrolysis</p>

1.2. Thermochemical conversion

1.2.1. Gasification

General description and operating principle: Gasification is an endothermic, thermochemical process running at 800 °C-1500 °C and at sub-stoichiometric conditions ($\lambda=0.2-0.5$, where λ is the oxygen to fuel ratio relative to the oxygen to fuel ratio required for complete combustion without oxygen excess). There are essentially two types of gasification technologies: auto-thermal (direct) and allothermal (indirect) gasification. In direct gasification, the heat required by the process is only internally generated by the partial combustion of the feedstock, whereas in indirect gasification energy is also delivered to the process via the gasification agent (steam). Furthermore, in direct gasification, all reactions occur in the same device, while in indirect gasification, combustion reactions occur in a separate chamber that communicates with the gasification chamber both with mass streams (bed material, char, ashes and feedstock to be combusted) and energy streams (heat carried by the thermal inertia of the bed material itself) (Sette et al., 2015). Several types of equipment are used (Basu, 2010), the main ones being entrained flow, and bubbling and circulating bed gasifiers (EFG, BFG, and CFG, respectively). For instance, indirect gasification systems can be of the dual fluidized bed (DFB) type, consisting of a primarily CFB used for heat generation which is connected to a BFB used as a gasifier (Thunman et al., 2018).

The raw product gas typically consists of a Syngas type of mixture (i.e., CO and H₂), together with CH₄, tar and char components. Depending on the technology and biomass used, impurities may include dust, ash, bed material, sulphur and chloride compounds (Reihnard et al., 2013). Various types of filters (e.g., textile bag filters are used at GoBiGas, Gothenburg, (Thunman et al., 2018)) can be used to remove the particles from the product gas; the maximum allowable temperature of the filter is an important parameter for avoiding fouling in the heat exchangers cooling the raw product gas. The components with poisonous effects for downstream catalysts are mainly sulphur and chloride compounds. Downstream of the filter water (typically > 30% volume) and polyaromatic compounds (i.e., mainly consisting of benzene, naphthalene and toluene, typically < 1% volume) are removed, for instance using scrubbing processes. For DFB systems (indirect gasification), in general, raw gas quality depends on the catalytic activity, which can be controlled by:

- primary circulation of the bed material and secondary circulation of other solid particles
- addition and removal of bed material as well as supplementation with inorganic compounds containing potassium, sulphur and calcium
- fuel ash temperature levels
- fuel load and steam-to-flow ratio

Using air as a gasification agent (direct gasification) results in a product gas rich in N₂. The H₂ content in the product gas for indirect gasification is higher than that of direct gasification, while the opposite is true for the content of CO. If syngas is the primary goal of gasification, then methane needs to be reformed (i.e., steam reforming) in an additional step to increase the syngas yield. For entrained flow gasifiers, the higher operating temperature in the gasifier increases the conversion in this direction. As a last step, the resulting CO₂ from the water-gas shift reactions needs to be removed, typically by physical or chemical liquid absorption processes. The synthesis gas will need to be compressed to the required downstream synthesis pressure, typically to 80-100 bar (Landälv et al., 2017).

Different methods for biomass thermal pre-treatment and grinding for feeding to a gasifier exist. For instance, for pressurized entrained flow gasifiers, drying, torrefaction, flash pyrolysis and dissolution of wood in organic solvents are some of these methods. Many parameters must be considered such as heating value, grinding energy needed, overall efficiency of conversion (from raw biomass to fuel), auxiliary energy needed, fluidization properties, pneumatic feeding properties, pumping, viscosity and possible changes of properties of liquids/slurry, storage, microbial attack, emissions from thermal pre-treatment and overall integration with pressurized entrained flow gasification (Svoboda et al., 2009).

The important parameters defining gasification technology are summarized in Table 3.

Table 3: Definitions for gasification technology: input, process and output parameters

Input Parameters	Definition
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Capacity with respect to Feed	The size of the technology as the maximum rate of biomass that can be gasified (e.g., dry tonnes of biomass/day, MWth biomass)
Biomass Feedstock	A well characterised feedstock according to Chapter 4 in D1.3; of special interest is the moisture content), ash content, ash melting point, chlorine content, lower heating value and bulk density ²
Pre-treatment	Grinding and thermal pre-treatment methods including drying, torrefaction, flash pyrolysis and treatment with organic liquids are some typical examples
Process Parameters	Definition
Gasification agent	Steam (Indirect gasification), Oxygen (Direct gasification)
Operating Temperature	800-1500 °C
Operating Pressure	1-30 bar
Main Equipment	Entrained flow, fluidized beds (circulating or bubbling in a dual-bed setup)
Auxilliary Equipment	Heat exchangers, Gas cleaning filters, Scrubber/Absorption columns
Gasification agent to fuel ratio	Important for controlling the catalytic activity in DFB systems and the λ ratio
Solid circulation	Primary circulation of bed material and secondary circulation of ash fractions
Supplementation of inorganics	Inorganic compounds containing potassium, sulphur and calcium for improving the activity of the catalytic bed
Catalytic Bed	The type of catalyst used in the fluidized bed (e.g., nickel based catalyst)
Output Parameters	Definition
Capacity with respect to Product	The size of the technology as the maximum rate of the main product (e.g., MW of syngas)
Type of main product	Syngas (Mixture of primarily CO and H ₂ , that can also contain amounts or traces of CO ₂ , H ₂ O, CH ₄ , alkenes, alkynes, inert gases; the composition can vary depending on raw gas treatment)
Type of additional products	Mainly aromatics (e.g., benzene) but also heavier tar components, either single (e.g., naphthalene) or in the form of mixtures, can be recovered and used in various market applications

² Indicative operating threshold for moisture and ash content: 35% for fluidized bed combustors, 20-30% for gasification reactors, ash content more than 5% is unacceptable and an alkali index above 0.34 kg/GJ will cause fouling (Tanger et al., 2013). Thresholds of all these parameters for the biomass reference technologies, will be explicitly reported in D3.2.

1.2.2. Pyrolysis

General description and operating principle: Pyrolysis is one of the thermochemical technologies for converting biomass in the absence of oxygen into energy and chemical products consisting of liquid bio-oil (also referred to as pyrolysis oil, pyrolysis tar, bio-crude, wood liquid, wood oil or wood distillate), solid bio-char (also referred to as charcoal), and pyrolytic gas. A number of parameters affect the biomass pyrolysis process, yields and properties of products, including the biomass type and pre-treatment, reaction atmosphere, and heating and residence times. For instance, depending on the heating rate and residence time, biomass pyrolysis can be divided into slow (conventional), fast and flash pyrolysis aiming at maximising either the bio-oil or bio-char yields (Kan et al., 2016). The highest yield of liquid fraction is obtained by thermal fast pyrolysis, opening up decentralized concepts for producing the pyrolysis oil locally and transporting and upgrading it in centralized larger plants (Landälv et al., 2017). Fast pyrolysis takes place at around 500 °C in the order of seconds, typically 0.5-10 seconds, involving high heating rates, typically 50-200 °C/s (Demirbas and Arin, 2002). The heating medium is typically sand and catalysts are also used (i.e., catalytic pyrolysis).

Bio-oil yield can be as high as 50-70 wt% of dry biomass basis. Even higher heating rates of 1000-10000 °C/s can achieve bio-oil yields of up to 80 wt% (Amutio et al., 2012). Gas and bio-char yields amount to 13-25 wt% and 12-15 wt% of dry biomass feed basis, respectively. In catalytic pyrolysis, the bio-oil typically has a lower oxygen content but lower material and energy yields are achieved.

Biomass pyrolysis reactors can be fixed bed, fluidised bed, heated kiln, rotating cone, screw feeder/auger and vacuum pyrolysers (Bridgwater, 2000). From these reactor types, bubbling and circulating fluidised beds, heated kiln and rotating cone have been commercialised, while others remain at the demonstration or pilot stage. Typical capacities for commercial scale are in the range of 0.2-20 tonnes/hour, at feed moisture less than 10 wt%, and feed size of 0.2-50 mm and bio-oil yields of 70-75% wt%.

The biomass feedstock requires some form of pre-treatment before pyrolysis to enhance the pyrolytic efficiency. The pre-treatment typically consists of destroying the lignocellulosic structure. The pre-treatment methods can generally be those mentioned in paragraph 3.1 or a combination thereof. For instance, smaller particles (i.e., through milling or grinding of biomass) promote heat and mass transfer to form uniform temperatures within particles during pyrolysis and enhance bio-oil production by restraining the char formation and secondary cracking of vapours. On the other hand, extrusion of biomass under high pressure to produce pellets of large diameters increases the char and gas yields (Kan et al, 2016). Biomass drying prior to pyrolysis increases the energy efficiency of the pyrolysis process and improves the quality of

the bio-oil product. Reducing the ash content through water or acid washing reduces the presence of inorganic minerals (e.g., alkali and alkaline-earth metal salts) which affect the mechanism of biomass pyrolysis leading to lower bio-oil yields.

It is generally accepted that further upgrading (e.g., through catalytic cracking, high-pressure hydroprocessing) of the bio-oils is needed prior to practical application in engines (Ballat, 2011). Bio-oil can also be used to produce syngas through steam reforming and gasification (Xiu and Shahbazi, 2012).

The important parameters defining pyrolysis technology are summarized in Table 4.

Table 4: Definitions for pyrolysis technology: input, process and output parameters

Input Parameters	Definition
Capacity with respect to Feed	The size of the technology as the maximum rate of biomass that can be pyrolysed (e.g., dry tonnes of biomass/day, MWth biomass)
Biomass Feedstock	A well characterised feedstock according to Chapter 4 in D1.3; of special interest is the particle size (e.g., less than 2 mm for fast pyrolysis and 200 μm for flash pyrolysis), moisture content, lignin content, extractives content, mineral matter content and composition ³
Pre-treatment	Combination of methods mentioned in the pre-treatment section (3.1); bigger particles, higher moisture and (acid) washing leads to lower bio-oil yields
Process Parameters	Definition
Heating rate	The gradient of temperature increase (e.g., 10-200 $^{\circ}\text{C}/\text{s}$ for fast pyrolysis)
Residence time	0.5 to 10 seconds; shorter residence times favour bio-oil production; interaction between residence time and temperature on product quality
Operating Temperature	450-650 $^{\circ}\text{C}$ (fast pyrolysis), 800-1000 $^{\circ}\text{C}$ (flash pyrolysis)
Pyrolysis atmosphere	Typically inert gases; steam for partial gasification; CH_4 for increasing the bio-oil yields and H_2 for increasing the HHV
Type of equipment	Bubbling and circulating fluidised beds, heated kilns, rotating cone, auger/screw feed, vacuum
Output Parameters	Definition
Capacity with respect to product	The size of the technology as the maximum rate of the main product
Type of main product	Bio-oil typically comprises of water (15-35 wt%) and hundreds of organic compounds, such as acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds and miscellaneous oxygenates, as well as solid particles

³ Indicative operating threshold for moisture: 10% (Tanger et al., 2013). Thresholds of all these parameters for the biomass reference technologies will be explicitly reported in D3.2.

	Oxygen content: 35-40 wt% (dry basis), HHV: 15-20 MJ/kg, pH: 2-3.7, specific gravity: 1.2, pour point: -33 °C
Type of additional products	Bio-char typically containing unconverted organic solids, carbonaceous residues, and a mineral fraction. Carbon content: 53 to 96 wt%, HHV: 20-36 MJ/kg Pyrolytic gas typically contains CO ₂ , CO, H ₂ , hydrocarbons such as CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈ , and small amounts of other gases such as NH ₃ , NO _x , SO _x , and alcohols of low carbon numbers

1.3. Biochemical conversion

General description and operating principle: Biochemical conversion of lignocellulosic biomass comprises a number of options that can be roughly separated into sugars to alcohols, sugars to hydrocarbons, hemi- and cellulosic material to bio-methane via anaerobic digestion and gas to alcohols and hydrocarbons. The ADVANCEFUEL project focuses on the first route (sugars to alcohols) in accordance with the scope of the project presented in Figure 1.

C6 sugars are fermented by bioengineered microorganisms, most commonly derived from traditional yeasts. C5 sugars are fermented by genetically modified yeasts developed in recent years. Despite the unquestionable advantages of lignocellulosic biomass as a feedstock for ethanol production (availability, price, non-competitiveness with food, waste material), the recalcitrant structure of the material requires extensive pre-treatment (Morales et al., 2017) to yield fermentable sugars, and a relatively low concentration of monosaccharides in the medium that hinder the achievement of ethanol concentrations comparable with those obtained using first generation feedstocks. These low concentrations typically require a high amount of energy for downstream separations and ethanol purification (Landälv, 2017). Moreover, the presence of both pentose and hexose sugars in the fermentation broth, the price of cellulolytic enzymes, and the presence of toxic compounds that can inhibit cellulolytic enzymes and microbial producers of ethanol are other major issues. Several technological options exist, including simultaneous saccharification and fermentation (SSF), simultaneous saccharification and fermentation with delayed inoculation (dSSF), consolidated bioprocesses (CBP) combining production of cellulolytic enzymes, hydrolysis of biomass and fermentation in one step, separate hydrolysis and fermentation (SHF) processes, approaches combining utilization of both pentose and hexose sugars, use of immobilized enzymes and cells (Paulova et al., 2015) under low or high gravity fermentation conditions (Xiros and Olsson, 2014).

Generally, the 2nd generation cellulosic ethanol plants produce low ethanol concentration as a result of the low concentration of sugars available for fermentation as the feedstock does not allow for an increase in fermentable solids in batch reactors; the relevant technical problems include high viscosity, a low amount of free water due to its absorption in the biomass, a high

content of inhibitors, nutrient levels and heat and mass transport (Modenbach and Nokes, 2013). On the other hand, it has been estimated that bioethanol from lignocellulosic biomass can become economically attractive at concentrations exceeding 40 g/l (Uppugundla et al., 2014). For instance, ethanol concentrations for 2nd generation ethanol production around 100 g/l will be required to be compared with 1st generation performance (Chen and Fu, 2016). The upgrading of ethanol from lower concentrations for application as biofuel requires a series of evaporations (45 wt%), rectification (96 vol%) and dehydration (99.5 vol%) for blending into gasoline. The latter can be performed using zeolite adsorbents in a vacuum swing adsorption process. Annual production of ethanol in 2nd generation cellulosic plants ranges today from 5400 to 75000 m³.

Table 5: Definitions for fermentation technology for ethanol production: input, process and output parameters

Input Parameters	Definition
Capacity with respect to feed	The size of the technology as the maximum rate of biomass that can be fermentes (e.g., dry tonnes of biomass/day)
Biomass Feedstock	A well characterised feedstock according to Chapter 4 in D1.3
Pre-treatment	Combination of methods mentioned in the pre-treatment section (3.1) A typical sequence involves: drying, grinding, slurry preparation and treatment, (detoxification), and hydrolysis. Detoxification may be required before and/or after hydrolysis
Detoxification	Removal of inhibitors formed mainly after the physical pre-treatment steps which can seriously affect the hydrolysis and fermentation steps. It can increase significantly the cost of industrial applications and should be avoided or combined with more tolerant microorganisms to inhibitors
Process Parameters	Definition
Process configuration	Separate hydrolysis and fermentation (SHF), Simultaneous saccharification and fermentation without (SSF) or with delayed inoculation (dSSF)
Cultivation conditions	Configuration, temperature, pH, concentration of solids, type and amount of nutrients
Separate hydrolysis and fermentation (SHF)	Separately optimised hydrolysis and fermentation steps (e.g., enzymatic hydrolysis at 50 °C and microbial strain based fermentation at 30-35 °C, reduced medium viscosity prior to fermentation allowing higher solid content and thus higher concentrations, enzyme cocktail can be optimised for the type of biomass)

	<p>End product inhibition slows the rate of hydrolysis and decreases the overall yield of ethanol; high xylan content and the respective degradation products further inhibit cellulotic enzymes</p> <p>Increased chance of contamination due to long period process, high solid content reduces activity of cellulotic enzymes but does not affect the microbial strain performance of the ethanol production step</p> <p>Typical ethanol concentrations: 15-30 g/l (depending on the type of biomass and pre-treatment steps) Theoretical ethanol yield: 84-98% Typical productivity: 0.15-0.35 g/l/h</p>
<p>Simultaneous saccharification and fermentation without (SSF) or with delayed inoculation (dSSF)</p>	<p><u>For SSF:</u> Hydrolysis and fermentation steps performed in one reactor avoiding glucose accumulation and thus enzyme inhibition, increasing ethanol yields, reducing equipment costs, and lowering the risk of contamination</p> <p>Discrepancy in temperature conditions from the separately optimised processes affects the activity of cellulotic enzymes and slows down the metabolism of the microbial strain, reduces productivity and lowers concentration of ethanol</p> <p>Inhibition of cellulases by ethanol typically less than that by glucose</p> <p>Low ethanol productivity in the early stages due to glucose deficiency</p> <p>High solids content affects enzyme activity due to high concentration inhibitors (mainly for acid pretreated biomass feedstock) and thus requires an additional detoxification step</p> <p>The biomass pre-treatment method also plays a role, e.g., for olive tree wood it has been reported that steam explosion followed by hot alkaline peroxide treatment increased ethanol yield</p> <p>The amount of enzyme can play a role in the ethanol concentration, increasing the cellulose to glucose conversion</p> <p>Optimal feeding strategies (fed-batch operations) can increase sugar concentrations by spreading the dose of the substrate over a longer time period and decreasing viscosity compared to the typical batch mode</p>

Typical ethanol concentrations: 16-40 g/l (depending on the type of biomass, pre-treatment steps, and SSF temperature, duration and solid content)

Theoretical yield: 70-85%

Typical productivity: 0.20-0.70 g/l/h

For dSSF:

The broth from chemically or physically pretreated biomass is firstly prehydrolysed with cellulases at the optimum temperature (45-55 °C) then cooled on the optimum SSF temperature (30-35 °C), and immediately inoculated without enzymes being inactivated. It overcomes the discrepancy in the temperature optima for enzymes and microorganisms, increasing the cellulose hydrolysis rate in the early process stages and also generally decreases the viscosity prior to inoculation (i.e., allowing high solid loadings) and eliminates glucose limitation at the later process stages

The key point for a successful implementation and combination of the SHF and SSF advantages is the length of prehydrolysis to not let glucose accumulate above the end product inhibition critical value. This optimum presaccharification period depends on many factors, such as substrate, concentrations, pre-treatment type and microbial strain

In the case of a process with high solid content many parameters need to be optimised (i.e., trade-off between concentration and cellulose to glucose conversion)

Typical ethanol concentrations: 17-40 g/l (depending on the type of biomass, pre-treatment steps, SSF conditions and duration of the presaccharification step)

Theoretical yield: 50-85%

Typical productivity: 0.20-0.45 g/l/h

Hexose and pentose fermentation (e.g., glucose and xylose co-fermentation)

Microorganisms capable of efficiently fermenting both hexose and pentose. Typically used microorganisms (e.g., *Saccharomyces cerevisiae*) are unable to ferment pentose). Metabolic engineering strategies are of high importance (but of low TRL).

Consolidated bioprocessing (CBP)

The most challenging task is the selection or design of suitable microorganism to express appropriate hydrolytic enzymes matching the lignocellulosic feedstock, and produce ethanol.

Although theoretically the feedstock of CBP should not require any special physical, chemical or enzyme pre-

	<p>treatment, sometimes it is supplemented by saccharifying enzymes or chemical pre-treatment.</p> <p>There is an increased interest in this technology, although still of low TRL with respect to the design of efficient microorganisms and process conditions.</p> <p>Typical ethanol concentrations: 3-35 g/l (depending on the microorganism, feedstock and process conditions) Theoretical yield: 30-90% Typical productivity: 0.03-0.2 g/l/h</p>
Use of immobilised biocatalysts	<p>This technology focuses on reducing input costs, particularly cellulosic enzymes and the production of strains. Both can be efficiently immobilised to be separated and reused in consecutive processes</p> <p>The main immobilisation methods include entrapment in a polymer matrix, adsorption on a solid carrier, covalent linking to a solid support, affinity interactions and cross-linking of enzyme aggregates</p> <p>The reported data, however, do not support the efficient reuse of the immobilised biocatalysts because of relatively fast loss of their enzyme activity (e.g., 20-60% within a few hours)</p>
Type of Equipment	Reactor vessels, (e.g., 50-400 m ³ are typical sizes), distillation and pressure swing adsorption columns
Output Parameters	Definition
Capacity with respect to product	The size of the technology as the maximum rate of the main product (e.g., m ³ of ethanol)
Type of main product	Ethanol (99.5 vol%)
Type of additional products	The bottom liquid from the fermentation broth that contains residual lignin, unreacted cellulose and hemicellulose, ash, enzymes, organisms, and other components. Although this is typically sent to wastewater treatment or burned as fuel to power the process, it has significant potential to be converted to other co-products

Besides ethanol, there is significant interest in butanol as a biofuel because of its energy content (e.g., 29.2 MJ/l for butanol compared to 21.2 MJ/l for ethanol) and other more adequate properties, such as lower vapor pressure and flammability, hydroscopic nature, and supply in existing gasoline channels and pipelines (Qureshi and Ezeji, 2008) to use in a gasoline blend (i.e., 85% butanol/gasoline blends can be used in unmodified gasoline engines). Some bacteria naturally produce butanol, but those used for ethanol can also be engineered to produce butanol (Lee et al., 2008). Both n-butanol and iso-butanol can be produced, although iso-butanol has a high value as an intermediate for the production of chemicals. In general, the same types of process

parameters affecting ethanol production (Table 5) are also significant for butanol production. Butanol tolerance of microorganisms is lower, and this results in lower titer levels and lower productivity, and additional purification issues with respect to energy consumption (Nanda et al., 2014). It is also acknowledged that another big challenge for industrialization of the butanol fermentation is the fermentation of acetone and ethanol as byproducts.

One way to overcome these drawbacks is to develop robust strains with improved butanol yield and tolerance. In various efforts butanol yielded concentrations of 5-20 g/l and butanol productivities of 0.05-0.15 g/l/h (Cao et al., 2016).

To overcome the problem of butanol toxicity, recovery technologies such as liquid-liquid extraction, pervaporation, gas stripping, and adsorption have been proposed as alternatives that can be integrated with the conventional fermentation process (Jang and Choi, 2018). Among them, the adsorption technology is both energy efficient and simple and can be designed either as in-situ or ex-situ with respect to its integration with the fermentation process (Qureshi et al., 2005).

1.4. Downstream chemical synthesis and refining

Regarding downstream chemical synthesis, two types of processes are within the scope of the ADVANCEFUEL project: the Fischer-Tropsch (FT) synthesis for liquid biofuels (including bio-LNG from methane via liquefaction at $-162\text{ }^{\circ}\text{C}$) and the production of methanol and dimethyl ether (DME).

In the FT process, the clean syngas is converted into a mixture of alkanes, alkenes and oxygenates using iron and cobalt catalysts. The low temperature technology ($200\text{-}220\text{ }^{\circ}\text{C}$, and less than 30 bar) provides outputs primarily for diesel production, and the high temperature technology ($300\text{-}350\text{ }^{\circ}\text{C}$) results in a mixture which is more compatible with gasoline. The raw product should undergo a series of upgrading processes typically used in oil refineries, such as hydro-treatment and hydrocracking. The involved separation processes are also typical for oil refineries. Thus, the FT process parameters for bio-syngas to liquid fuels is similar to that of coal or gas to liquid fuels. However, the biomass derived synthesis gas can contain significant amounts of contaminants like alkali and alkaline earth species, sulfur (H_2S , COS), nitrogen (NH_3 , HCN), dust, and tars. The H_2/CO ratio in synthesis gas derived from biomass is typically lower than the ratio obtained from natural gas reforming, but higher than the ratio from coal gasification. Due to the high oxygen content of biomass, a significant concentration of CO_2 is usually present in the synthesis gas (Lilebo et al., 2013).

Methanol is industrially formed from syngas in the presence of copper catalyst at $260\text{ }^{\circ}\text{C}$ and pressures higher than 60 bar (i.e., typically up to 100 bar). The conversion is exothermic and

very selective, transferring almost 80% of the syngas energy content to methanol. Methanol is separated from the co-produced water by distillation. Dimethyl ether (DME) can be formed by methanol dehydration in the presence of silica-alumina in a slightly exothermic reaction. DME can be stored in the liquid state at 5 bar and ambient temperature, similar to liquefied petroleum gas (Landälv et al., 2017). The process can also be performed in a dual catalytic system in the same reactor (performing both methanol synthesis and dehydration) without prior isolation of methanol. Again, the main link to the biomass conversion technologies (other than the process integration potential) is the impurities in the syngas feedstock of these processes as a result of the biomass gasification. This may increase the gas cleaning requirements and the requirements for additional renewable hydrogen (e.g., from electrolysis technologies, see Figure 1) toward more favourable H₂/CO ratios.

Bio-oil is a complex mixture of water (20–30 wt%) and organic oxygenates (70–80 wt%) that are derived from the thermal decomposition of the lignocellulosic feed. It has higher energy density and can be handled more easily than solid biomass, and is therefore more suitable for storage and transportation. However, it is composed of highly reactive oxygenates that are responsible for many adverse properties, such as instability, immiscibility with hydrocarbon fuels, low heating value and corrosivity. These properties render bio-oil a low quality product that is difficult to introduce into the world energy market. Bio-oil can be upgraded to a higher quality product with improved properties via downstream catalytic cracking or hydrodeoxygenation (Stefanidis et al., 2018).

During catalytic cracking, raw bio-oil is vaporized at intermediate temperatures and the vapours come in contact with a heterogeneous acidic catalyst. Catalytic reactions remove oxygen from the vapours via formation of water, CO₂, and CO, and the resulting oil is a less oxygenated mixture of aromatic hydrocarbons and less problematic oxygenates. However, the instability of raw bio-oil and its hydrogen-deficit nature cause significant charring and formation of coke, which lead to severely diminished oil yields, rapid catalyst deactivation and increased formation of solid byproducts. In addition, the resulting upgraded liquid product is only partially deoxygenated and still requires further upgrading.

Alternatively, raw bio-oil can be almost completely deoxygenated and converted into a mixture of liquid hydrocarbons via hydrodeoxygenation (Elliott, 2015). Hydrodeoxygenation is carried out at intermediate temperatures (200–350 °C), high pressure (50–150 bar) and under a hydrogen atmosphere in the presence of a heterogeneous hydrogenation catalyst (Bridgwater, 2012). Due to the instability of raw bio-oil, and in order to ensure continuous processing, complete hydrodeoxygenation needs to be carried out in multiple steps (Elliott, 2015), which adds to the complexity of the process. Moreover, due to the high oxygen content of raw bio-oil (typically, 30–45 wt%), a significant amount of hydrogen is consumed for complete deoxygenation, which can lead to significantly high operating costs. In order to avoid high operation costs, partial hydrogenation/hydrodeoxygenation can be carried out at milder conditions with less hydrogen



consumption. This milder process results in an oxygenated oil (hydrodeoxygenated oil, HDO) that is more stable than raw bio-oil and can be more easily processed further to produce fuels (Venderbosch et al., 2010).

Another potential technology to overcome some of the above challenges is the co-processing of bio-oil with petroleum feeding into conventional refinery processes. This approach has several important advantages, such as the utilization of existing refinery infrastructure, which significantly reduces the capital cost required for bringing second-generation biofuels to the market. Co-processing can potentially be carried out in refinery processes such as fluid catalytic cracking (FCC) and hydroprocessing. Since FCC is one of the main processes in the refinery for the conversion of heavy petroleum feeds into lighter products such as gasoline, liquefied petroleum gas (LPG), and light cycle oil (LCO) and can handle a variety of impure feedstocks, it is potentially the most suitable process for the introduction of bio-oil into the refinery.

2. Concluding remarks

The conversion technologies of the ADVANCEFUEL project are defined in this document with respect to their basic characteristics for feed, process conditions and output products. Both qualitative and quantitative information is provided to better explain the relevant technology parameters and definitions.

The information is relevant for creating a superstructure of technological paths (i.e., linking conversion technologies based on the reported input-process-output information) characterise them based on their TRL and efficiencies and identify benchmark technological paths. Thus, this information will be used in D3.2 for defining biomass reference technologies with respect to TRL and will also support detailed calculations for the relevant technology performance indicators.

The information of this document will also be used as a reference throughout WP3 for identifying needs for development and potentials for innovations for high efficient and low risk biomass conversion technologies, and positioning them with respect to key European fossil-fuel infrastructures.

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