CERESiS: ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies

D1.3: Assessment of clean liquid biofuel value chains

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NOMENCLATURE

AH:	Aromatic Hydrocarbon
BtL:	Biomass to Liquids
CC:	Catalytic Cracking
CE:	Carbon Engineering
DAC:	Direct Air Capture
DDGS:	Distiller's dried grains with solubles
DME:	Dimethyl ether
DW:	Dry Weight
EC:	Electrochemical
ECF:	Electrochemical Filtration
ETBE:	Ethyl Tertiary Butyl Ether
ETH:	Eidgenössische Technische Hochschule
FFA:	Free Fatty Acids
FT:	Fischer–Tropsch
GHG:	Greenhouse Gas
HHV:	Higher Heating Value
HM:	Heavy Metal
HMCB:	Heavy metal contaminated biomass
HTL:	Hydrothermal Liquefaction
LHV:	Lower Heating Value
MEA:	Monoethylamine
MPC:	Maximum permissible concentration
PAH:	Polycyclic Aromatic Hydrocarbons
PARC:	Palo Alto Research Center
PCDD:	Polychlorinated dioxins
PCDF:	Polychlorinated furans
PS:	Particle Size

PSA: Pressure Swing Adsortpion

PtG: Power to Gas

PtL: Power to Liquids

PtX: Power to X

SCWG: SuperCritical Water Gasification

SHF: Separate Hydrolysis and Fermentation

SRC: Short Rotation Coppice

SSF: Simultaneous Saccharification and Fermentation

TSA: Temperature Swing Adsorption

US: United States

WGSR: Water Gas Shift Reaction

ZSW: Zentrum für Sonnenenergie- und Wasserstoff-Forschung

EXECUTIVE SUMMARY

The aim of D1.3 “Assessment of clean liquid biofuel value chains” is to identify and examine the preliminary alternative liquid biofuel value chain scenarios, based on analysis of existing chains, focusing on the required adaptations needed for clean biofuel production. In this task, the incorporation of contaminated biomass was examined, to specify the requirements and constraints of integrated pathways.

Recent need for sustainable energy pathways has led to the development of new technologies involving biomass-derived liquid biofuels. Existing liquid biofuel value chains can be categorized in first generation (commodities that are used for food purposes), second generation (lignocellulosic crops), third generation (algae-derived biomass) biofuels and electrofuels (based on CO2 of non-biogenic origin and biomass-based CO2). By identifying the most common stages in existing value chains (including pre-processing, conversion to liquid biofuel, post-processing techniques) four basic value-chain scenarios were configured. An additional criterion for selecting the existing chains was the level of relevance to the CERESiS framework. This means that electrofuel and algae feedstock related chains were not selected as cases to be further examined for adaptations in order to deal with contaminated feedstocks. The alternative biofuel value chains have been defined (and will be further refined in forthcoming deliverables), aiming to provide a liquid fuel with comparable HM load to existing fossil transport fuels.

These chains selected to be examined for contaminated load adaptations are:

Value chain 1: Sugar to alcohols

Value chain 2: Oil crops to biodiesel

Value chain 3: Biomass to Liquids (BtL) via gasification

Value chain 4: Biomass to Liquids (BtL) via pyrolysis

In this scope, the presence of contamination in the above-mentioned cases was reviewed, to assess the effect of contaminants (e.g., heavy metals, polycyclic aromatic hydrocarbons etc.). Their effect was studied in each of the typical stages of the existing value chains. More specifically there was focus on the gasification and pyrolysis conversion processes, emphasizing on the fate of contaminants along each process. Among others, parameters such as temperature, pressure, heavy metal type and concentration in the gasification process have been studied and proved to be significant. On the other hand, in pyrolysis, residence time, reactor temperature, pre-treatment and post-treatment methods are some of the primary variables which influence the fate of contaminants along the process.

Towards defining the clean biofuel chains, suitable pre-processing treatments have been described in section 3.1. As provided by the relevant literature, it is possible in some cases to capture the HM load before the main conversion stage, thus potentially addressing the issue of excessively contaminated feedstocks. However, options for managing the

hazardous effluent should be further investigated in the forthcoming tasks and deliverables.

Unfortunately, there is very limited information available for mineral oil and aromatic hydrocarbon contaminated feedstocks. Relevant open literature sources are mostly dealing with the formation of PAH contaminants during thermochemical conversion of biomass or focusing on the effects of biomass yield of crops growing in correspondingly contaminated soils, while the subsequent stages towards liquid biofuels are not thoroughly examined. The main reason is because, due to their hydrophobic nature, hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in environmental matrices are rapidly adsorbed on particles and organic matter of soils. Consequently, soils are the ultimate repository for most hydrophobic organic contaminants that cannot be extracted by a plant since they cannot be dissolved in the aqueous phase moving from the soil to the vascular system of the plant. However, biomass grown on soils with organics contamination presents this kind of contamination mainly due to soils particles adhering the external surface of the plant.

Nevertheless, T1.3 has successfully defined the alternative value chain scenarios in the case of heavy metal contamination, after processing and summarizing the information from a considerable number of relevant literature. This is an important contribution, which will be the starting point of Task 1.7, in which the final definition of alternative value chains will take place.

1 EXISTING LIQUID BIOFUEL VALUE CHAINS

1.1 Main types of liquid biofuels

This section provides background information on existing types of established and promising liquid biofuels.

1.1.1 First Generation liquid biofuels

The three main types of first generation biofuels used commercially are biodiesel (bio-esters), ethanol, and biogas of which worldwide large quantities have been produced so far and for which the production process is considered 'established technology'. Biodiesel is a substitute of diesel and is produced through transesterification of vegetable oils, and residual oils and fats, with minor engine modifications; it can serve as a full substitute as well. Bioethanol is a substitute of gasoline and it is a full substitute for gasoline in so called flexi-fuel vehicles. It is derived from sugar or starch through fermentation. Bioethanol can also serve as feedstock for ethyl tertiary butyl ether (ETBE) which blends more easily with gasoline. Biogas, or biomethane, is a fuel that can be used in gasoline vehicles with minor adaptations, however it is not herewith examined since the work focuses on liquid biofuels. At present, biodiesel, bioethanol and biogas are produced from commodities that are also used for food. The demand of edible oils is increasing, therefore using the agricultural food crop for biofuel production becomes correspondingly less attractive and sound from a sustainability perspective [1]

1.1.2 Second Generation liquid biofuels

Second-generation biofuels are derived from lignocellulosic crops. These biofuels can be manufactured from different forms of biomass which can be renewed rapidly as part of the carbon cycle. Second generation biomass is considered the residual nonfood parts of current crops, such as stems, leaves, and husks, that are left behind once the food crop has been extracted. In addition, other kinds of crops that are not used for food purposes, such as switch grass, miscanthus, reed canary grass, rye, wheat straw, cereals, etc. can also be extracted. [2][3]

The development of second-generation biofuel technologies has emerged because first-generation biofuel manufacture has important limitations. The production of first-generation biofuels is comprised of biodiesel from vegetable oils and bioethanol from sugar containing plants. This type of production relies on well-established technologies and the actual exploitation of the final products is excellent. One major disadvantage is that these biofuels exhibit significant costs mainly due to the limited feedstock species that they account for. In addition, a competition was developed between the biofuel and the food industries over the subject of feedstock availability and other potential imbalances (mostly economical) that the use of these materials for fuel production would have on the food industry and society in general. Furthermore, great consideration is taken as well about the use of land, water, and chemical fertilizers for the cultivation of these plantations (and their environmental and economic impact). [4]

Second-generation biofuels are capable of solving these problems and can supply a larger proportion of biofuel sustainably and affordably with greater environmental benefits. Furthermore, the goal of second-generation biofuel processes is to extend the amount of biofuel that can be produced sustainably by using biomass. [2]

1.1.3 Third Generation liquid biofuels

The second generation biofuels face steep challenges in the form of technical difficulties during pretreatment processes and inefficient conversion of lignocellulosic materials due to their complex structures. For this reason, there is a need for viable and cost-effective alternatives to fossil fuels. Many studies have reported the superior capabilities of algae-derived biomass for the production of an improved version of biofuels: “third generation” biofuels. Algae are highly diverse micro- and macro-plants that are found almost everywhere on planet Earth. They provide food, feed, and vital nutrients as well as supplying up to 60% of the required oxygen to all living beings vital for their survival, so it plays an important role in many ecosystems [5]. Recently though, algal cultures have been used to produce vitamins, feed, and other products on an industrial scale. Microalgae have high photosynthetic conversion efficiency, so they are reported to be a promising alternative for the production of fuels and chemicals. Moreover, these organisms are unicellular, contain carbon, hydrogen, oxygen, and nitrogen, and are categorized as aquatic biomass. Their development is heavily dependent on the availability and intensity of light, the availability of nutrients like phosphorus and nitrogen, CO_2 and O_2 levels, temperature, and the type of culture system used.[6]Algae are simple plants which range from microscopic (microalgae) to large seaweeds (macroalgae), from small green dots to larger cyanobacteria and the tinsel diatoms. Furthermore, there are nine major groups of algae which include cyanobacteria (Cyanophyceae), green algae (Chlorophyceae), diatoms (Bacillariophyceae), yellow-green algae (Xanthophyceae), golden algae (Chrysophyceae), red algae (Rhodophyceae), brown algae (Phaeophyceae), dinoflagellates (Dinophyceae), and “picoplankton” (Prasinophyceae and Eustigmatophyceae). It must be mentioned that microalgae like Spirulina, Chlorella, Dunaliella, and Haematococcus are currently cultivated commercially to produce photosynthetically grown biomass from a few tons to several hundred tons annually. [5]

To sum up, algae represent a promising, everlasting source of fuel and other valuable products. They have the ability to produce crude oil which may, then, be easily processed into diesel and gasoline. Furthermore, particular algae may be genetically modified so that the carbon metabolic pathway facilitates the production of important end-products like ethanol. They also possess the ability to produce more energy per acre of land compared to other conventional feedstock crops such as sugarcane and corn [7]. As a result, microalgae are considered to have the maximum potential to act as a substitute for petroleum-derived transport diesel without adversely affecting food supply and other crop products. [5]

1.1.4 Electrofuels

Electrofuels or e-fuels are advanced fuels, produced with hydrogen that is obtained from the electrolysis of water. The term electrofuels is referring to the process rather than the fuels itself. These are similar or identically to the ones produced with different processes. The terms for the conversion processes of electricity and variable renewable energies (e.g. solar or wind power), to produce electrofuels, are: Power-to-X (PtX), Power-to-Gas (PtG) and Power-to-Liquid (PtL), as shown in Table 1.

Electrofuels / E-fuels	Power-to-X (PtX)	Power-to-Gas (PtG)	Power-to-liquid (PtL)
Hydrogen (H_2)	X	X	
Methane (CH_4)	X	X	
Ammonia (NH_3)	X	X	
DME (C_2H_6O)	X	X	
Methanol (CH_3OH)	X		X
FT-liquids	X		X
Gasoline components	X		X
Diesel components	X		X
Jet components	X		X

Table 1: Classification of Electrofuels [8]

For the production of carbon based electrofuels, electricity and carbon dioxide are needed. During the electrolysis, electricity is used to split water into oxygen and hydrogen. The hydrogen produced by electrolysis is either used as such or combined with carbon, to form gaseous or liquid hydrocarbons through synthesis processes. Depending on the desired product, these synthesis processes use different catalysts to produce either methane, methanol, FT-fuels, etc.

The sustainability and particularly the GHG emission reduction potential of electrofuels is determined by the origin of electricity and carbon. Using excess and/or renewable electricity or biogenic carbon increases the sustainability. Following, a list of different carbon sources [8] :

- Electrofuels from non-biogenic origin: CO_2, which would have been emitted through e.g. fossil fuel burning, is captured and re-used. For the purposes of this project, these electrofuels will not be further studied, as they do not include sustainable feedstock options.
- Biomass based electrofuels: CO_2 from biomass processing such as fermentation, anaerobic digestion, gasification, combustion is captured and re-used.
- Direct air capture (DAC): CO_2 is directly captured from air and re-used.

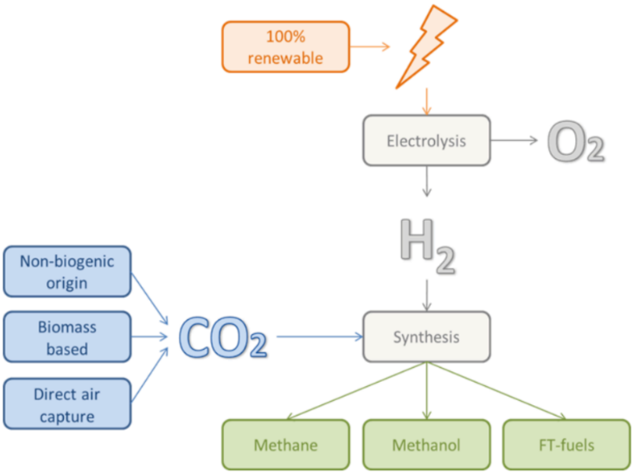


Figure 1: Schematic production of electrofuels [8]

1.2 Identification and general description of stages

Biofuel chains encompass several different stages such as feedstock production (agricultural phase), feedstock transport, feedstock processing, biofuel production, and biofuel distribution, storage, dispensing, and combustion[9]. It has been shown that the magnitude and scale of impacts vary significantly between the different stages of the life cycle of biofuels.

The biofuel supply chain is quite complex, as it encompasses all activities from feedstock production, biomass logistics of storage and transportation, biofuel production, and distribution to end consumers. Similar to most other supply chains, a biofuel supply chain involves various distinct stages with different ownership entities such as farmers, biorefineries, distributors, and oil companies, and its performance highly depends on the network design, planning, and operations. Figure 2 depicts a schematic overview of an advanced biofuel supply chain network. Specifics of the intermediate processes and logistics steps (conversion, conditioning, storage, and transportation) may vary depending on the types of biomass feedstocks, conversion technology, and biofuel form. However, the fundamental mechanism and flow of the process are very similar.

The present work focuses on the production of liquid biofuels, therefore the general stages relevant to this scope are pre-processing of feedstock, conversion to biofuel and post-processing towards transport quality fuel (Fig. 2). These stages are presented according to the type of the liquid biofuel to be produced at the end of the respective value chain: First, second and third generation, plus the case of electrofuels.

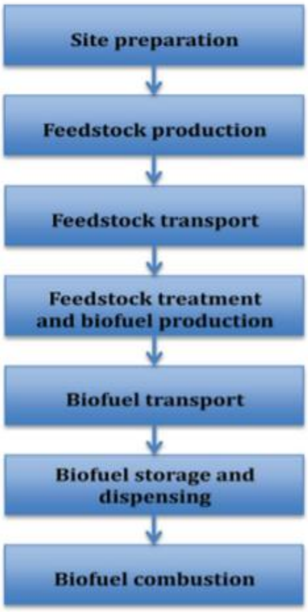


Figure 2: The seven stages of the biofuel life cycle [9]

The three major value chains relevant to D1.3 are shown in Fig 3:

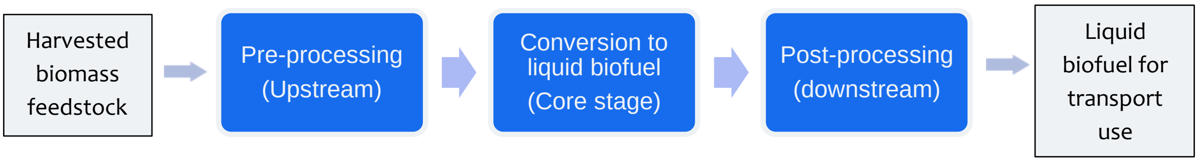


Figure 3 Major value chains relevant to D1.3

1.3 Pre-processing of biomass feedstock (upstream processes)

The pre-processing stage is herewith presented according to the type of the liquid biofuel to be produced at the end of the respective value chain.

1.3.1 Pre-processing of first generation liquid biofuels

This is the initial process herewith considered, following the agricultural operations of ground preparation, planting, cultivation and harvesting. In-field handling and transportation aim to collect biomass from where it is initially grown, usually with special mechanical equipment, and to move it to a point where it can be easily accessible by road transportation vehicles. This process sometimes includes some form of pre-treatment, such as chipping or even pelleting, in order to homogenize or reduce the size of the material collected. The processing is often performed to facilitate handling and to prevent significant loss of material during transportation and handling, such as baling (for loose materials). Pelleting is an expensive and energy-consuming step, which produces a fuel (pellets) of high density, high homogeneity, high heating value as well as low moisture content. Therefore, it makes it more appropriate for long-distance transportation, when pellets are the final product required or when the biomass is used in plants located in urban areas[10]

After these steps, the biomass needs to be loaded onto road transportation vehicles for conveyance to the energy conversion facility. The biomass will have to be unloaded from the vehicles at the biofuel conversion facility. The loading and unloading equipment heavily depends on the form and the type of the biomass, and whether it has been already somehow processed. It is often more efficient for the biomass to be in a form that standardized loading and unloading equipment (or agricultural equipment) may handle, so that this equipment may be used in other operations when not needed for biomass, in order to spread the fixed ownership cost over longer harvesting or operational periods[11]. In order to avoid high costs, an attractive option is using standardized equipment with a small number of interchangeable parts to better fit the biomass specifications.[10]

Next step is transportation. Taking into account that the typical locations of biomass availability, the transportation infrastructure is usually such that road transportation will be the only potential mode for collection and transportation of the fuel. Other factors that favor the use of road transportation are the relatively short distances over which the fuel is transported and the greater flexibility that it can offer in comparison with other modes. Other transportation modes, such as ships or trains may be considered when long distance biomass transportation is examined. Long-distance biomass transportation is not prohibitive from a financial perspective, as biomass may be procured and purchased at lower prices[12]. On the other hand, longer transportation distances lead to higher emissions from the biomass supply chain, therefore reducing to a certain extent the environmental advantages of renewable energy generation. [10][12]

The biomass supply chain system includes storage. Many types of biomass are characterized by seasonal availability, as they are harvested at a specific time of the year, but since a steady fuel supply is required at the power station on a year-round basis, it is therefore necessary to store them. The storage point could be at a farm, forest or other collection point, at the energy conversion facility or at an intermediate site. [10]

1.3.1.1 Bio-ethanol from maize

By definition, alcohol produced from sugar by yeast is ethanol. Feedstock preparation and pretreatment techniques play a major role in the process of bioethanol production from maize. In the case of maize, wet milling and dry milling can be both used as pre-processing steps, followed by liquefaction and saccharification. Regarding bio-ethanol production from maize, the usual pre-processing steps are presented below:

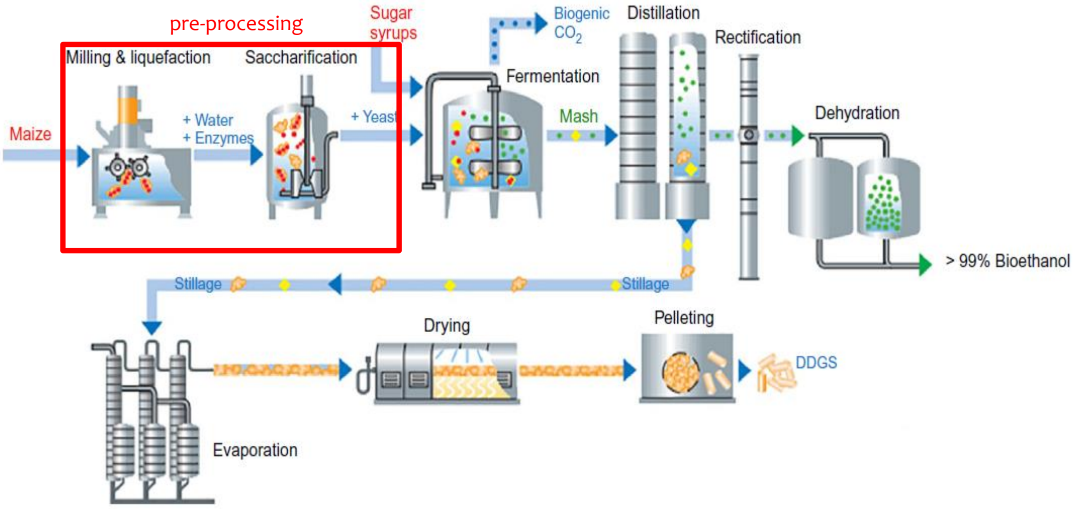


Figure 4 : Dry grind milling of maize to ethanol.[13]

Besides producing fuel ethanol, wet milling is used to produce many products. Compared to dry grind, maize-processing wet mills are large scale and capital intensive, and produce varied products such as high fructose maize syrup, biodegradable plastics, food additives such as citric acid and xanthan gum, maize oil used for cooking oil, and livestock feed too.

The first step in the wet milling process involves soaking the grain in water (steeping). For that reason, the word “wet” is used for this milling process. Soaking softens the grain and makes it easier to separate the various components of the maize kernel. The process of separating soaked maize into many other components is called “fractionation.” The process of fractionation separates wet maize grains into starch, fiber, and germ. Once they are separated, they are processed to make a variety of products. The major by-products of wet milling fuel ethanol production are two commercially available feed products: maize gluten meal, which contains high protein (40%) and is used for human consumption, maize gluten which contains low protein (28%) and is used as animal feed; and maize germ, which is further used to produce maize oil used for cooking purposes. [2]

In the dry-grind ethanol process, the whole grain is processed, and the residual components are separated at the end of the process. There are six major steps in the dry-grind method of ethanol production: Milling involves processing maize through a hammer mill with screens between 3.2 and 4.0mm to produce a flour [14]. This maize flour is then slurried with water and heat stabilized along with an enzyme called α-amylase. The slurry is then cooked through a process known as "liquefaction." It is performed using jet cookers that inject steam into the flour slurry to cook it at temperatures above 100°C. The heat and mechanical shear of the cooking process breaks apart the starch granules present in the kernel endosperm, and the enzymes break down the starch polymer into small fragments. The cooked maize mash is then allowed to cool to 80–90 °C, the additional α-amylase enzyme is added, and the slurry is allowed to continue liquefying for at least 30min [13]. After milling and liquefaction, the maize slurry is now called "mash," which is furthered cooled to approximately 30°C, and a second enzyme, glucoamylase, is added to the mash. Glucoamylase completes the breakdown of the starch into a simple sugar (glucose). This step is called "saccharification" and often occurs while the mash is filling the fermenter in preparation for the next step of fermentation and continues throughout the next step. [13]

1.3.1.2 Bio-ethanol from sugar cane

The conversion of sugar cane to ethanol consists of two steps: preprocessing and processing.

Preprocessing: The first step is harvesting cane. In many sugar-producing countries, including Brazil and India, mechanical harvesters are used to cut the cane into small pieces and load it into trucks during the harvesting operation. Trucks then deliver the harvested sugar cane to the processing mill. Each truck is weighed to check how much cane it is delivering. Samples are removed to test the quality of the cane. Sugar cane must be processed as soon as possible to avoid its sugar content to deteriorate. Most cane is delivered within 24 hours of harvesting. One ton of sugar cane produces around 85L of ethanol.

The truck unloads the cane onto preparation conveyor belts that carry the cane to the crushing system. Sugar cane juice is extracted by crushing the chopped cane through a series of rollers and the juice flows out. Cane fiber called bagasse goes to boilers to be burned. The heat turns water into high-pressure steam for electricity. Bagasse in the ethanol industry is used for electricity production. [13]

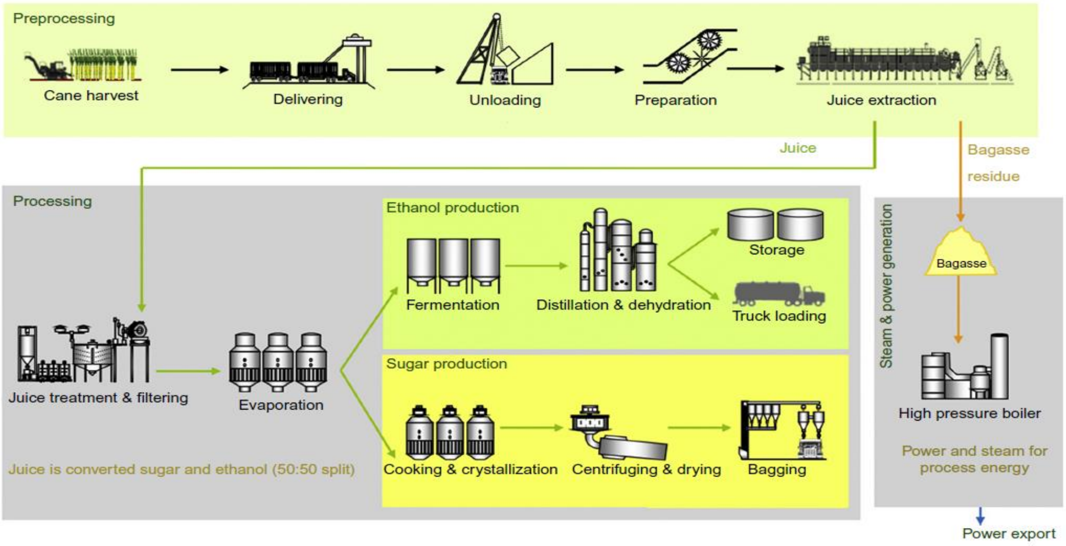


Figure 5: Conversion of sugar cane to ethanol and sugar [13]

1.3.1.3 Biodiesel

Oil crops are the base for biodiesel production. In Europe, rapeseed is the most common feedstock for biodiesel production. In the United States, Argentina, and Brazil, soybean oil is the most dominant biodiesel fuel feedstock. In Indonesia and Malaysia, palm oil is the main feedstock cultivated. Besides the most prominent oil crops (palm, soybean, rapeseed, and sunflower), many other crops such as canola, mustard, flax, jatropha, coconut, hemp, and pennycress are good sources of oil. The use of corn oil is also gaining momentum in the United States, where large volumes of maize are used in ethanol production.[13]

Oilseed crops store energy from the sun through photosynthesis during the process of producing their own food. The seeds are harvested from the oilseed crops and the harvesting mechanism differs from one oilseed-producing crop to another. The following upstream processes (transportation, storage, etc.) are identical to the case of handling typical cases of seeds for vegetable oil production. The next step is cleaning, drying, and preparing the seeds for crushing. Foreign particles such as stone, glass, and metal are removed, and then drying is performed while avoiding contact with combustion gases unless natural gas is used. In the solvent extraction process, the clean and dried seeds are crushed and heated to break them into two components: oil and solvent. The process separates the oil from the seeds/beans. The preprocessed seeds/beans are treated in a multistage countercurrent process with solvent until the oil content is reduced to the lowest possible level. Hexane is commonly used as extraction solvent. The miscella is a mixture of oil and solvent. It is separated by distillation into its two components: crude vegetable oil and solvent. The solvent is recycled for reuse in the extraction process. The crude oils are then refined to remove the gums or crude lecithins and FFA from the oil ensuring the quality and stability of the refined vegetable oil. The biodiesel is derived from vegetable oil through the process of transesterification. Along with producing biodiesel the process generates glycerol as a by-product, which is used extensively in both the food and cosmetics industries. The entire procedure of conversion of oilseed crops to biodiesel is shown in the figure below (Fig. 6). [13]

Figure 6: Conversion of oilseed crops into biodiesel. [12]

Seeds with high oil content, such as rapeseeds and sunflower seeds, are usually mechanically pressed after a preheating step. The pressed cake contains up to 18% of oil and is further treated in the extractor. In some cases, the pressed cake undergoes deep expelling. This brings oil levels down to below 10% and results in an expeller sold for feed purposes. Soybeans have a relatively low oil content. They are thermally treated and mechanically crushed into raw materials/flakes that are further extracted. Sometimes the oil-containing raw material is pressed without heating; such oils are known as cold-pressed oils. Since cold pressing does not extract all the oil, it is practiced only in the production of a few special edible oils for example olive oil. [12]

1.3.2 Pre-processing of second generation liquid biofuels

Operations vary depending on whether the biomass is a secondary residue harvested after a primary grain harvest (for example corn grain and stover) or a primary energy crop harvest (for example switchgrass). If the biomass is a dedicated energy crop, it does not contain a separate grain element (or some other marketable fraction) that must be harvested. [3]

The harvested biomass from regional farms is first collected and staged at the nearby shipping terminal or elevators and then subsequently shipped to a nearby conversion facility. Receiving and preprocessing at the facility encompasses all the processes associated with weighing and unloading incoming trucks, moving baled feedstock into short-term storage (queuing), moving bales from queuing into the preprocessing system for grinding and feeding, and moving the ground feedstock into the conversion process. [3]

An essential part in the second-generation solid biofuel value chain is feedstock preparation techniques for any thermochemical method. It must be noted that thermochemical methods of conversion have certain advantages in terms of processing of biomass. There is no requirement for the separation of all the components of biomass, so no chemical pretreatment is needed. Although, to achieve the high bio-oil yields it is mandatory to prepare the solid biomass feedstock in such a way in order to facilitate the required heat transfer rates. The main parameters considered in the pretreatment of lignocellulosic biomass are size distribution, particle shape, moisture content, bulk and particle densities, compressibility and compact ratio. [15]

After the harvest and collection of biomass the next step focuses on the reduction of biomass size. Biomass size reduction, also referred as comminution, takes biomass from its as-received condition (for example baled, log, or coarse shredded) to the final particle size specification required by the end user. [3] In addition, particle size of biomass feedstock has a major impact on the heating rate of solid fuel, making it an important parameter. In other words, particles need to be very small to fulfill the requirements of rapid heating and to achieve high liquid yields. [15] The particle size depends on several factors, such as biomass physical and material properties, process variable of the comminution system, shear and impact forces imparted by the comminution system, and the size opening of the screen used to retain material in the system until the material is sufficiently processed to pass through. The most widespread technology for biomass comminution is hammer mills due to their high throughputs and versatility in processing a wide range of materials. Moreover, milling operations at hammer mills typically involve two steps to arrive at the final particle size specification. The first step of the size reduction process takes the as-received biomass and converts it, through processes such as grinding or chipping, into a product that can be further preprocessed. Then for the second step, another grinder is used to reduce the particle size further to meet particle size distribution requirements. Usually, a common second-stage size reduction process will use a 3/4 to 1-in. screen to produce a mean particle size of 1/9 to 1/8 in. According to other reports, feed specifications can range from less than 200 mm for rotating cone reactors to less than 2 mm for fluid beds and less than 6 mm for transported or circulating fluid beds. [16] The conventional milling processes usually achieve the desired mean particle size. However, they often have wide particle size distributions, with a large percentage of undersized particles referred to as fines. This problem can be solved with fractional milling design which is used at advanced supply systems by introducing a separation step between the first- and second stage grinding operations to remove the material that already meets the size specification. As a result, only the remaining oversized material is proceeded for further size reduction. [3]

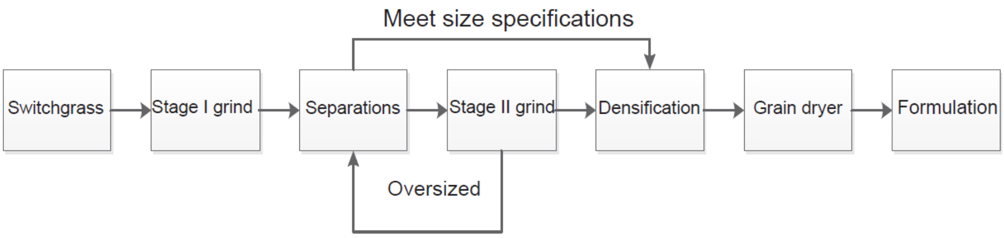


Figure 7: Size reduction process for lignocellulosic biomass [16]

Once size reduction has been achieved, the next step is usually drying and densification of the biomass. This is done in order to achieve consistent properties (such as size and shape, bulk and unit density, and durability), that heavily influence storage, transportation, and handling characteristics and, by extension, feedstock cost and quality [3]

Drying and densification is a process which converts raw biomass into a biomass pellet. Conventional biomass pellet production includes an initial size reduction to a 2-in. particle which is followed by drying to 10-12% moisture content with a rotary drier. Then, the dried biomass is passed through a second stage grinding process to reduce the particle size to less than 3/16-in., steam conditioned, and pelletized. In addition, a large amount of energy is consumed for drying (about 70% of the total pelletization energy). [3]

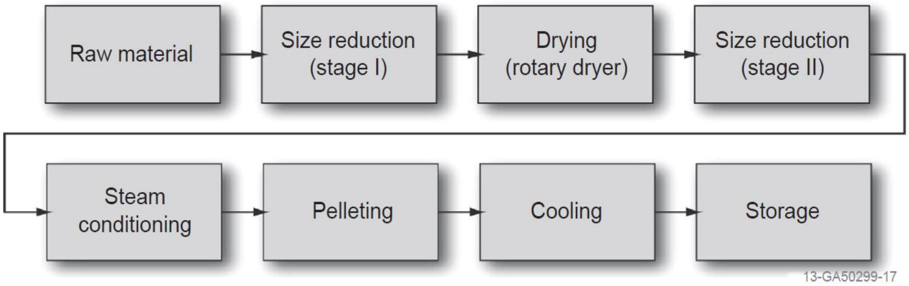


Figure 8: Conventional Drying and Densification System [3]

Improvements to the conventional drying and pelleting processes are possible with high-moisture densification because it eliminates the energy-intensive rotary drying prior to pelleting. During this process, the high-temperature (typically 160-180 °C) drying step is replaced with a low temperature (approximately 110 °C) and short duration (usually several minutes) preheating step. As a result, the combination of preheating along with the additional frictional heat generated in the pellet die results in a reduction of feedstock moisture content by about 5-10 points (for example from 30% down to 20-25%). However, the pellets produced still have a high moisture content and require further drying to about 7% in order for pellets to hold up during storage and transportation. [3]

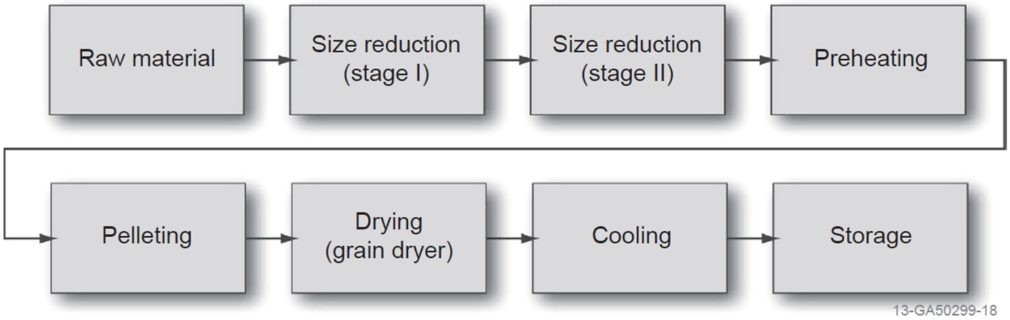


Figure 9: Advanced Drying and Densification System which includes Pre-Heating [3]

Transportation is a crucial part of the value chain. Usually, it is expected that energy crops like switchgrass will be trucked to a depot where preprocessing addresses quality (moisture content, ash content) along with density issues to allow for more efficient high-capacity transportation and handling. Furthermore, densification increases material uniformity and flowability, which is advantageous in transportation activities. [3]

1.3.3 Pre-processing of third generation liquid biofuels

In microalgae systems, the biomass quantities are present in very dilute streams, which must normally be concentrated during the harvesting process. Pretreatment processes play a major role in removing unwanted material such as lignin and facilitating the release of polysaccharides from biomass, while enzymes act on these polysaccharides and convert them into their respective monomers. [17]

Some preprocessing schemes might be required prior to the extraction of the desired components in the algae biomass and their subsequent conversion into bioenergy carriers. Specifically, these are the removal of foreign objects (ie, debris, stone, sand and litter picked up during harvesting.), dewatering of the biomass quantities, and possibly milling or cellular disruption of the algae biomass. Dewatering methods include flocculation, centrifugation, filtration and screening, flotation and electrophoresis techniques [18]. For microalgae production, the removal of foreign objects is not much of an issue. However, it becomes quite important with regard to macroalgae biomass, which could have stones, sand, litter, and other debris forms that might have been taken up during the harvesting process. Furthermore, milling (for macroalgae biomass) or cell disruption techniques are useful for the reduction of biomass structures to particle sizes and to improve the availability of the cellular contents for subsequent processing and conversion schemes. The technique that will be used is highly dependent on the planned bioenergy product intended for the algae biomass. For example, the dewatering demand for macroalgae is much less than that required for microalgae biomass. Moreover, depending on the intended fuel application of the algae biomass, it could be directly dried and densified into pellets and briquettes for direct use in heat and power applications (via combustion in power plants). [19]

Because algae biomass has a high-water content (80%), drying should be avoided where possible due to the amount of energy required to meet this goal. Therefore, the production of solid fuels is not a suitable fuel product consideration when using algae biomass. Extensive dewatering might not be required if the algae biomass is intended for biofuel conversion processes such as anaerobic digestion, alcohol fermentation, and hydrothermal liquefaction. Such processes have a water requirement or a high tolerance for water presence in the biomass. On the other hand, a dry feedstock is usually required for processes such as biodiesel or bio-oil production. Biomass drying can be achieved with the se of solar energy, waste process heat, or heat pumps [19].

Another option is chemical pretreatment methods, which are acid and alkali treatments of biomass. They are widely acceptable because they are less energy intensive, efficient processes for the removal of unwanted materials together with the release of sugar [20].

1.3.4 Pre-processing of electrofuels

The case of electrofuels differs from the previous biofuel chains, in the sense that there is no solid biomass feedstock to be processed. Nevertheless, the carbon contained in the liquid fuels produced can originate from a biogenic source, therefore “pre-processing” can be assigned to the according CO_2 supply options [8]:

- Biomass based electrofuels: CO_2 from biomass processing such as fermentation, anaerobic digestion, gasification, combustion is captured and re-used.
- Direct air capture (DAC): CO_2 is directly captured from air and re-used. There is no biogenic origin, however the DAC operation resembles to photosynthesis as regards the absorption of atmospheric CO2.

Biogenic CO_2 sources are biogas-upgrading plants, CO_2 from ethanol plants, and CO_2 from the combustion of biogas and solid biomass. The CO_2 content of biogas ranges from 25 to 55% [21]. The CO_2 can be separated from the biogas stream via scrubbing with amines or via pressure swing adsorption (PSA). Both technologies provide sufficient CO_2 purity (99%). Alternatively, if methane is the desired product, the biogas stream including the CO_2 is fed directly into a methanation reactor (direct methanation)[22]. The CO_2 fraction is converted to methane. The methane gas is swept through the methanation reactor like an inert gas. In this case, no CO_2-separation step is required [9].

The state-of-the-art approach is to extract CO_2 from flue gas via scrubbing with amines such as monoethanolamine (MEA). The scrubbing agent washes the CO_2 from the gas stream, and is regenerated through heating. Another process describes that the CO_2 is washed out from the gas stream via scrubbing with K_2CO_3 solution. The CO_2 concentration in the scrubbing agent is then elevated via electrodialysis and stripped out by a vacuum pump [9][11]

Pure CO_2 with a very low oxygen content is needed to avoid damaging the catalysts used for methanation and synthesis. The CO_2 is purified via liquefaction. The process is based on an existing CO_2 liquefaction plant with onsite carbon storage at an ethanol plant in Lüdinghausen in North Rhine-Westphalia in Germany, which has been in operation since 2013. The temperature of liquefied CO_2 is about -25°C at an elevated pressure, and the purity amounts to 99.999% (vol.) [23]. The oxygen content after liquefaction is less than 5 ppm [24], which is sufficient for the catalysts used in methanation and synthesis [9].

Various technologies for extracting CO_2 from the air exist. One option involves using a scrubbing agent such as sodium hydroxide (NaOH) or potassium hydroxide (KOH), which is converted to sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3). The decomposition is done via electrodialysis.

The Center for Solar Energy and Hydrogen (ZSW) research process is based on absorption with sodium hydroxide (NaOH), stripping the CO_2 with sulphuric acid (H_2SO_4), and regenerating the Na_2SO_4 via electrodialysis. The specific electricity consumption depends on the current density of the electrodialysis system. The higher the current density, the higher the specific electricity consumption. [9]

A process developed by the Palo Alto Research Center (PARC) uses KOH as a scrubbing agent . The electricity consumption is indicated with 300 kJ per mole of CO_2 (of that, 100 kJ is for the electrodialysis of the $KHCO_3$ solution from CO_2 absorption with KOH), which results in about 6.8 MJ per kg of CO_2.

The process developed by the Canadian company Carbon Engineering (CE) consists of CO_2 absorption with KOH, formation of $CaCO_3$ from K_2CO_3 and regeneration of the $CaCO_3$ via calcination and subsequent conversion to $Ca(OH)_2$. [11]

Another option is the technology developed by the Swiss company Climeworks. Climeworks (an ETH Zurich spinoff) uses an adsorption/desorption cycle to extract CO2 from the air. The CO_2 is chemically bound on a sorbent (in contrast to most adsorption processes, this uses chemisorption instead of physisorption). The regeneration of the sorbent is carried out at low temperatures (95°C) [25]. The process can also be referred to as a temperature swing adsorption (TSA) process [25]. TSA has been applied at Sunfire's power-to-liquid plant in Dresden, which uses high-temperature electrolysis with downstream Fischer-Tropsch synthesis.[9]

1.4 Conversion to liquid biofuel

1.4.1 Conversion processes of first generation liquid biofuels

Regarding first generation biofuels, the most common conversion processes are stated below. [1]

1.4.1.1 Bio-ethanol

A wide variety of carbohydrates containing raw materials have been used for production of ethanol by fermentation process. These raw materials are classified under three major categories: (a) Sugar containing crops: Sugar cane, wheat, beet root, fruits, palm juice, etc. (b) Starch containing crops: Grain such as wheat, barley, rice, sweet sorgum, corn, etc. and root plants like potato, cassava. (c) Cellulosic biomass: Wood and wood waste, cedar, pine, wood, etc. agricultural residues, fibers.

The term fermentation can generally be defined as the metabolic process in which an organic substrate goes under chemical changes due to activities of enzymes secreted by micro-organisms. There are two basic types of fermentation (a) aerobic and (b) anaerobic depending upon oxygen needed in the process or not. There are thousands of micro-organisms in nature capable of providing fermentative changes. Some of these are capable of producing ethanol from sugar and starch. The microorganisms employed for ethanol production are classified into three categories viz. yeast (saccharomyces species), bacteria (zymomonas species), and mold (mycelium). These micro-organisms found in nature and are very selective in their fermentation characteristics, some of these ferment specific to hexoses or pentose, or mixtures of both. Efforts are being made by various researchers to produce an ideal micro-organism, which will be able to produce ethanol from any carbohydrate.

Considering the production from sugar cane, the juice is heated and treated with sulfur, lime, and thickener. The mixture is pumped to rotating filters that separate the juice from most impurities. These form a crumbly residue, known as filter cake, which is used as natural fertilizer on fields. The filtered juice passes through sieves that remove any remaining impurities. The pure juice then goes to the evaporation process to remove the extra water content. Finally, the thick sugar juice goes either to make sugar or to make ethanol. This process is very popular in Brazilian sugar mills where both sugar-processing and ethanol fermenting facilities exist under one roof. Therefore the mill managers make the decision as to how much sugar and ethanol to produce depending on the demand for each (sugar and ethanol) product. Water and yeast are added to ferment the liquid sugar cane juice to produce ethanol. Like maize starch-based ethanol the fermented liquid, called “beer,” passes through centrifuges. The yeast is removed, treated, and reused. The liquid flows through two distillation columns that heat it to remove water. This produces dehydrated ethanol, which is blended with petrol for use as a transport fuel. The liquid by-product, called vinasse, is sprayed onto fields as fertilizer. At the pump, Brazilian motorists choose between pure ethanol and a petrol/ethanol blend. Some liquid flows into a third distillation column that further heats the liquid to remove more water. This produces anhydrous ethanol, which contains less water. It is considered to be>99% pure bioethanol and could be blended with gasoline at any percentage. The efficient industrial mills process sugar cane into ethanol in around 12–15hours. The ethanol flows into tanks to be stored and then transported to the market. If the mill manager chooses to produce sugar, then the sugar cane juice is further cooked to evaporate the last portion of the water under very tight controls in a vacuum pan. Seed grain (pulverized sugar) is fed into the pan as the water evaporates and crystals begin to form. The mixture leaves the vacuum pan as a thick crystal mass and is sent to a centrifuge, a large perforated basket spinning very rapidly much like a washing machine in the spin cycle, where it is spun and dried, yielding golden raw sugar, which is bagged according to weight. [13]

Other grains, mainly wheat and barley, are used extensively in Canada and many parts of Europe to produce ethanol. The process of harvesting gains varies according to the grain. Once the sugar is extracted from the grains the ethanol is obtained through the process of fermentation. The more general structure of converting grains to ethanol is shown in Fig. 10, which shows that any crops that contain a significant quantity of sugar starch could go through the process of extraction and fermentation to generate ethanol. [13]

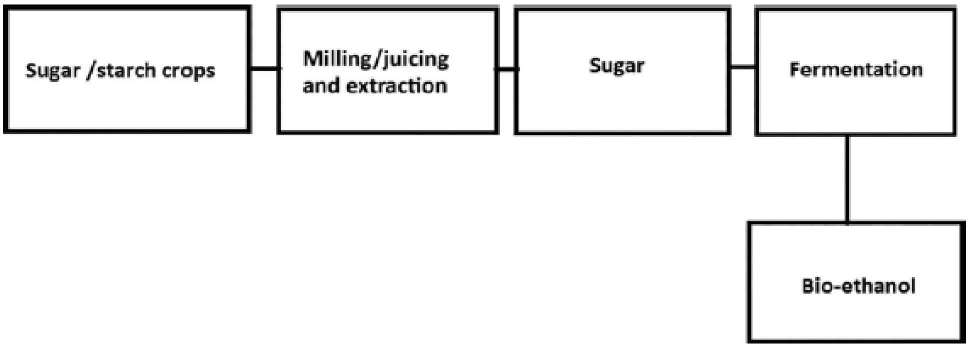


Figure 10: Schematic diagram of the conversion of grains to ethanol [12]

1.4.1.2 Bio-diesel

Almost all biodiesel is produced by the process called "transesterification." It is the most economical process requiring only low temperatures and pressures while producing a 98% conversion yield. The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol (methanol) to form esters and glycerol. A triglyceride has a glycerin molecule as its base with three long-chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerin. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. Transesterification of natural glycerides with methanol to methyl esters is a technically important reaction that has been used extensively in the soap and detergent manufacturing industry worldwide for many years. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the monoalkyl ester or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. Potassium hydroxide has been found more suitable for ethyl ester biodiesel production, but either base can be used for methyl ester production. The products of the reaction are the biodiesel and glycerol. A successful transesterification reaction is signified by the separation of the methyl ester (biodiesel) and glycerol layers after the reaction time. The heavier coproduct glycerol settles out and may be sold as it is or purified for use in other industries, for example pharmaceuticals, cosmetics, and detergents. After the transesterification reaction and the separation of the crude heavy glycerin phase, the producer is left with a crude light biodiesel phase. This crude biodiesel requires some purification prior to use [13].

1.4.2 Conversion processes of second generation liquid biofuels

Two basic paths are identified: thermochemical processing and biochemical processing.

1.4.2.1 Thermochemical processes

One of the thermochemical methods applied to lignocellulosic biomass is gasification. It is a conversion process that involves reacting biomass with air, oxygen, or steam to produce a gaseous mixture of CO, CO_2, H_2, CH_4, N_2 along with a rich spectrum of hydrocarbons, either known as producer gas, synthesis gas or syngas, depending on the relative proportions of the component gases [26]. The main objective of gasification is to maximize the yields of gaseous products and simultaneously minimize the amounts of condensable hydrocarbons and unreacted char. Furthermore, the exact composition of product gas depends on different parameters such as the type of process feeds, their feed ratios, process parameters and the type of gasification reactor used [27]. The produced syngas has roughly half the energy density of natural gas and can be utilized for its heat value in steam cycles, gas engines, fuel cells, as well as turbines to generate power and heat. In addition, syngas is also considered an intermediate feedstock for the production of liquid fuels and a large number of commodity chemicals, (such as hydrogen, synthetic natural gas, naphtha, kerosene, diesel, methanol, dimethyl ether and ammonia). Moreover, for the transportation fuels, the main syngas derived routes to fuels are hydrogen by Water Gas Shift Reaction (WGSR), hydrocarbons by Fischer–Tropsch (FT) synthesis or methanol synthesis followed by further reaction to produce hydrocarbon or oxygenated liquid fuels [15]. In other words, the main steps that take place for the production of transportation fuels from lignocellulosic biomass via gasification, include syngas generation, followed by syngas cleanup and Fischer–Tropsch synthesis. [28]

The syngas is generated in a gasifier. Gasifiers are capable of gasifying almost any kind of organic feedstock, including many types of wood, agricultural residues, and municipal solid waste. If an atmospheric fluidized bed gasifier is used, then a mixture of feed with bed material is fluidized by the gasifying agents, such as air, oxygen and/or steam, entering at the bottom of the bed. After that, heat is supplied to the gasifier either directly or indirectly to raise the gasification temperature to 600–1000 °C [29]. Also, the typical residence time for the gasification reaction is 3–4 s [30]. At the end of the gasification process the resulting gas is called raw gas. In the next step, the raw gas is cooled in a heat exchanger and after that, it is fed to a gas–solid separator (for example cyclone) in order to facilitate the separation of solid particles carried by exhaust gas [31].

Then, the syngas is by passed over supported metal catalysts (Fe, Co, Ru, Rh and Ni) in a Fischer-Tropsch (FT) reactor for the production of hydrocarbons. The product from the FT synthesis is a syncrude, which is a mixture of linear hydrocarbons (such as n-alkanes and n-alkenes) which bears close resemblance to crude oil. On the other hand, it also contains aromatics and oxygenates like 1-alkanols, aldehydes, ketones, carboxylic acids, and as a result, a different upgrading than the crude oil is required. Also, the syncrude is a multiphase mixture containing three to four different phases. As a result some upgrading techniques are required to convert most of the syncrude phases into a single "crude oil". These include various cracking, isomerization, hydrotreating, alkylation, aromatization and oligomerization procedures. The goal is to produce a higher quality oil end-product which can then be marketed as a synthetic crude oil to refiners [32].

Pyrolysis is defined as a thermo-chemical decomposition process in which lignocellulosic material is converted into a carbon-rich solid and volatile matter by heating in the absence of oxygen [33]. The most popular configurations used are fluidized beds and circulating fluidized beds due to their ease of operation [16]. Furthermore, fast pyrolysis is characterized by high heating rates, short vapor residence times, moderate and carefully controlled temperature. Rapid cooling or quenching of the pyrolysis vapors are two other important factors. Feedstock should be prepared as small particle sizes and a heat transfer rate to the particle within a range of 600-1000 $W \cdot cm^{-2}$. In addition, residence time should be limited to some seconds to minimize char formation [15]. Moderate temperatures (in the range of 450–550°C) are implemented depending on the species of crop and end-product [34]. Vapors need to be removed quickly from the presence of the hot solids. If this is not done, then these compounds can crack further into smaller molecular weight fragments and/or polymerize into larger fragments, both at the expense of fragments making up the desired liquid product [15].

The result from the rapid quenching of the pyrolysis vapors and aerosols, three product phases are formed: pyrolysis oil, non-condensable gases and char. The yields of each phase depend on these parameters: operating conditions, reactor design and feedstock characteristics, including ash content as well as the relative amounts of cellulose and lignin. The fast pyrolysis liquid, which is considered the main product, is obtained in yields of up to 80 wt% on dry feed, along with the by-product char and gas, which can be used within the process to avoid waste streams. The fast pyrolysis liquid, also known as bio-oil is obtained after vapor condensation. Additionally, the product bio-oil contains less than 30 wt% of water and hundreds of oxygenated components [35]. It is mostly immiscible in hydrocarbon liquids and can be upgraded by hydrotreating to lower the oxygen content and decrease hydrophilicity. The char, which is a by-product, is mainly composed of carbon and it is separated from the fast pyrolysis vapors and aerosols with the use of a cyclone. It is important to note that this solid product can be used as fuel. Lastly, the non-condensable gases are collected during vapor condensation. These gases could be made to good use, because they can be recycled internally as fluidizing gas to the fast pyrolysis reactor and/or collected for fuel use [15].

To sum up, the major advantage of fast pyrolysis is that it can directly produce a liquid fuel. This can be especially beneficial when biomass resources are remote from where the energy is required since the liquid can be readily stored and transported. In other words, pyrolysis bio-oil is a promising candidate to replace petroleum fuels [15].

Supercritical fluid extraction under supercritical conditions is defined as the thermal disruption process of the lignocellulose or other organic materials in a temperature range of 250–400 °C under high pressure (4–5 MPa). With this process extraction and separation of organic compounds from a matrix can be accomplished effectively [36]. During the process, a mixture of liquid and gas at equilibrium is heated and the thermal expansion causes the liquid to become less dense while the gas becomes denser as pressure increases. The densities of the two phases become identical and the distinction between them disappears at the critical point. The supercritical conditions offer unique properties, such as the strong dependence of the solubility of a material in a supercritical fluid to its density and good contact between oxidants and reactants, that make supercritical fluid extraction ideal for separation and extraction of useful products and for oxidation of organic materials [15]. However, lignocellulosic biomass is the most difficult one to deconstruct efficiently to produce biofuel due to its heterogeneous and recalcitrant structure [37]. The biofuels obtained from biomass using supercritical fluid extraction are significantly affected by extraction parameters such as extraction temperature, extraction time, biomass/solvent ratio, and pressure [36]. For most of the studies regarding supercritical extraction of biofuels from lignocellulosic biomass have been carried out using either ethanol or methanol as solvents, which have high reactivity, approachable critical temperatures and pressures, and low corrosiveness. The major advantages of the supercritical fluid extraction compared to the other conversion methods are fast kinetics, higher biomass conversion, ease of continuous operation and elimination of the use of catalysts. However, the main concerns are the high temperature and high pressure, which increase the operation costs. [15]

1.4.2.2 Biochemical processes

Bioalcohol such as ethanol, propanol, butanol, isobutanol, etc. can all be produced by fermentation. Most of them are produced using food crops, such as corn, potato, sugarcane, and cassava. However, due to food security issues, researchers are now focusing on the use of nonfeed stock (biomass) as a raw material for bioalcohol production. The main methods used for bioalcohol production are hydrolysis, fermentation, and distillation.

Ethanol: Ethanol is characterized by a high-octane number and can be mixed with gasoline to produce fuel. It must be noted that more than 97% of gasoline sold in the U.S. contains 10% ethanol to oxygenate the fuel and reduce pollution. Moreover, various wild and engineered microbes have been reported for bioalcohol production, starting from biomass as feedstock. Some of these are: Saccharomyces cerevisiae, Mrakia blollopis, a co-culture of cellulolytic (Clostridium phytofermentans) and ethanogenic (Saccharomyces cerevisiae cdt-1).

Butanol: Butanol is also a renewable fuel and can be used as a replacement for gasoline. In addition, it has similar energy content and octane number as gasoline and can be used directly in engines without modification. Also, butanol is immiscible with water, and has low vapor pressure, which makes it easy to handle. However, butanol has a lower octane rating as compared to gasoline, and its combustion yields more greenhouse gases. There are many microbes and feedstocks that have been reported for butanol production. Some of these include oil palm trunk sap as raw material, coculturing of Clostridium acetobutylicum and Bacillus subtilis by Abd-Alla and coworkers etc. [38]

1.4.3 Conversion processes of third generation liquid biofuels

The processes used for transforming microalgal biomass into different energy sources can be split into these categories: biochemical conversion, thermochemical conversion, chemical reactions, and direct combustion. For the production of bio-oil the most common processes that are utilized are biochemical and thermochemical methods [5].

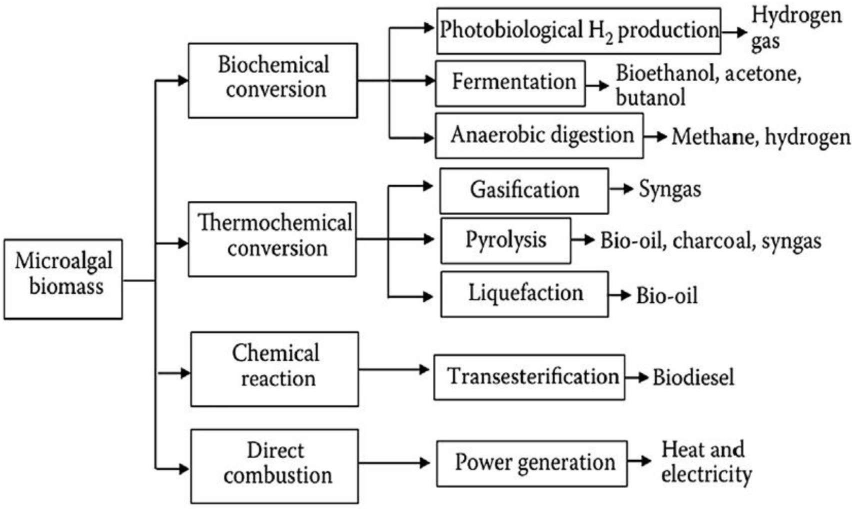


Figure 11: Processes for the conversion of third generation biofuels [5]

1.4.3.1 Thermochemical processes

The processes mentioned in this section are the same as the processes used for the conversion of second-generation biomass into biofuels. Therefore, the information in this section refers to the processes used for the conversion of third-generation biomass.

To produce yield though Hydrothermal Liquefaction (HTL), several crucial parameters must be considered. These include oleaginous microalgal strains, biomass concentration, reaction type, type of catalyst, temperature, and heating rate, among others [39]. Some research reports focus on the gasification of algal biomass. Firstly, Chlorella vulgaris using Ru/TiO2 as catalyst was found to be rich in hydrogen [40]. In addition, the composition of syngas obtained by Duman et al. after gasification of biomass of N. occulata was 40–53% H2, 30–40% CO2, 10% CH4 and 6% CO. Studies have shown that the catalyst plays a very important role in the conversion of biomass to syngas as it improves tar degradation and facilitates hydrogen production [41]. Regarding pyrolysis, studies have shown that the biomass of Chlorella sp. can be subjected to pyrolysis in a microwave oven and produce bio-oil approximately 28.6% wt/wt of the biomass [42]. The produced bio-oil is composed of both aromatic and aliphatic hydrocarbons, phenols, nitrogenous compounds, and higher chain fatty acids. In addition, Wang et al. reported that the bio-oil produced from algal biomass shows a poor calorific value, but better oxidation stability compared with the bio-oil produced after pyrolysis of lignocellulosic biomass [43]. Moreover, within the algal bio-oil are dissolved solid and nitrogenous substances, which need to be further upgraded by the process of cracking and hydrogenation [44]. Lastly, rapid pyrolysis of C. vulgaris and C. protothecoides biomass was found to produce 53% and 57.9% bio-oil by weight, respectively [43][45]. Throughout pyrolysis of the algal biomass, char is used as an enhancer, due to the fact that it acts as an adsorbent [46].

1.4.3.2 Biochemical processes

For the production of bio-oil, the main biochemical method that is used is fermentation. Following the algal biomass pretreatment, the next step is microbial fermentation, in which the recovered sugar is converted into bioethanol. There are two well-known fermentation processes involved in the production of bioethanol: separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF). [20]

1.4.4 Conversion processes of electrofuels

Synthetic electrofuels or efuels are gaseous and liquid fuels produced from hydrogen and captured carbon dioxide using sustainable electricity as the principal power [47]. They are also known as power-to-gas/liquids/ fuels (PtX) or synthetic fuels. Figure 2 gives a schematic showing the production of efuels. The principal advantages of efuels are that they have a relatively high energy density, they use the existing energy infrastructure and are compatible with existing internal combustion engines, albeit with slight modifications [48]

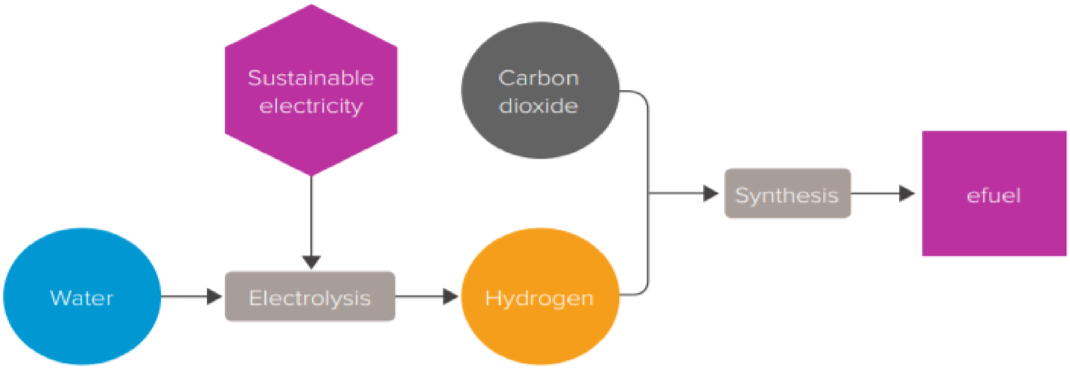


Figure 12: Production of synthetic electrofuel [48]

There are many different efuels, all produced using the following key process steps[48]:

i. **The production of hydrogen**. The most common industrial process to generate hydrogen is steam methane reforming which uses natural gas and produces carbon dioxide as a by-product. There are several methods of producing low-carbon hydrogen and they are discussed in the Royal Society policy briefing document Producing low-carbon hydrogen at scale [49]. Low-carbon hydrogen can be produced by the electrolysis of water using renewable electricity. The source of the sustainable electricity will also affect the cost, as intermittent sources (eg wind turbines) will increase the cost of electrolysers due to the more challenging intermittent duty cycle. [48]

ii. **The capture of carbon dioxide.** High concentration carbon dioxide sources, such as from industrial processes (eg steel works) or power generation, provide a cheaper source of carbon, however it can also be obtained from the air through direct air capture (DAC). Technologies currently being tested include supported amine absorption and the lime-soda process. [48]

iii. **Synthesis – reacting carbon dioxide with hydrogen to form fuels and chemicals.** Common processes for fuel synthesis include Fischer Tropsch and methanol synthesis. Very large scale plants using these processes are in operation and produce, for example, methane and methanol from carbon monoxide and hydrogen. With research, these processes can be modified to use carbon dioxide as the carbon source, requiring modifications to maintain conversion efficiencies and yields. There are already a number of demonstration processes either on-line or in preparation.[48]

Electrolysis. Producing low-carbon hydrogen through the electrolysis of water will become more commercially viable as the price of renewable electricity falls and the electrolysers become more efficient. Research is underway to improve the costs of electrolysis and is already starting to yield benefits. [48]

Solar to fuels. Solar or photocatalytic conversion of carbon dioxide has been actively studied for a number of years. It involves the activation of catalysts using light to convert carbon dioxide directly into fuels such as methanol. Catalysts based on titanium dioxide are most commonly used because of their high efficacy. Despite progress, there have been a number of challenges limiting its widespread uptake and in particular, more work needs to be done on conversion rates, overall yields and selectivity.[48]

1.5 Post-processing

1.5.1 Post-processing of first generation liquid biofuels

After fermentation, the liquid portion of the slurry has 8%–12% ethanol by weight. Because ethanol boils at a lower temperature than water, the ethanol can be separated by a process called "distillation." Conventional distillation systems can produce ethanol at 92%–95% purity [13]. The azeotropic composition of an ethanol/water mixture obtained from distillation at atmospheric pressure contains about 95% of ethanol, which is the maximum achievable purity of ethanol in an atmospheric rectification column. The residual water is then further removed using a molecular sieve process called "rectification" that selectively the water from an ethanol/water vapor mixture, resulting in nearly pure ethanol (>99%) [13]. As mentioned, pure ethanol cannot be obtained from distillation since it forms an azeotrope with water at 95%. Fuel ethanol or absolute alcohol is produced by dehydration of rectified spirit (ethanol). Commercially available technologies for the dehydration of rectified spirit are azeotropic distillation and molecular sieve technology:

Azeotropic distillation*:* To dehydrate ethanol from azeotropic concentration, a third substance called an entrainer (trichloroethylene, benzene, toluene, cyclohexane, etc.) is added to the mixture of ethanol and water. An entrainer breaks the azeotropic point of ethanol and water, i.e., it alters the relative volatility of water making it more volatile. The ternary azeotropic mixture formed at the top of the dehydration column, allows the removal of water and thus dehydrates the alcohol. The azeotropic mixture is heterogeneous and the "heavy" phase which is high in water content is extracted by decantation. The regeneration column allows water extraction from the "heavy" phase and entrainer recycling.

Molecular sieve technology*:* Molecular sieve technology works on the principle of pressure swing adsorption. Here water is removed by adsorption on the surface of "molecular sieves" under pressure and then cyclically removed under low pressure at different conditions. This process carries out dehydration of mixed ethanol and water by adsorption of water into zeolite balls, which are molecular sieves. The dehydration unit operates with two adsorbers according to alternate steps of adsorption and desorption. Adsorption occurs in the vapor phase and under pressure. Desorption regenerates water-saturated molecular sieves. This step is performed under vacuum. Part of the dehydrated alcohol is used for molecular sieve desorption. Alcoholic effluent from desorption is regenerated within the distillation column.

For example, in the case of ethanol production from maize, described in the previous chapters, the residual water and solid maize that remain after the distillation process are called "stillage." The stillage is then centrifuged to separate the liquid (thin stillage) from the solid fragments of the kernel (wet cake or distillers grains). Some of the thin stillage (backset) is recycled to the beginning of the dry-grind process to conserve the water used by the facility. The remaining thin stillage passes through evaporators to remove a significant portion of the water to produce thickened syrup. This process is often called "evaporation." Usually, the syrup is blended with the distillers grains and dried through the process of "dying" to produce DDGS. When feedlots are close to the plant, the by-product may be sold without drying as distillers grains or wet distillers grains.[13]

The ethanol from the biorefinery is subsequently transported to blending facilities and blended with gasoline. After this stage, the biofuel is ready to be distributed as a commercial transportation fuel. Most existing vehicles today can run on biofuel. A notable biofuel blend example is E10 which is a blend of 10% of ethanol and 90% gasoline. The use of bioethanol helps reduce toxic air pollutant emissions and increase octane components; for example, ethanol used in E10 contains 35% oxygen allowing a more complete burn in the engine leading to better combustion and fewer emissions [50]. Higher ethanol content blends such as E15, E20 have also been introduced in some states in the U.S. (e.g., E15 is available in many midwestern states) and other countries (e.g., E20 has been used in Brazil since 1970s). E85, a blend of 85% of ethanol and 15% gasoline, is another commonly used biofuel that can be used by flexible-fuel vehicles [13]

1.5.2 Post-processing of second generation liquid biofuels

1.5.2.1 Thermochemical upgrading processes

The most common upgrading technologies utilize heat and pressure to initiate chemical reactions and address bio-oil deficiencies (e.g., energy density and corrosiveness), as well as separate bio-oil into distinctive fractions that can be altered via catalytic treatments and hydrotreating. It has been observed that petroleum refinery technologies that utilize high temperature and pressure have shown potential for upgrading bio-oil and other biomass-based intermediate products using various upgrading practices (e.g., hydroprocessing and fluid catalytic cracking). This is an important part of the value chain because bio-oil is incompatible with existing infrastructure and requires stabilization due to its high water and oxygen content [51]

Catalytic cracking (CC) is a process that produces biofuel via the breakdown of bio-oil into low carbon aromatics and light olefins; alkylation of aromatics with olefins produced C8–C15 hydrocarbons similar to diesel. Upgraded bio-oils using CC have met some fuel requirements based on the combustion heat, viscosity, and freeze point, which represents a promising substitute for the use in conventional petroleum refineries. Zeolite remains as one of the most highly effective catalysts for CC treatment in order to reduce bio-oil oxygen levels as reported in recent studies. [51]

Hydrocracking, which is a variant of CC, uses supplemental H2 in addition to high temperature (400 °C) along with a catalyst to break longer molecular chains (carbon-carbon bonds) and achieve conversion yields of up to 20% for gasoline fractions. Bio-oil compounds react with hydrogen through a catalyst at high temperatures to reduce oxygen and water content. In this process, bio-oil vapor reacts with H2 molecules to create alkanes, in other words a molecular chain that comprises high-grade hydrocarbon fuels, such as cyclohexane. [51]

Hydrotreatment refers to conventional processes, used in today's petroleum refineries, operating at high-temperature (310–375 °C) in conjunction with supplemental H2 and catalyst to remove oxygen and sulfur in the form of H2O and hydrogen sulfide (H2S). Some hydrotreating processes are hydro-deoxygenation, hydrogenation, and hydro-desulfurization. The main goal of hydrotreating is breaking the carbon-nitrogen, carbon-oxygen, and carbon-sulfur bonds in reaction with H2 [52] to produce benzene and cyclohexane and increasing the H:C ratio. In a similar way that steam reforming allows for hydrogen production from hydrogen-rich gas (e.g., natural gas, methane, and syngas); hydrogen could be produced during thermochemical processing of biomass feedstocks. [51]

1.5.2.2 Other upgrading processes

Physicochemical treatments lack the effects of externally applied heat, chemicals, or catalysts. Rather, physical treatments benefit from lower hazards, fewer consumable inputs, and generally enhanced sustainability. As emerging technologies, they have not proven as effective as thermochemical. [51]

Electrochemical stabilization and upgrading of bio-oil does not require external hydrogen like some thermochemical methods. Moreover, it can be performed at a wider range of temperatures and pressures. EC upgrading uses electricity to generate hydrogen protons (H^+) on the anode side of an electrochemical cell. After that, H^+ is transferred to the cathode side through a cation exchange membrane, where the hydrogenation of the organic bio-oil molecules proceeds [51]

In ultrasonic cavitation an ultrasound generator uses a transducer, amplifier, and probe to convert approximately 60 Hz into high-frequency mechanical energy (~20 kHz)[53].Ultrasound equipment is easy to use and operates under mild conditions, such as low pressure and temperature. Furthermore, a range of frequencies may be utilized for different purposes, e.g., high frequency causes cavitation and blending while the low frequency can encourage compound separation. [51]

Another option for addressing bio-oil deficiencies is blending untreated bio-oil with other hydrocarbons (such as diesel and gasoline) or alcohols (e.g., ethanol and methanol) in small fractions. It should be noted that traditional practices (e.g., mechanically blended biofuels) can result in diminished performance, which creates issues such as fuel separation and oxidation. Other problems can occur, such as the fact that the acidity and corrosiveness of bio-oil results in damage to fuel delivery components of a diesel engine during extended testing [54]. Nevertheless, microscopic fuel blends (for example: emulsion fuels) can increase blended fuel stability if surfactants (for example: chemical modifiers) are used during blending to mitigate long-term stability issues and enable usage in existing equipment. [51]

1.5.3 Post-processing of third generation liquid biofuels

The main methods that are utilized for upgrading the bio-oil derived from algal are the same as the methods used for lignocellulosic biomass. These include various catalytic cracking, hydrocracking, hydtrotreatment methods and physiochemical methods as well. Details on these methods can be found on the section of second generation biofuels.[51]

Other upgrading methods include solvent addition, emulsification. For the homogenization and the reduction of viscosity of biomass oils, polar solvents have been used for many years such as ethyl acetate, acetone, methanol, and ethanol. It has been reported that adding solvent can increase the heating value since the solvent has a higher heating value than that of the most bio-oils. Furthermore, solvent addition reduces bio-oil viscosity due to physical dilution and chemical reaction between solvent and bio-oil components that prevents further chain growth and ageing reactions.[52]

Another method for bio-oil upgrading is emulsification with other fuels. Although, it must be noted that pyrolysis-derived bio-oil is not miscible with petroleum-derived fuels, but it can be emulsified with biodiesel and diesel oil by using surfactants. This method is considered a relatively simple upgrading technique, but it is also costly due to surfactant addition and high energy cost for high production of emulsions [52]. Bio-oil emulsions have desired ignition properties; however, higher corrosion levels were observed in engine applications compared to bio-oil or diesel alone. Emulsification does not require chemical reaction, and it seems to be a short-term approach for bio-oil upgrading. This method has been proven to improve some characteristics of bio-oil such as ignition characteristics, but improving other fuel properties such as heating value, corrosiveness, and cetane number were not satisfied [55]. Recently, supercritical fluids have been used in hydrothermal liquefaction of biomass for bio-oil production in order to increase bio-oil yield or quality. However, supercritical fluids can also be utilized for bio-oil upgrading. Many solvents in supercritical conditions for bio-oil upgrading including ethanol, methanol, and water. When alcohol and acid catalyst are used, this method bears close resemblance to esterification. With this treatment there is an increase in higher heating value and decrease in acid number, oxygen and nitrogen contents, and viscosity. [52]

1.5.4 Post-processing of electrofuels

The product from Fischer–Tropsch synthesis is a synthetic crude oil, or syncrude for short. This syncrude, like crude oil, has to be further refined to produce transportation fuels. Yet, despite significant activity in the field of Fischer–Tropsch synthesis, little attention has been paid to the refining of Fischer–Tropsch syncrude. It is possible to adapt technologies that were developed for crude oil refining, for the refining of Fischer–Tropsch syncrude. The most important conversion technologies for Fischer–Tropsch refining are olefin dimerisation/oligomerisation, aromatic alkylation, pentene skeletal isomerisation with etherification, hydrotreating (oxygenates and olefins), hydroisomerisation, hydrocracking, nonacidic Pt/L-zeolite reforming and alcohol dehydration [56].

1.6 Summary

This chapter has provided details on the processes involved with the upstream, core conversion and downstream part of existing and promising biofuel value chains. According to the context of CERESiS, the following four major value chains are selected to provide the basis for the determination of evaluation benchmarks.

1.6.1 Value chain 1: Sugar to alcohols

In general, sugars obtained from sugar crops, starch crops and lignocellulose are fermented into alcohols (Fig. 4). 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). Bioethanol is the expected product, while biobutanol can be produced if engineered yeast with special bacterias is used. Lignin can be obtained as co-product, useable as energy carrier, animal feedstock, food ingredient, etc.

1.6.2 Value chain 2: Oil crops to biodiesel

Biodiesel is produced from oil crops through transesterification (Fig. 5). The most prominent oil crops are rapeseed, sunflower (both mainly in Europe), soybean (US, Argentina, Brasil) and palm seeds (southeast Asia). A by-product of transesterification is glycerol, which is used extensively in both the food and cosmetics industries.

1.6.3 Value chain 3: Biomass to Liquidσ (BtL) via gasification

Any lignocellulosic material such as wood from forestry, short rotation coppice (SRC) or energy crops is suitable for feedstock. Biomass from dedicated felling of forestry wood is also lignocellulosic but is not considered sustainable. Syngas is produced with gasification, while the Fischer Tropsch (FT) process, combined with upgrading steps, can provide usable liquid fuels [57].

1.6.4 Value chain 4: Biomass to Liquid (BtL) via pyrolysis

In parallel to Chain 3, any lignocellulosic material can be used. The desired product is called bio-oil or bio-crude, obtained from the condensation of the gaseous components originating from biomass decomposition during pyrolysis. Bio-oil can be currently used to replace natural gas or heating oil. It may be upgraded and co-fed in existing refineries into advanced biofuels that have the same combustion properties as conventional fossil transport fuels [57].

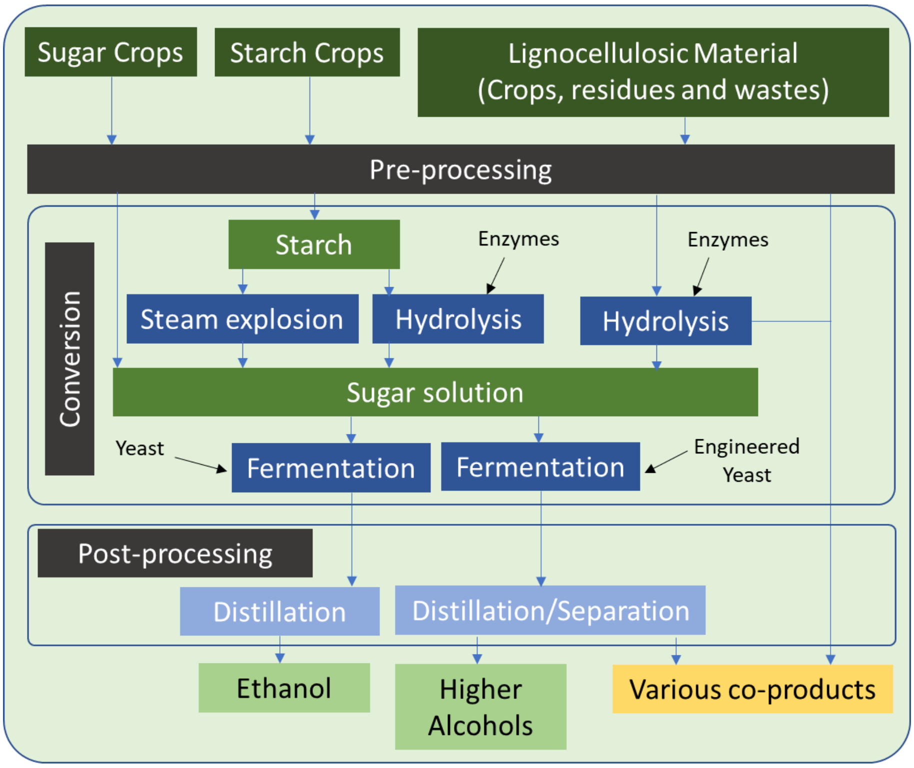


Figure 13: Existing biofuel value chain 1 (Sugar to alcohols) (Adapted from [57]).

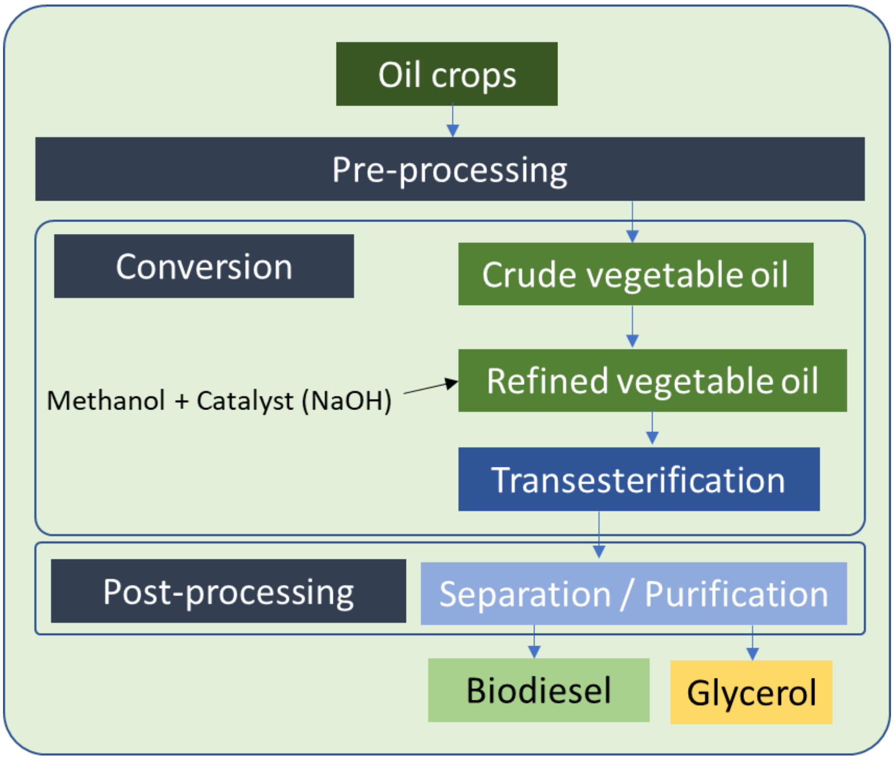


Figure 14: Existing biofuel value chain 2 (Oil crops to biodiesel [57]).

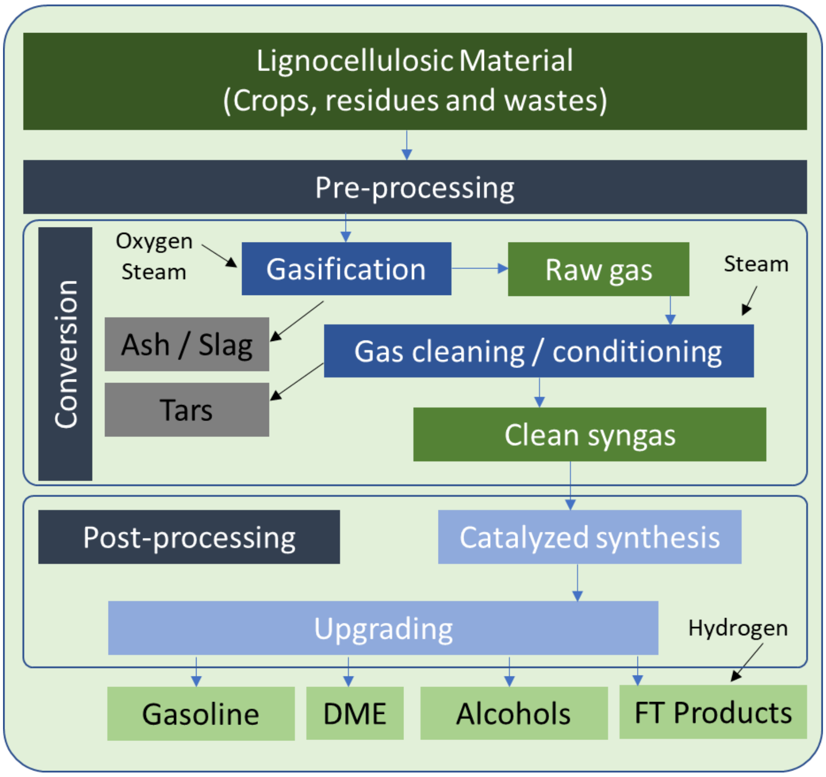


Figure 15: Existing biofuel value chain 3 (BtL via gasification) (Adapted from [57]).

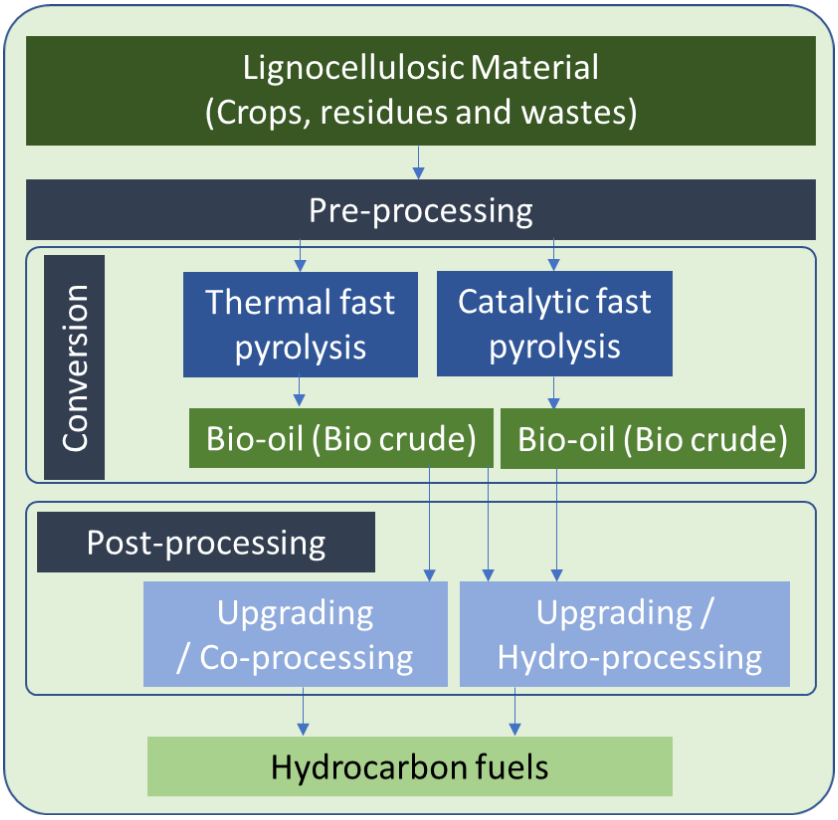
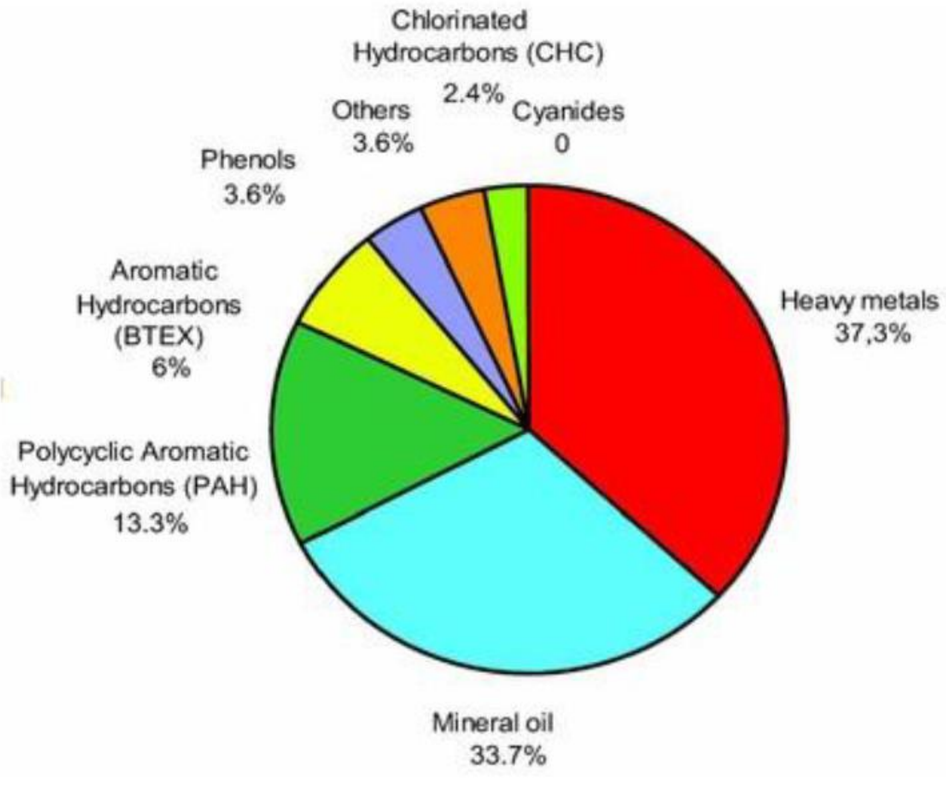


Figure 16: Existing biofuel value chain 4 (BtL via pyrolysis) (Adapted from [57]).

2 CONTAMINATED BIOMASS FEEDSTOCKS FROM PHYTOREMEDIATION/PHYTOEXTRACTION ACTIVITIES

The contaminated biomass feedstocks to be examined in CERESiS are expected from various types of polluted soils. According to the European Environmental Agency's Signals data for 2019, the range of polluting activities vary considerably across Europe, with the most important sources being industrial and commercial activities and the treatment and disposal of waste. Reports from countries across Europe indicate that heavy metals and mineral oil are the most frequent soil contaminants at investigated sites, while mineral oil and chlorinated hydrocarbons are the most frequent contaminants found in groundwater. These estimates are based on the frequency a contaminant is reported at the investigated site.



Source: *https://www.eea.europa.eu/themes/soil/soil-threats*

Figure 17: Types of contaminants in soil across Europe [adapted from deliverable D1.4]

Soil contamination with HM is being researched and remediation techniques if possible are proposed in a wide range of papers. Many of such publications bear examples of concentrated soil point-source pollution, like industrial and mining sites, wood impregnation stations, landfilling sites, accidental spills, etc. Although, HM concentrations exceed MPC manifold, due to the limited area it is possible to apply narrow spectrum chemical and physico-chemical remediation methods. Marginal land includes not only areas with a lack of precipitation or nutrients, but also land with the diffuse HM contamination from agricultural or industrial activities. The latter territories are not suitable for food and fodder production. However, the application of traditional remedy solutions is not reasonable due to the vastness of the contaminated territory and often relatively low mobility of contaminants. Phytoremediation as an environmental clean-up biotechnology, incorporating selection of HM accumulating plant species, can be seen as an alternative to the above mentioned process-based methods (Table 3). The idea that plants can uptake HM from the soil together with other necessary elements is very old and cannot be assigned to any particular author. Phytoremediation as a civil-engineering solution emerged in recent decades. Terms of phytoextraction and phytoremediation are often taken as synonyms. However, phytoremediation is a concept while phytoextraction is one of five clean-up biotechnologies that incorporate plants (other four technologies are rhizofiltration, phytostabilization, phytovolatilization, phytodegradation). Phytoextraction is identifiable above all other phytoremediation techniques and for that reason it gains increased attention from scientists. [58].

Unfortunately, there is very limited information available for mineral oil and aromatic hydrocarbon contaminated feedstocks. The relevant literature[59][60]focuses on the problems associated with the bioremediation process of PAH (such as reduced biomass yield). The main reason is because, due to their hydrophobic nature, hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in environmental matrices are rapidly adsorbed on particles and organic matter of soils [61]. Consequently, soils are the ultimate repository for most hydrophobic organic contaminants that cannot be extracted by a plant since they cannot be dissolved in the aqueous phase moving from the soil to the vascular system of the plant. Moreover, several xenobiotic organic substances are degraded by soil microorganisms through both aerobic and anaerobic processes. However, biomass grown on soils with organics contamination presents this kind of contamination mainly due to soils particles adhering the external surface of the plant. Literature lacks in studies dealing with their fate during the biomass processing. The major relevant findings are presented in chapter 4.

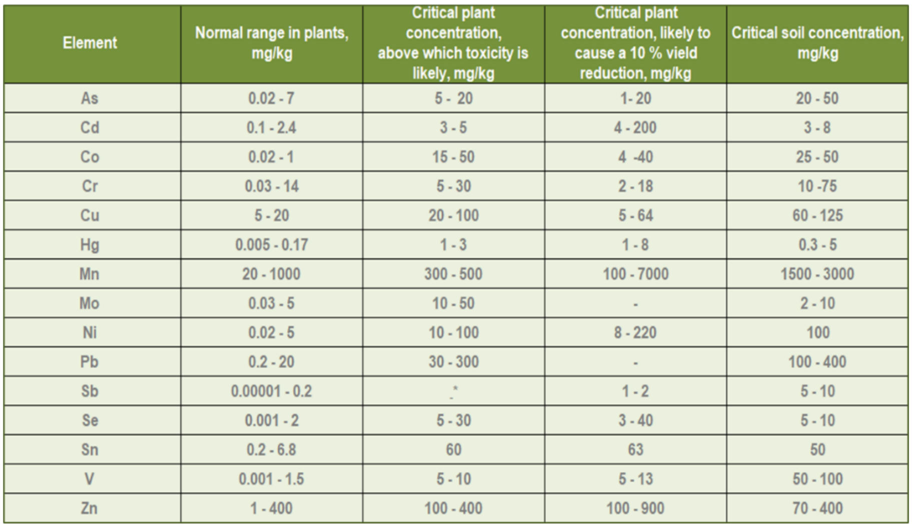
Therefore, the present analysis deals mostly with heavy metal contaminated feedstocks. Several studies have described the performance of heavy metals uptake by plants. It is reported that phytoremediation technology is an alternative to treat heavy-metal contaminated side which will be more admitted in order to remediate the environment.

2.1 Heavy metal contaminated feedstocks

Heavy metals are potentially toxic elements that cannot be degraded like organic pollutants. This conspicuous characteristic poses a great challenge for environmental engineers. At a certain moment, the process has a dead-end mass transfer where the metal toxicity must be dealt with. In the past decade, several technologies have been tested to reduce the contaminated biomass by thermal processes and find a potential use of the process streams, including the recovery of the metal [65]. The latter has been traditionally regarded as a separate technology known as phytomining. However, following the concept of closed-cycle processes, phytomining and energy recovery increasingly accompany thermal treatments [65].

At present, there are two main phytoextraction strategies available: the first is the use of hyperaccumulators. These plants are wild species that can accumulate large amounts of specific metals in their shoots, but they are often slowly growing (low biomass plants). Hyperaccumulation implies concentrations in dry matter above 0.01% for Cd, 0.1% for Pb and 1% for Zn. The second strategy is the use of fast-growing plants (high biomass plants) that are usually not metal-specific and have low to average heavy metal concentrations. [65][66]. The highest accumulation of As in plant tissue can reach more than 0.7 mg As/g dry weight of plant. Several plants could accumulate Pb in their tissue of more than 50 mg/g dry weight of plant. Among those, Brassica species could accumulate more than 100 mg Pb/g dry weight. Furthermore, Brassica species could accumulate more than 1 mg Hg/g dry weight of plant, while the other plants only accumulate less than 0.2 mg Hg/g dry weight[64] .

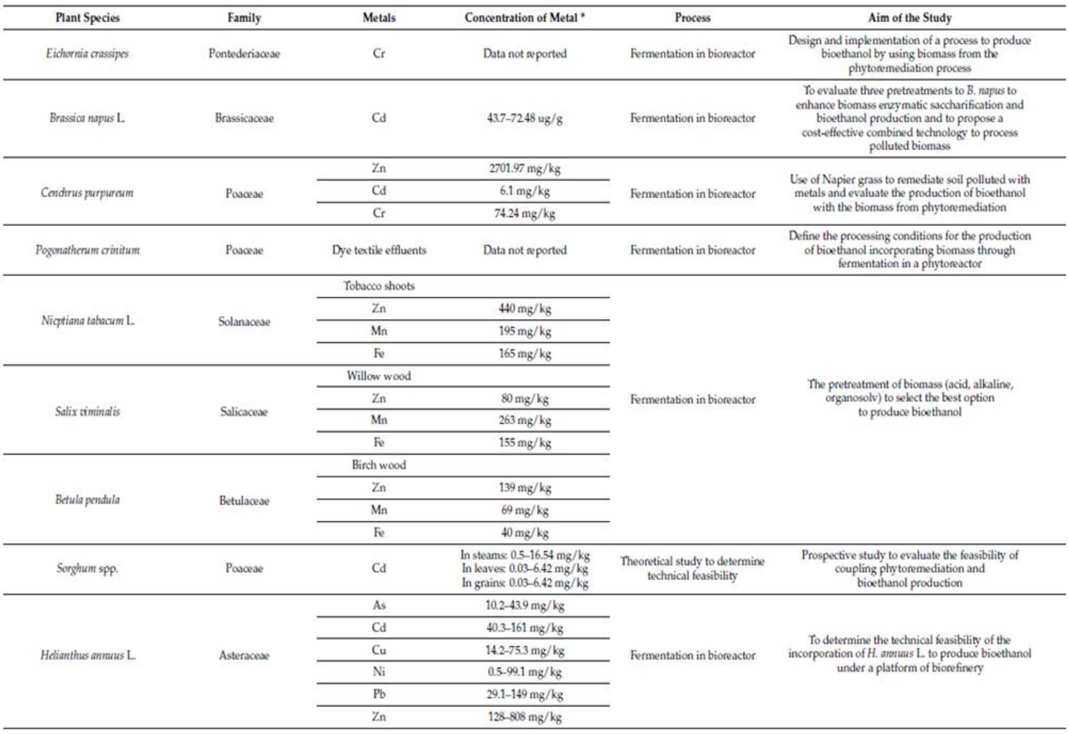
Normal ranges of HM concentrations in plants are given in Table 2 as well as critical concentrations to plants. These concentrations are likely to be fatal or cause a significant yield reduction. Table 2 also presents critical HM concentrations in the soil. Plant-metal interactions may be beneficial, have no effect or be harmful depending on metal species and concentrations.



Element	Normal range in plants, mg/kg	Critical plant concentration, above which toxicity is likely, mg/kg	Critical plant concentration, likely to cause a 10 % yield reduction, mg/kg	Critical soil concentration, mg/kg
As	0.02 - 7	5 - 20	1- 20	20 - 50
Cd	0.1 - 2.4	3 - 5	4 - 200	3 - 8
Co	0.02 - 1	15 - 50	4 -40	25 - 50
Cr	0.03 - 14	5 - 30	2 - 18	10 -75
Cu	5 - 20	20 - 100	5 - 64	60 - 125
Hg	0.005 - 0.17	1 - 3	1 - 8	0.3 - 5
Mn	20 - 1000	300 - 500	100 - 7000	1500 - 3000
Mo	0.03 - 5	10 - 50	-	2 - 10
Ni	0.02 - 5	10 - 100	8 - 220	100
Pb	0.2 - 20	30 - 300	-	100 - 400
Sb	0.00001 - 0.2	-*	1 - 2	5 - 10
Se	0.001 - 2	5 - 30	3 - 40	5 - 10
Sn	0.2 - 6.8	60	63	50
V	0.001 - 1.5	5 - 10	5 - 13	50 - 100
Zn	1 - 400	100 - 400	100 - 900	70 - 400

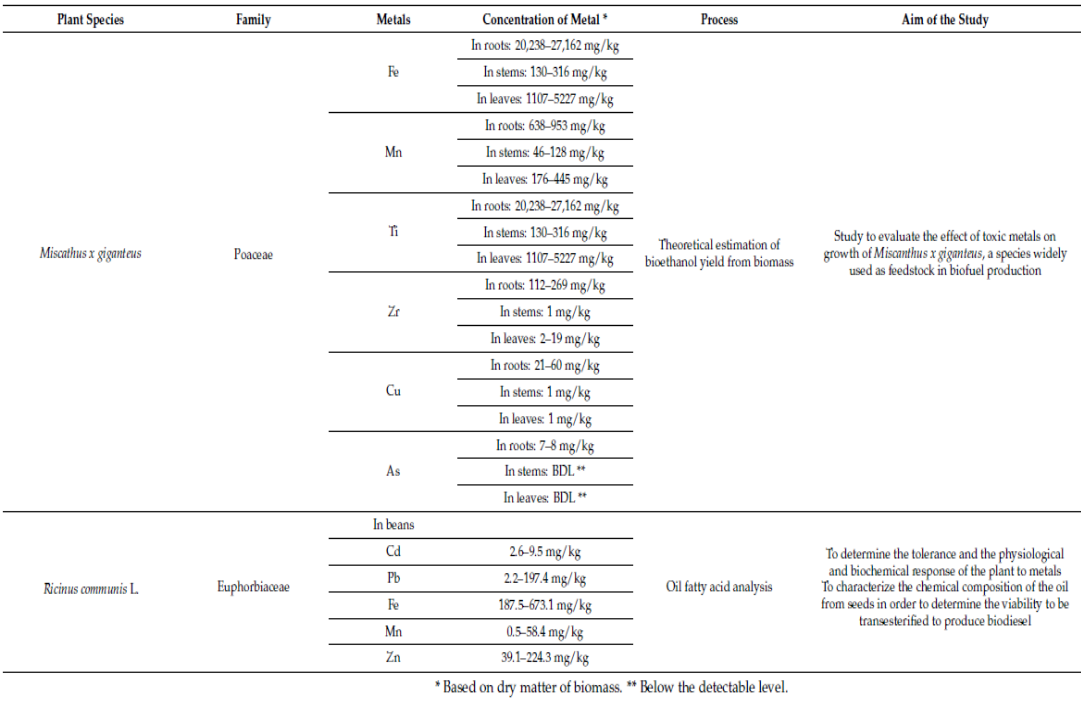
Table 2: Normal heavy metal ranges in plants and critical concentrations both in plants and soils [58]

A recent review on coupling heavy metal contaminated biomass and bioenergy production [65] provides a detailed table of relevant studies. The following table presents the cases reported to use phytoremediation biomass to produce liquid biofuels, alongside with the metals encountered and the respective concentrations in the feedstocks considered.



Plant Species	Family	Metals	Concentration of Metal *	Process	Aim of the Study
Eichornia crassipes	Pontederiaceae	Cr	Data not reported	Fermentation in bioreactor	Design and implementation of a process to produce bioethanol by using biomass from the phytoremediation process
Brassica napus L.	Brassicaceae	Cd	43.7–72.48 ug/g	Fermentation in bioreactor	To evaluate three pretreatments to *B. napus* to enhance biomass enzymatic saccharification and bioethanol production and to propose a cost-effective combined technology to process polluted biomass
Cenchrus purpureum	Poaceae	Zn	2701.97 mg/kg	Fermentation in bioreactor	Use of Napier grass to remediate soil polluted with metals and evaluate the production of bioethanol with the biomass from phytoremediation
		Cd	6.1 mg/kg		
		Cr	74.24 mg/kg		
Pogonatherum crinitum	Poaceae	Dye textile effluents	Data not reported	Fermentation in bioreactor	Define the processing conditions for the production of bioethanol incorporating biomass through fermentation in a phytoreactor
Nicptiana tabacum L.	Solanaceae	Tobacco shoots		Fermentation in bioreactor	The pretreatment of biomass (acid, alkaline, organosolv) to select the best option to produce bioethanol
		Zn	440 mg/kg		
		Mn	195 mg/kg		
		Fe	165 mg/kg		
Salix viminalis	Salicaceae	Willow wood			
		Zn	80 mg/kg		
		Mn	263 mg/kg		
		Fe	155 mg/kg		
Betula pendula	Betulaceae	Birch wood			
		Zn	139 mg/kg		
		Mn	69 mg/kg		
		Fe	40 mg/kg		
Sorghum spp.	Poaceae	Cd	In steams: 0.5–16.54 mg/kg In leaves: 0.03–6.42 mg/kg In grains: 0.03–6.42 mg/kg	Theoretical study to determine technical feasibility	Prospective study to evaluate the feasibility of coupling phytoremediation and bioethanol production
Helianthus annuus L.	Asteraceae	As	10.2–43.9 mg/kg	Fermentation in bioreactor	To determine the technical feasibility of the incorporation of *H. annuus* L. to produce bioethanol under a platform of biorefinery
		Cd	40.3–161 mg/kg		
		Cu	14.2–75.3 mg/kg		
		Ni	0.5–99.1 mg/kg		
		Pb	29.1–149 mg/kg		
		Zn	128–808 mg/kg		

Table 3: Use of phytoremediation biomass to produce liquid biofuels - 1 [65]



Plant Species	Family	Metals	Concentration of Metal *	Process	Aim of the Study
Miscathus x giganteus	Poaceae	Fe	In roots: 20,238–27,162 mg/kg	Theoretical estimation of bioethanol yield from biomass	Study to evaluate the effect of toxic metals on growth of *Miscanthus x giganteus*, a species widely used as feedstock in biofuel production
			In stems: 130–316 mg/kg		
			In leaves: 1107–5227 mg/kg		
		Mn	In roots: 638–953 mg/kg		
			In stems: 46–128 mg/kg		
			In leaves: 176–445 mg/kg		
		Ti	In roots: 20,238–27,162 mg/kg		
			In stems: 130–316 mg/kg		
			In leaves: 1107–5227 mg/kg		
		Zr	In roots: 112–269 mg/kg		
			In stems: 1 mg/kg		
			In leaves: 2–19 mg/kg		
		Cu	In roots: 21–60 mg/kg		
			In stems: 1 mg/kg		
			In leaves: 1 mg/kg		
		As	In roots: 7–8 mg/kg		
			In stems: BDL **		
			In leaves: BDL **		
Ricinus communis L.	Euphorbiaceae	In beans		Oil fatty acid analysis	To determine the tolerance and the physiological and biochemical response of the plant to metals To characterize the chemical composition of the oil from seeds in order to determine the viability to be transesterified to produce biodiesel
		Cd	2.6–9.5 mg/kg		
		Pb	2.2–197.4 mg/kg		
		Fe	187.5–673.1 mg/kg		
		Mn	0.5–58.4 mg/kg		
		Zn	39.1–224.3 mg/kg		

* Based on dry matter of biomass. ** Below the detectable level.

Table 4: Use of phytoremediation biomass to produce liquid biofuels - 2 [65]

3 EFFECTS OF HEAVY METALS ALONG THE EXISTING CHAINS

In this chapter, the presence of contamination in the value chains examined will be assessed to study the effect of contaminants, focusing on heavy metals. Their effect will be studied in each of the typical stages of the existing value chains, including pre-processing, conversion, and post-processing steps. Specifically, there will be focus on the gasification and pyrolysis conversion processes, reviewing the fate of contaminants along each process. In the gasification process parameters such as temperature, pressure, heavy metal type and concentration will be examined. At the same time, in pyrolysis the considered parameters will be among others, but not limited to, residence time and reactor temperature. Few relevant data were made available for the case of biodiesel production (Value chain 3), therefore this chain is partially addressed.

3.1 Pre-processing

3.1.1 Value chain 1: Sugar to alcohols

Asad et al. [67] investigated the pretreatment of HM-enriched nonwoody lignocellulosic (tobacco) and woody (birch and willow) biomasses. Three processes (dilute acid, alkali-catalyzed and ethanol organosolv pretreatments) were evaluated, all of them being among the most widely used and studied technologies for cellulosic bioethanol production. The fractionation of phytoremediation biomasses for the production of bioethanol is also described. In aqueous acidic conditions, a wood pretreatment performed at 170 °C in presence of 2% w/w of sulfuric acid allows an efficient extraction of the metals (for Zn, Fe, and Mn) recovered in the water effluent producing a clean pulp. In alkaline conditions the metal extractability was low, especially at a high temperature. As a result, during a soda pretreatment of a metal-rich biomass performed at 170 °C or above the metals were mostly recovered in the cellulosic pulp, producing clean liquid stream and lignin for further utilizations. For organosolv, metal concentrations were in a decreasing order were: pulp ≫ water effluent > lignin. Metal extraction in the liquid phase depended on the metal and the plant species but was generally low. Metal extractability increased with the water content but decreased with the temperature. Wu et al. [68] implement three optimal chemical pretreatments. As a result, two optimal chemical pretreatments (12% H2SO4, 4.0% NaOH + 2.0% H2SO4) could release 99% (of total in raw stalk) Cd from the mature stalks.

3.1.2 Value chain 3: Biomass to Liquids (BtL) via gasification

There are many pre-treatment methods that can be implemented on the biomass feedstock. Dry pre-treatment methods can be utilized, however there have been no reports on how heavy metals affect the yield and quality of the syngas, and their distribution as well [44]. On the other hand, according to a study by **Yu et. al** [69] the wet pre-treatment method of leaching with distilled deionized water can reduce the ash content of the product significantly. Although, with the extraction of contaminants (organic and inorganic) the composition of the residual solids can be changed leading to complex properties.

3.1.3 Value chain 4: Biomass to Liquid (BtL) via pyrolysis

The effects of dry pretreatment (i.e. crushing, preheating, and torrefaction) and wet pretreatment (using various acids, solvents, etc.) on heavy metal contaminated biomass (HMCB) have been investigated to explore their effects on bio-oil yield and HMs content. Mostly feedstocks crushed to the particle size (PS) of < 2.00 mm have been introduced to different reactors [70][71]. Wiinikka et al. [72] demonstrated that feedstock with PS < 0.25 mm had a higher conversion rate, whilst the product converted from feedstock with PS of 0.50–1.00 mm had a lower conversion rate with a high amount of volatiles that was almost comparable to the raw material. Switchgrass species with modest levels of Pb content can serve as both promising phytoextraction agent and biofuel feedstock [44][73].

The demineralization of HMCBs is anticipated to cause the increase of bio-oil yield and quality, however, it is been reported that the presence of HMs, like Zn, Cu, etc., in biomasses could also perform as an efficient catalyst to promote the gas yield and bio-char formation while reducing the liquid production [74][75][76].

According to Wigley et al. an integrated acid leaching and torrefaction pretreatment led to a demineralized and stabilized biomass, which consequently limited the catalytic upgrade of pyrolysis vapors using water, organic acids, and inorganics present in the biomass [77]. After direct pyrolysis or application of phosphate-assisted approach, HMs may reduce their harm to the environment by probable transferring from the toxic state of ions into some amorphous states in the bio-char [78] [79](in the form of phosphate minerals [80][81]) or being stabilized with external materials, including Al2O3, FeCl3, CaCO3, and NaOH [82]. Therefore, it can be inferred that pyrolysis assisted by phosphate and/or other materials can be mainly recommended for the safe disposal of HMCBs rather than bio-oil recovery.[44]

3.2 Conversion

The foundation of thermal treatments is the transformation of the organic fraction of the accumulator biomass under different thermochemical conversion processes into solids (e.g., ashes, biochar), liquids (e.g., oil), or gases (e.g., syngas, biogas) [83][72]. Simultaneously, the metal mass fraction must ideally be concentrated in a controlled and predictable way in one of these products. The metal partition in the different streams will determine the destiny of the product, and low concentrations may render it useful for further processing (compost material, catalyst material, or energy recovery), while high concentrations will limit downstream processing or must include another mass transfer operation to separate the metal fraction [84][85][86]

Then, the main constraint of any thermal process using this raw material is not only the partition of the metals between by-products but also its possible remobilization to the environment. Cui et al. [87] performed an extensive review of the available thermal technologies and concluded that the fate of metals responds to complex and multifactorial processes in all the available thermo-conversion formats.

Although there are no available predictive constants for any process, it has been observed through experimental testing that some metals like Pb or Zn have wide temperature ranges (220–900 ◦C), where they can be largely (>90%) captured in the solid phase [52][53]. On the other hand, other metals and metalloids like Cd [52] or As [54] are susceptible to leaving the system [66]. Few relevant data were made available for the case of biodiesel production, therefore this chain is partially addressed.

Taking into consideration the above factors, there is a risk in the process of using biomass to extract mixtures of metals. To bypass this constraint, specialized products can also be obtained as secondary products of plant biomass processing. For example, by-products containing metals have been conceptualized as catalytic materials that can be upgraded—through upstream processes—to obtain acetate/furan. The solid by-products can be refunctionalized as metal adsorbents after metal leaching, and the gas streams can be employed as syngas rich in hydrogen and methane. An alternative use of metal-contaminated streams in [66], where it is demonstrated that vegetal biochar can be transformed with plating wastewater into reusable Cd-biochar acting as nano Cd-S with photocatalytic activities and tested the concept in dye removal from water.

3.2.1 Value chain 1: Sugar to alcohols

In [59], enzymatic hydrolyses of HM-enriched pulps and metal-free pulps were investigated to examine the metal influence on the enzymatic hydrolysis into monomeric sugars. Metals (i.e., Zn, Fe, and Mn) have little or no effect on polysaccharide hydrolysability. Sayago [88]concludes that experimentation with two types of E. crassipes biomass loaded with different concentrations of chromium showed that they could be used to produce bioethanol or other biofuels because their affectation is not significant. Nevertheless, the chromium samples produced 33% less ethanol than the "clean" hydrolyzed biomass of E.

crassipes (8000 mg/L vs 12100 mg/L after 25h). On the contrary, Wu et al. [68] claim that the Cd accumulation in rapeseed stalks could significantly enhance biomass enzymatic saccharification and bioethanol production under twostep (4.0% NaOH + 2.0% H_2SO_4) chemical pretreatment. In particular, the ethanol yield (% dry matter) was increased by 8% and 12% in two respective Cd-contaminated samples.

The positive impact of Cd in SSF (simultaneous saccharification and fermentation) is confirmed in [89], while Cr presence is also beneficial for the same process. On the other hand, negative impacts of biomass Zn and Cd contents on the previous process of enzymatic hydrolysis were observed, even higher for lower enzyme dosages. However, the biomass Cr content demonstrated positive impacts on enzymatic hydrolysis at all three enzyme dosages. Smaller negative impacts of biomass Zn content were observed on bioethanol SSF processes.

3.2.2 Value chain 2: Oil crops to biodiesel

However, some crucial questions about the content of heavy metals in biodiesel, obtained from the oil of plants used for the phytoremediation of soils polluted with heavy metals, remain unanswered. In a study on the accumulation and distribution of heavy metals in oil crops [90] the content of the heavy metals Cd, Cu, and Pb in plant organs and in the oil of rape seed (Brassica napus L.), which were grown in a polluted area is reported. The distribution of heavy metals in the organs of crops had a selective character that decreased in the following order: leaves > stems > roots > fruit shell > seeds. Although the concentration effect of heavy metals was the lowest in the seeds (which contain the pure plant oil), the quantities of Pb, Cu and Cd in the rape seed oil were higher than the accepted maximum permissible concentrations for human consumption. If biodiesel exhaust fumes from such rape seed plants – specifically selected for their high heavy-metal uptake capacity – will have hazardous metal emissions is virtually unknown. [90]

3.2.3 Value chain 3: Biomass to Liquids (BtL) via gasification

One common type of contaminant in biomass is heavy metals, which can cause problems to the gasification process. The emissions of heavy metals can contribute to corrosion, fouling, and erosion of the gasification facilities. Another common issue is catalyst deactivation [91][83]. Moreover, during the gasification process many unwanted products are formed such as ash and tar [92][93]. The tar, which sometimes contains HMs, can cause significant problems such as plugging and filter blockage, corrosion, and engine failure. [92]

Studies have heavily focused on the different parameters of the gasification process which contribute to the transfer and distribution of heavy metal compounds into the gas phase.

Many experiments and modelling simulations have been implemented that deduced different results. A study from Jiang et. Al [91] concluded that temperature and heavy metal content of the biomass are critical parameters that influence the fate of heavy metals in the gasification process. Some elements (As, Cd, Zn, Pb) volatized at temperatures above 600 °C, others (Ni, Cu, Mn, Co) transferred to the syngas at temperatures 1000°C-1200°C and Cr, Al and Mg remained in the solid phase even at temperatures higher than 1200°C. As for the pressure it was found that it increases product yield and raises the heavy metal transition temperature by 100°C-200°C [91]. According to the experiments done by Cui et. al, most heavy metals volatized into the gas phase, except for Al and Fe. It must be noted that Pb and Zn were the most abundant in the gas phase. From the analysis of the content of syngas [87]. Syc et. al studied the distribution of heavy metals in the gasification system. The experiment focused on the gasification of energy crops (flax, mixed hardwood). The results showed that the heavy metals Cd, Zn, Pb, Ni and Cu were found in the bed ash, cyclone, ash, and downstream syngas. Also, the heavy metal content in the syngas was found to be in the range of 0.37-4.2 mg/m^3. [94]

In another experiment from Pudasainee et. al, which involved the gasification of slurry (glycol and straw char), it was deduced that heavy metals were distributed in many sections of the gasification systems, such as the cooler, boiler, and the syngas cleaning devices. Furthermore, the total concentrations of the heavy metals were Ni (53,2 $\mu g/Nm^3$) > Cr > Pb > As > V > Cd > Hg (24 $\mu g/Nm^3$) [83]

The volatilization temperatures of heavy metals in the gasification process, according to empirical and theoretical studies ([83],[95],[96])can be categorized as follows:

1. Some HMs may be totally condensed in gasification gas under cleaning and emission conditions (Mn)
2. Some others may get mainly enriched in the gas phase (Hg and Cd)
3. Some elements (Co) could be totally or partially in the gas phase at the temperature of hot gas cleaning systems 500-800 °C
4. Other elements (As, Zn, Cd, Pb, Cr, Ni, Sb) would be present in the gas phase even at <500 °C

From the simulations and experiments that are mentioned above it is apparent that the heavy metals that are contained in the contaminated biomass are volatilized into the gas phase. However, the type and amount of heavy metals that transfer to the gas phase is heavily dependent on temperature and pressure. The most common heavy metals that can be found in the syngas are Zn, Cu, Pb, Cd. Generally, temperature < 1000 ° C and higher pressure up to 30 atm are considered optimum gasification conditions, in order to limit the transfer of many volatile HMs. [91]

It is important to note that, no general benchmark values have been set for the maximum acceptable level of inorganic compounds and HMs contents neither in bio-oils nor other biofuels ([94],[97],[72]). The concentration of < 0.10 % wt% for particles as well as for HMs have been recommended [84]

In addition, the distribution of heavy metals depends on [44]:

1. Chemical speciation of metals and dynamics of fluidization

2. Operating conditions (temperature pressure)
3. Nature of HMCBs
4. Implementation of pre/post treatment processes
5. Type of gasifier system (fluidized bed, fixed bed, entrained bed)
6. Impact of fluidized bed materials
7. Type of gasification agent

The type of gasifier that is used is an important parameter. It has been observed that the countercurrent downdraft fixed bed gasifier is more efficient compared to the fluidized bed gasifier. The emissions from the first were almost one magnitude lower than those of a fluidized bed gasifier ([97],[85]). Additionally, the steam fluidized is better than the air fluidized bed gasification when it comes to the volatilization of HMs ([86],[98]). The steam fluidized bed not only reduces the HM emission, but also has a better catalytic role and produces syngas that has a higher LHV. However, it has been observed that the type of the gasification agent (such as H_2O, O_2, CO_2) is not the most important parameter that influences heavy metal transfer to the syngas [99].

3.2.4 Value chain 4: Biomass to Liquid (BtL) via pyrolysis

Flash pyrolysis is an eligible processing method for metal contaminated biomass and meets the requirements to accomplish the research goals: the rather low pyrolysis temperature – unlike combustion – prevents metals from volatilization and valuable pyrolysis oil is produced[100].

Different biomasses contain mineral matter in various amounts. Generally, the main elemental constituents of biomass minerals are Si, Ca, K, Na and Mg, with smaller amounts of S, P, Fe, Mn and Al and trace amounts of heavy metals (e.g. zinc). These constituents occur as oxides, silicates, carbonates, sulphates, chlorides and phosphates. The mineral or ash content has an influence on pyrolysis yield distribution, the rate of devolatilization and the initial decomposition temperatures of biomass; consequently it has an influence on the properties of the pyrolysis products (adsorptive properties of char, heating value and the elemental composition) [101][74][102]. Pyrolysis process parameters affecting the yield of the different pyrolysis products are: reactor temperature, residence time, heating rate, physicochemical pre-treatment, particle size, geometrical configuration of the reactor and solid heat carrier [102][33][103]

There are mainly three goals in the pyrolytic conversion of contaminated biomass [66]:

1. to produce metal-free bio-oils,
2. to avoid HMs emission via gaseous phase (in the form of free ions or hydroxide and carbonates), and
3. to accumulate HMs in the bio-char.

Individual metal and metalloid elements behave differently to heat treatment, as shown in an experiment that determined biochar could be mixed with contaminated biomass to contain heavy metals during pyrolysis. The experimenters noticed the capacity of Pb to remain immobilized by itself during the pyrolysis process of a contaminated biomass conducted at 673 K.[104]

It has been reported that a number of factors (i.e. plants type, pretreatment [97][105],operating conditions, and post-treatment stages [97][100]) have various impacts on the characteristics and quality of bio-oil and bio-char. At the same time, a study has been conducted by Zhong et al. [106] on slow and fast pyrolysis of a hyperaccumulator (S. plumbizincicola) with high concentrations of HMs, including Zn (9838), Cd (560), Pb (62.50), Cu (77.60), Cr (45.40), Fe (642), and Al (13,976 mg kg^{-1} of HMCB). The higher temperatures and heating rates increased the HMs emission rate into bio-oil with different trends for each element. For example, at 450–650 °C at least 66.30% of Zn remained in the bio-char, while, 87.60% of Cd and 73.60% of Pb transferred into the bio-oil; but no HMs were detected in the gaseous phase. It was concluded that fast pyrolysis of the HMCB studied at 650 °C could produce bio-oil with highest yield and quality (in terms of more alkenes and low levels of oxygenated compounds).

A different experiment operated a lab-scale pyrolysis reactor to process a feedstock composed of sunflower contaminated with Cu, Cd, Pb and Zn and indicated a temperature of 623 K as a favorable heat level to avoid volatilization of elements like Cd and Zn in the condensable and non-condensable fractions, while Cu and Pb could remain immobilized in the solid fraction in a temperature range from 623 K to 873 K . Each element is affected by the temperature and the feedstock in a specific way that will determine whether it will leach in the liquid and gas fractions or not. [103]

Furthermore, a high temperature treatment raises the pH of the liquid fraction and, by doing so, diminishes the solubility of the heavy metals and the concentration of the water extractable Cu and Ni. [107]

Stals et al. [100] investigated the flash pyrolysis of contaminated willow (a mixture of stem and leaves based on naturally weight ratio of plant organs). The results revealed that by increasing temperature from 350 to 550 °C, a lot more quantity of Cd volatilized to the gaseous phase while Zn majorly transferred into the bio-oil. However, a negligible level of Pb in the bio-oil was detected even at highest testing temperature. Based on the yields, properties and content of target metals in pyrolysis oil in this study, 350–450 °C deemed as preferable pyrolysis temperature range at which generally high yields of bio-oil were achieved and lower amounts of HMs were found in the bio-oil: Zn < 7.80 mg kg^{-1} (1%), Cd < 0.80 mg kg^{-1} (13%), and Pb < 0.60 mg kg^{-1} (7%) of initial concentrations, respectively. Even though, at the lowest temperature, HMs majorly concentrated in the bio-char, and the bio-oil did not meet other optimal indexes, i.e. bio-oil yield (41%), gas yield (38%), bio-char yield (21%), water content (49%), and high heating value (HHV 21.90 MJ kg−1) [100].

According to Leijenhorst et al. [97], using fast pyrolysis of agricultural residues in the temperature range of 400–600 °C, over 95 wt% of total inorganic elements present in contaminated biomass were separated from the produced bio-oil, and HMs largely remained in the bio-char.

Generally, the easy transfer of HMs to gaseous phase in thermochemical decomposition of HMCBs is affected by

1. their high volatilization at higher temperatures [100][106],
2. the bonding of HMs with initial biomass structure [75][108][109]and produced organic vapor [99].

Dilks et al. [107] have presented an overall scheme for pyrolysis of HMCBs using a reactor equipped with a cyclone as the posttreatment for phase separation to produce cleaner bio-oil, whilst, no wet-chemical pretreatment was considered to eliminate the HMs directly from the feedstock prior to conducting pyrolytic conversion. According to some studies, the produced bio-char obtained from the pyrolysis of HMCBs is unsuitable for free disposal into the environment and metals extraction/recovery [107][100].

Generally, biomass type, feedstock particle size/distribution, pyrolysis operating conditions, as well as pre- and post-treatments can affect HHV, the yield and quality of bio-oil, and HMs and solids transfer amounts. Koppolu et al. [118] showed that the fluidized bed reactors allow the utilization of higher pyrolysis temperatures up to 600 °C without compromising the sequestration of the HMs in the biochar. On the contrary, Stals et al. [100] have suggested a lower temperature, i.e. ~350 °C, for flash pyrolysis of HMCB in a fluidized bed reactor equipped with a hot-gas filter.

The higher temperatures of pyrolysis process by 700 °C lead to further tar cracking and higher oxygen content resulted from the increased oxygen functionality of bio-oil structure [103][111], and consequently resulting in lower heating values of bio-oil (~16.80–19 MJ kg−1) that is less than desired HHV of conventional fossil fuels (40–45 MJ kg−1) [103][112][113]. However, pyrolysis at lower temperatures produces cleaner bio-oil [114][115], it leads to more bio-char formation [106][114]. As operating temperature can influence the contingency of HMs leaching from a contaminated bio-char, 350–450 °C has been stated as optimum operating temperature to produce a bio-char with maximum metal retention capacity from HMCBs, particularly those containing high contents of Cd and Pb [100][116].

Optimum operating temperature for HMCBs pyrolysis is 350–450 °C in terms of maximum HMs removal and acceptable bio-oil yield, which can be extended by 150–250 °C (i.e. threshold up to 600 °C) mainly depending on the type and concentration of HMs inside plants' organs, reactor configuration, and pre/post-treatment techniques. Sun et al. [124] showed that operating conditions, including temperature, processing method, and feedstock type, influence the physicochemical and biological properties of bio-chars and hydro-chars obtained from pyrolysis of biomass. [44]

Species effect on fate of contaminants

The lignocellulosic composition of biomass is one of the factors affecting the chemical composition of the bio-oil and its compounds distribution in the product [73]. Lievens et al. [103] have shown different HMCBs (i.e. birch and sunflower) end up to various pyrolysis fractions, i.e. bio-oil, bio-char, etc., with different yields, characteristics, and calorific values. It has been reported that different parts of HMCBs, i.e. stems, branches, and leaves, possess various concentrations of structural organic compounds [71] [109]and different bioaccumulation degrees of inorganic pollutants [75][108]. The difference in physical structure and composition of HMCB's organs may lead to different yields of bio-oil products with various HHVs, reactivity, and compositions [71]. Cd, Cu, Zn, and Pb have been the most phytoextracted HMs from brownfields [44][84][73][100].

3.3 Post-processing

3.3.1 Value chain 1: Sugar to alcohols

In [88] there is no contamination present in the produced ethanol, however chromium remains stuck in the waste of the plant and was finally disposed as a hazardous waste. Sayago [88] recommended a desorption process with chemical reagents such as sodium hydroxide (NaOH), for chromium recovery and reuse.

3.3.2 Value chain 3: Biomass to Liquids (BtL) via gasification

As it was mentioned above, increasing the operating temperature of the gasification process, then the volatilization rate of heavy metals and the ability of applied filters to capture elements with fine particulates in syngas is negatively affected [118][87]. Many heavy metals (Cu, Pb, Zn) are abundant in the gaseous stream, and as a result the syngas requires conditioning and clean-up before any further usage or syngas upgrading with catalysts [94][87][83][92]. According to another report, cyclones were not effective on capturing some heavy metals such as Cd, Zn, Pb and Cu because of the high temperature of syngas and their high volatilization [93].

It was also observed in other studies that the hot-gas filter is more capable of reducing the transfer of heavy metals into the syngas compared to the cyclone [95][97]. Gas streams are formed during pyrolysis making it possible for fine char particles to be entrained to the pyrolysis oil condensation vessel. Since pyrolysis oil is acidic and metal concentrations in char are over 100 times as large, it can strongly influence the results. To prevent entrained flow of particles, a hot-gas filter is installed in the upper part of the reactor housing and replicate experiments are run. Comparing experiments with and without this gas filtration, a significant reduction in zinc and cadmium concentration in the pyrolysis oil is measured for the willow stems experiments. The reduction induced by gas filtration is observed for all three tested temperatures (623, 723, 823 K), and the volatilisation increase with increasing temperature is only present for the case of cadmium. [100]

Electrostatic precipitators have been used for the collection of solid particles from the gaseous phase. They were shown to have a collection efficiency of 98-99% for solid particles with diameters 0.3-20 μm. On the contrary, the electrostatic precipitators had lower efficiency (75%) for other particle sizes such as 4-400 μm, 1.80-309 μm and 3.90-375 μm. Heavy metals (such as Cu, Zn, Cr and Ni) accumulated inside the electrostatic precipitators and the cyclone upstream, and not in the cyclone downstream of the gasifier [119]. Finally, the ash, which is a by-product of the gasification process, needs to be managed or disposed. If the ash from the gasification of contaminated biomass from heavy metals cannot be reused, landfilling seems to be a promising disposal method. [94]

3.3.3 Value chain 4: Biomass to Liquid (BtL) via pyrolysis

It was suggested to adopt HMs cleaning technologies (i.e. cyclone and spray tower) as posttreatment measures to recover Zn and Cd from bio-char and bio-oil, respectively. However, the bio-oil produced by such a process may not be suitable for real applications yet due to its high Cd and Zn content [[106].

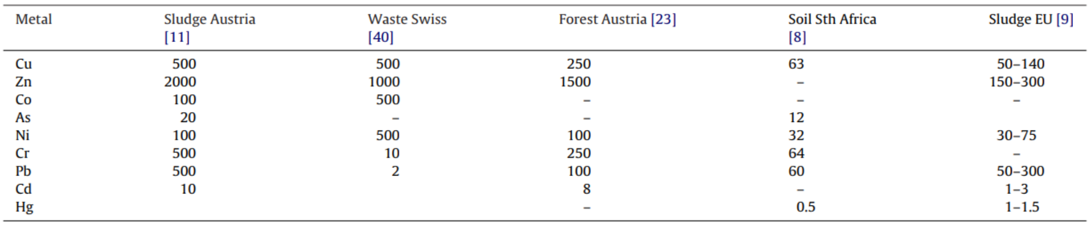
The issue of catalyst poisoning is of importance during the process. A number of studies have investigated and reported the catalytic roles of HMs (particularly Cu, Zn, Cr, etc.) present in contaminated biomass. Some studies indicated the positive roles of HMs towards improving activation energy and thermo-decomposition of biomass components, and consequently enhancing bio-oil yield and HHV [70][120][121][122][123]. The catalytic upgrading of bio-oils derived from HMCBs pyrolysis – using commercial catalysts – faces some obstacles, such as the deactivation and/or poisoning of catalysts by different factors, etc., which considerably affect the yield and the efficiency of the process technically, environmentally and economically. Some of those negatively affecting factors during the biomass pyrolysis generally are the high concentration of HMs, water content, and coke formation, which each one can reduce the catalytic activity significantly depending the nature and characteristics of the catalyst(s) used [97][124][125][126]. Mullen and Boateng [124] have indicated the increased concentration of two metals, i.e. Fe and Cu, on the HZSM-5 catalyst while other metals with a high concentration in HMCBs also can poison the active sites in different catalysts. The coke formation during pyrolysis process and its accumulation on the catalyst surface poisons the active site(s), and varies the catalyst topology and textural characteristics, thereby reducing the total liquid and organic fraction yields, as well as inhibiting the production of aromatics [127][128]. Some catalysts, like ZrO2, behave unusually in the deoxygenation of bio-oils because it inhibits the poisoning of its active site by carbon dioxide and water [129]. Finally, the alumina catalyst hardly demonstrated any catalytic function toward improving the properties of the bio-oil [112]

Typical concentrations of total metals in bio-oil even for non-contaminated biomass can reach up to 500 mg kg^{-1} [115]. To the date, no general benchmark values has been set for the maximum acceptable level of inorganic compounds and HMs contents neither in bio-oils nor other biofuels [33][72][94]. To minimize environmental and operational issues resulting from particles and HMs in bio-oils, the concentration of < 0.10 wt% for particles and that for HMs as low as possible have been recommended [84]. Some issues related to solid particles and metals in bio-oil are particle emissions, particle deposits on the surface of heating equipment, high temperature corrosion [84], as well as the increment of the bio-oil instability and contamination [130] and high heating value [70]. In some pyrolytic operations, the high, scattered, or inaccurate amounts of HMs (such as Cu, Ni, Zn, Cr, Al, and Mn) in the bio-oil or other phase have been attributed to biomass harvesting systems [97], reactor construction materials [97][100], heating carrier material [100] or bio-oil collecting system [72]. There has been reported feasibility of bio-oil production with negligible amounts of HMs using fast pyrolysis of various HMCBs even though without implementing any wet pretreatment and/or post-treatment [103][44][70][71].

Wiinikka et al. showed the feasibility of fast pyrolysis for the production of an almost metal-free bio-oil in a pilot-scale reactor, while HMs majorly concentrated in the solid residue [72]. Some other studies do not recommend the real applications of the bio-oil produced from the pyrolytic conversion of HMCBs, due to its high metals content, including Cd and Zn [106]. So, it is necessary to implement post-treatment to avoid, separate, or remove HMs from bio-oil toward cleaner product. In pyrolysis process, the transfer of HMs from solid phase to condensable phase has been introduced as the main migration route [97][72]. The use of adequate technologies for solid–gas/liquid separation before condensation has been recommended to provide an effective obstruction of the HMs migration from bio-char into bio-oil [97][72]. At the same time, a study demonstrated the effective and successful application of cyclone as the post-treatment of pyrolytic conversion of HMCBs at 650 °C for simultaneous metal-free bio-oil production and metals recovery [106].

3.3.4 Issues relevant to all Value Chains (1-4) considered

When considering the ultimate disposal of the residuals from thermal processing, their final repository will be the earth. An ash (in particular from the gasification value chain 3) is suitable for spreading on soil if the emission regulations are met, but alternatively if it is highly contaminated it will require interment in a secure landfill. Since all the metals apart from mercury and to a lesser extent Se and As are effectively retained in the ash, the concentration in the ash will be determined by the concentration of metals and ash-forming minerals in the feed. A number of legislative limits applying to heavy metals for application to soil are presented in Table 5, relating to sewage sludge and general waste materials. Some of the ashes described in this review were suitable for dispersion into soil, but there are some difficult materials.



Metal	Sludge Austria [11]	Waste Swiss [40]	Forest Austria [23]	Soil Sth Africa [8]	Sludge EU [9]
Cu	500	500	250	63	50–140
Zn	2000	1000	1500	–	150–300
Co	100	500	–	–	–
As	20	–	–	12	
Ni	100	500	100	32	30–75
Cr	500	10	250	64	–
Pb	500	2	100	60	50–300
Cd	10		8	–	1–3
Hg			–	0.5	1–1.5

Table 5: Some limits for heavy metal concentration in ash for application to soil (mg/kg)[99]

The separation of ash into different fractions can enable application of ash derived from HM-enriched biomass to be used as fertilizers on agricultural land. Maximum permissible values are established for HM in the ash to be used for agricultural and land reclamation purposes: 30 mg/kg dry weight (DW) for Ni and Cr, 5 mg/kg DW for Cd, 3 mg/kg DW for As, 50 mg/kg DW for Pb, 200 mg/kg DW for Cu, and 1500 mg/kg DW for Zn. [58]

4 PRESENCE OF AROMATIC HYDROCARBONS AND CHLORINATED COMPOUNDS ALONG THE EXISTING CHAINS

A type of contaminant which can be a cause of concern is polycyclic aromatic hydrocarbons (PAHs), that are a group of persistent organic contaminants with ≥2 aromatic rings. Relevant open literature sources are mostly dealing with the formation of PAH contaminants during thermochemical conversion of biomass or the effects of biomass yield of crops growing in correspondingly contaminated soils, while the subsequent stages towards liquid biofuels are not thoroughly examined. The main reason is because, due to their hydrophobic nature, hydrocarbons, corresponding chlorinated compounds and polycyclic aromatic hydrocarbons (PAHs) in environmental matrices are rapidly adsorbed on particles and organic matter of soils.

Therefore, soils are the ultimate repository for most hydrophobic organic contaminants that cannot be extracted by a plant since they cannot be dissolved in the aqueous phase moving from the soil to the vascular system of the plant. Moreover, several xenobiotic organic substances are degraded by soil microorganisms through both aerobic and anaerobic processes. However, biomass grown on soils with organics contamination presents this kind of contamination mainly due to soil particles adhering the external surface of the plant.

The following paragraphs present the major findings regarding the evaluation of volatilization and decomposition reactions of dioxins from contaminated soils and the formation of PAH during the conversion stage.

4.1 PCDD/PCDF formation and behaviour

Polychlorinated dioxins (PCDDs) and furans (PCDFs) consist of two aromatic rings and chlorine atoms in different positions. These can be carried with soil particles or formed throughout the gasification process. Specifically, they can occur through small organic compounds acting as their precursors or through the oxidative breakdown of residual carbonaceous materials. In the case of fly ash both requirements are met, supporting polychlorinated dioxins/furan formation.[133]

Some studies have investigated the evaluation of volatilization and decomposition reactions of dioxins from sediment by oxygen free pyrolysis, since large quantities of dioxin-contaminated residues have been found in ecosystems globally. These traces can cause direct toxic effects on aquatic life, as well as indirect risk to human well-being through the bioaccumulation of toxic contaminants in the food chain. As a result, there is need for these toxic substances of the sediment to be removed or made more chemically stable. It has been shown that 99.9999% has been removed in the case of total dioxins during oxygen free pyrolysis of Contaminated sediment, while PCDFs were not formed in the solid products over the retention time range of 30-90 min at 800°C. The removal of

PCDDs also reached 100% at a retention time of 30 and 90 min, respectively. Consequently, there is significant potential of oxygen free pyrolysis as useful technology to either prevent formation of PCDD/Fs or minimize the release of these compounds into the environment. [62]

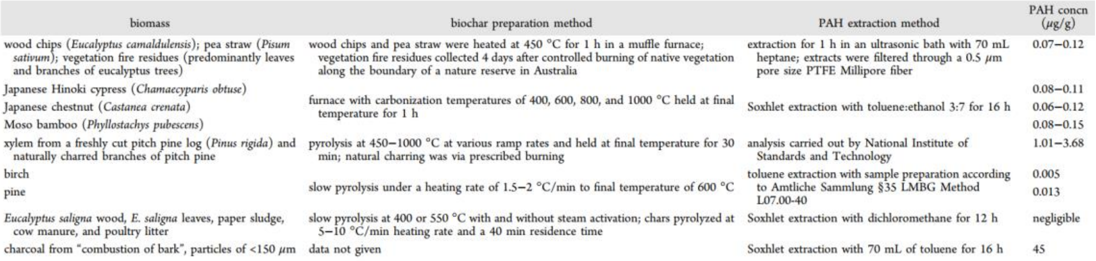
Other studies have focused on PCDD/PCDF behavior in low-temperature pyrolysis of PCP-contaminated sandy soil. In this case, considering cost and environmental impact, low-temperature pyrolysis in an oxygen-deficient atmosphere has been found as an efficient way to suppress PCDD/F formation in fly ash in the temperature range of 300–500 °C. It has been shown that temperature clearly affects the competition among formation, dechlorination, desorption and destruction of PCDD/Fs. Most PCDD/F removal from the soil was observed at 350 °C, and not much difference of PCDD/Fs was released into the gaseous phase between 350 °C and 400 °C. [63]

4.2 Polycyclic AH (PAH) formation during core processes

This type of contaminant is mainly derived from incomplete combustion of biomass or fossil fuel. While no PAHs are expected to be incorporated in the contaminated biomass (according to the introduction of this chapter), a significant proportion of PAHs could be inevitably formed during biochar production, and in turn pose a threat to the natural environment due to the increased rate of biochar application. PAHs have drawn the attention of both the general public and scientists because of their persistence in the environment and their carcinogenic, mutagenic and teratogenic effects on human health.

Polycyclic aromatic hydrocarbons can increase significantly in the gasification process. It was deduced that 2-ring and 6-ring PAHs increased significantly during the gasification process. It must be noted that phenols have been an important precursor of PAHs synthesis. [131]

Although PAH formation can be greatly suppressed under the pyrolysis conditions, certain amounts of PAHs can also be found in biomass pyrolysis products, especially in tar [111]. The contents and distributions of PAHs in the products (e.g., gas, tar, and bio-oil) of birch wood biomass pyrolysis were analyzed by Fagernas et al. [134]. They observed that PAHs were detected in incondensable gases, condensable liquids, and biochar. Most of the PAHs were found in tars, especially in the collected heavy tar. Zhou et al. [135] investigated the generation PAHs in the pyrolysis of nine different organic solid waste fractions including biomass and waste plastics. It was found that more PAHs were detected from plastics pyrolysis than biomass pyrolysis. For the chemical structures of PAHs, two-ring PAHs dominated all the tar samples, which varied from 40 to 70 wt %, while naphthalene was the most abundant two-ring PAH formed during the pyrolysis process. Phenanthrene and fluorene were detected as the most abundant three-ring PAHs, while the contents of chrysene and benzo[a]anthracene were notable in the tar of plastics. Compared with tar and the gas phase of the biomass pyrolysis, there are also considerable amounts of PAHs found in the solid biochar phase. For example, in the biochar obtained from slow pyrolysis, the content of total PAH is in the range 0.07–3.27 μg/g and varied with biomass source, whereas in the biochar obtained from fast pyrolysis, the total PAH contents remarkably increased to 45 μg/g. [111] The main reason for this phenomenon might be that the PAHs produced in the slow pyrolysis may escape to the gaseous phase, while during the fast pyrolysis process the produced PAHs might condense on the surface of biochar. For more information, Table 6 [111]summarizes the PAH concentrations in the biochar obtained from different biomass resources and under different pyrolysis conditions.



biomass	biochar preparation method	PAH extraction method	PAH concn (μg/g)
wood chips (*Eucalyptus camaldulensis*); pea straw (*Pisum sativum*); vegetation fire residues (predominantly leaves and branches of eucalyptus trees)	wood chips and pea straw were heated at 450 °C for 1 h in a muffle furnace; vegetation fire residues collected 4 days after controlled burning of native vegetation along the boundary of a nature reserve in Australia	extraction for 1 h in an ultrasonic bath with 70 mL heptane; extracts were filtered through a 0.5 μm pore size PTFE Millipore fiber	0.07−0.12
Japanese Hinoki cypress (*Chamaecyparis obtuse*)	furnace with carbonization temperatures of 400, 600, 800, and 1000 °C held at final temperature for 1 h	Soxhlet extraction with toluene:ethanol 3:7 for 16 h	0.08−0.11
Japanese chestnut (*Castanea crenata*)			0.06−0.12
Moso bamboo (*Phyllostachys pubescens*)			0.08−0.15
xylem from a freshly cut pitch pine log (*Pinus rigida*) and naturally charred branches of pitch pine	pyrolysis at 450−1000 °C at various ramp rates and held at final temperature for 30 min; natural charring was via prescribed burning	analysis carried out by National Institute of Standards and Technology	1.01−3.68
birch	slow pyrolysis under a heating rate of 1.5−2 °C/min to final temperature of 600 °C	toluene extraction with sample preparation according to Amtliche Sammlung §35 LMBG Method L07.00-40	0.005
pine			0.013
Eucalyptus saligna wood, *E. saligna* leaves, paper sludge, cow manure, and poultry litter	slow pyrolysis at 400 or 550 °C with and without steam activation; chars pyrolyzed at 5−10 °C/min heating rate and a 40 min residence time	Soxhlet extraction with dichloromethane for 12 h	negligible
charcoal from "combustion of bark", particles of <150 μm	data not given	Soxhlet extraction with 70 mL of toluene for 16 h	45

Table 6: PAH concentrations in the biochar obtained from different biomass resources and under different pyrolysis conditions [111]

5 CLEAN LIQUID BIOFUEL CHAINS

This chapter contains the preliminary definition of the alternative value chain scenarios, after processing and summarizing the information presented in the previous chapters. In the present document the term "clean biofuel chain" is assigned to a group of processes, capable of producing a biofuel carrying a minimum load of contaminants. Nevertheless, as commented in section 3.2.3, no general benchmark values have been set for the maximum acceptable level of inorganic compounds and HMs contents neither in bio-oils nor other biofuels (see Annex for existing biofuel specifications). As a consequence, there is not a commonly accepted level of HM contamination, below which a biofuel is considered "clean" or "HM-free".

Fossil transport fuels on the other hand contain only traces of heavy metals (averaging between 5 and 33 ppb or $\mu g\ kg^{-1}$) [136], therefore it would be reasonable to assume that a biofuel for transport applications should not exceed the existing HM concentrations. The above statement should apply, even if a contaminated feedstock is considered, since the "environmentally friendly" profile of a transport biofuel would be considerably compromised in the case of increased HM emissions.

As a consequence, the alternative biofuel value chains will be defined (and further refined in forthcoming deliverables), so as to (potentially) provide a liquid fuel with comparable levels of HM and other contaminant load to existing fossil transport fuels.

5.1 Preliminary alternative value chain scenarios

The alternative value chains are accordingly defined, in order to be able to provide a final biofuel product, having a HM contaminated biomass feedstock as input. The integration of the existing value chain defined in section 1.6 and the information collected and presented in chapter 3 has provided the preliminary alternative value chain scenarios herewith described.

5.1.1 Alternative value chain 1: Sugar to alcohols

According to the information based on the previous experience of producing bioethanol from HM contaminated feedstocks (sections 3.1.1, 3.2.1 and 3.3.1), a pre-processing stage is necessary towards extracting the HMs from the feedstock. The goal is to avoid large HM quantities from entering the hydrolysis/fermentation stages. A combination of acid and alkali treatment has been reported to capture almost all HM load and provide an HM rich effluent. There is no agreement on the effect of the small amount of HM entering the next process steps, probably due to the different HM species considered. Cd has been reported to increase the ethanol yield, while Zn and Cr have detrimental impacts. The final product has not been reported to contain any HM. Figure 18 summarized the main features of the alternative value chain 1: sugar to alcohols.

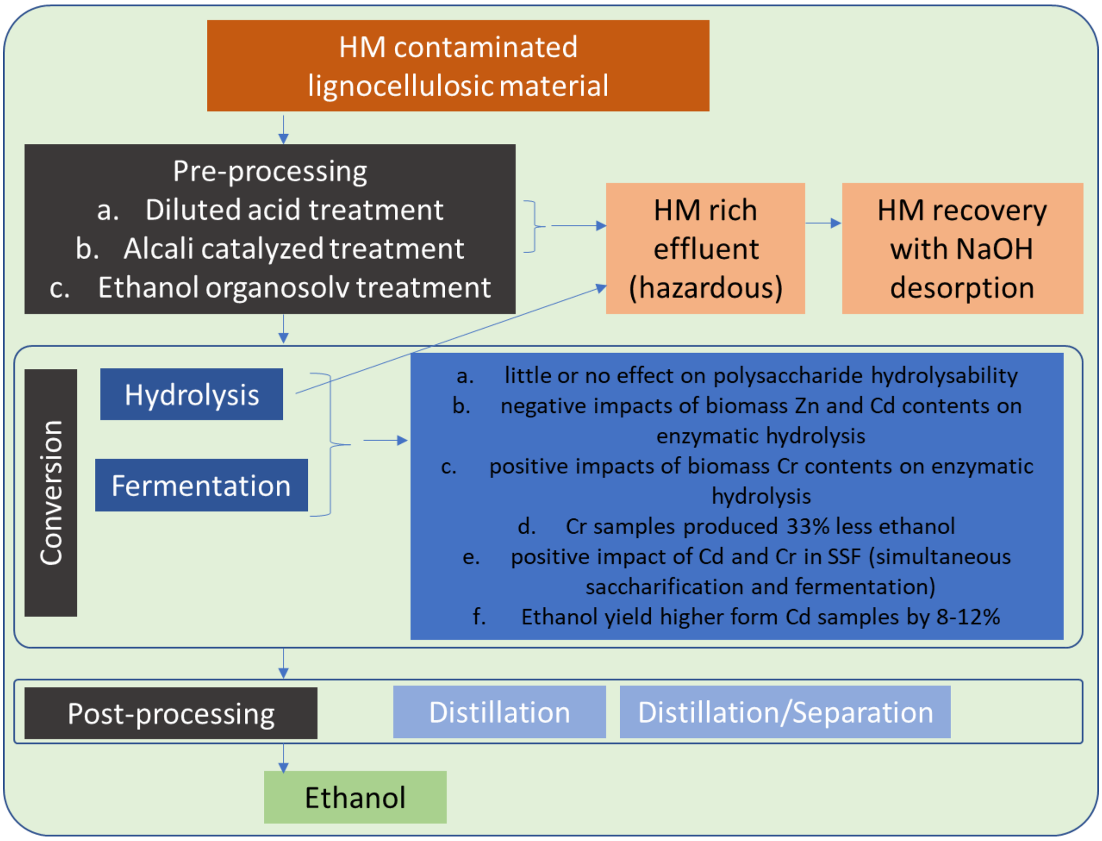


Figure 18 Alternative value chain scenario 1: Sugar to alcohol

5.1.2 Value chain 2: Oil crops to biodiesel

Unfortunately, there is no information retrieved regarding the effects or possible adaptations regarding the production of biodiesel from HM contaminated feedstocks. Therefore, Fig. 19 cannot be considered to represent an alternative value chain, nevertheless it summarizes a main positive outcome from relevant papers: The HM tend to concentrate less in the seeds of the oil crops. Since it is only the seeds that are processed for biodiesel production, this means that a comparatively lighter HM load can be expected to enter a potential conversion stage.

5.1.3 Value chain 3: Biomass to Liquids (BtL) via gasification

Regarding the gasification value chain, all pre-processing treatments identified for value chain 1 are applicable, since the same type of lignocellulosic feedstock is considered. Additionally, treatment with de-ionized water is reported, as presented in section 3.1.3. In a typical gasification process, HMs are expected to concentrate mostly in bottom and fly ash, therefore the decontamination refers to the capture of ashes and particles. Nevertheless, some HMs can be volatilized and transferred to the syngas, which is not desirable. For this reason, gas cleaning is applied, through cyclones, hot filtering and electrostatic filters. The abovementioned measures are expected to provide a HM-free syngas for further processing (Fig. 20).

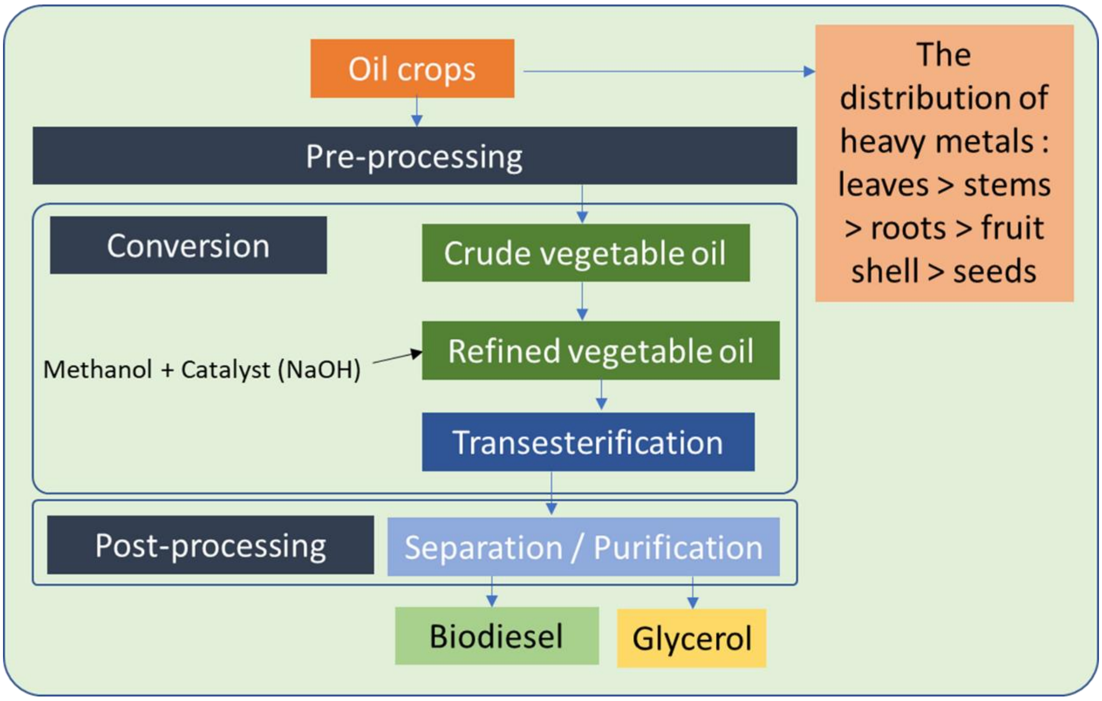


Figure 19 Alternative value chain scenario 2: Oil crops to biodiesel

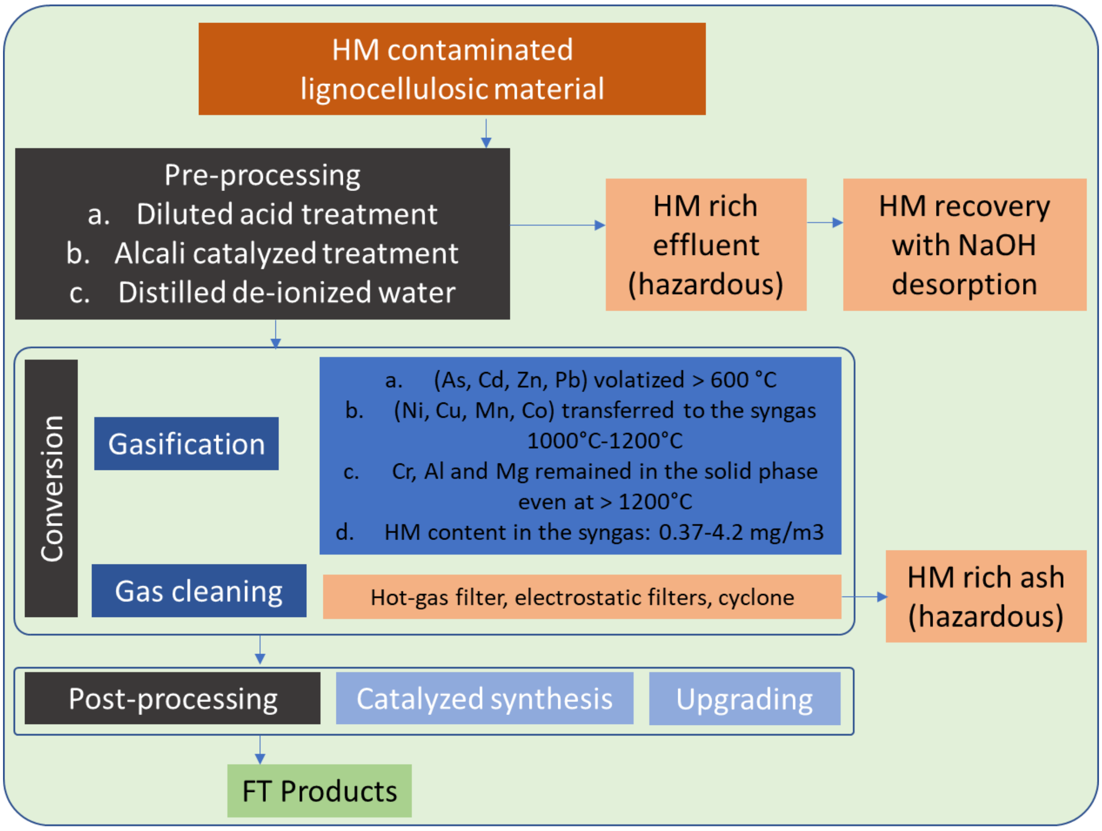


Figure 20 Alternative value chain scenario 3a: BtL via gasification

A different gasification approach will be followed in CERESiS, adopting SuperCritical Water Gasification (SCWG). This will provide a HM-rich sludge (instead of ash residues) to be evaluated for further treatment towards final disposal or reuse (fig. 21).

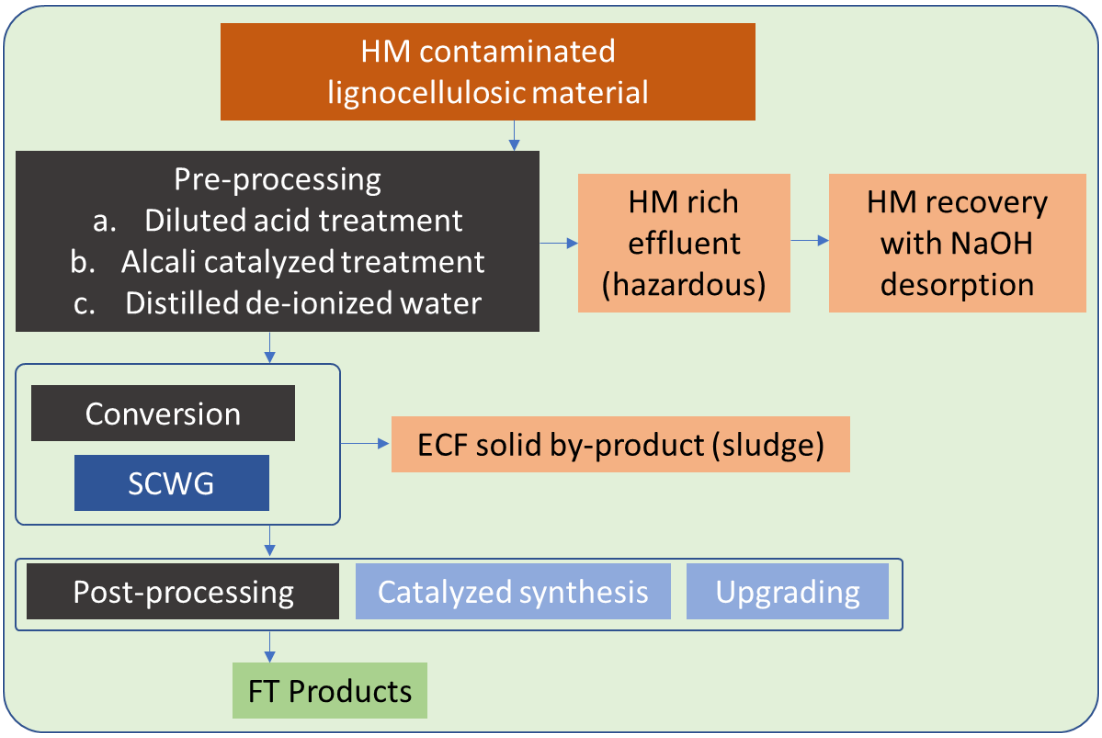


Figure 21 Alternative value chain scenario 3b: BtL via SCWG

5.1.4 Value chain 4: Biomass to Liquid (BtL) via pyrolysis

In parallel to Chain 3, all pre-processing treatments identified for value chain 1 are applicable, since the same type of lignocellulosic feedstock is considered. In this case, HMs have three optional routes: Bio-char (expected to contain most of the load), Bio-oil (not desirable route) and carried by particles in the off gas of the process. The process temperature is considered critical, with a level of <500 °C to be the best compromise between bio-oil yield and HM load carried (fig. 22). Hot gas filtering is reported to be beneficial towards reducing the HMs in bio-oil, which can be further decontaminated with micro-filtration, as suggested in the CERESiS framework.

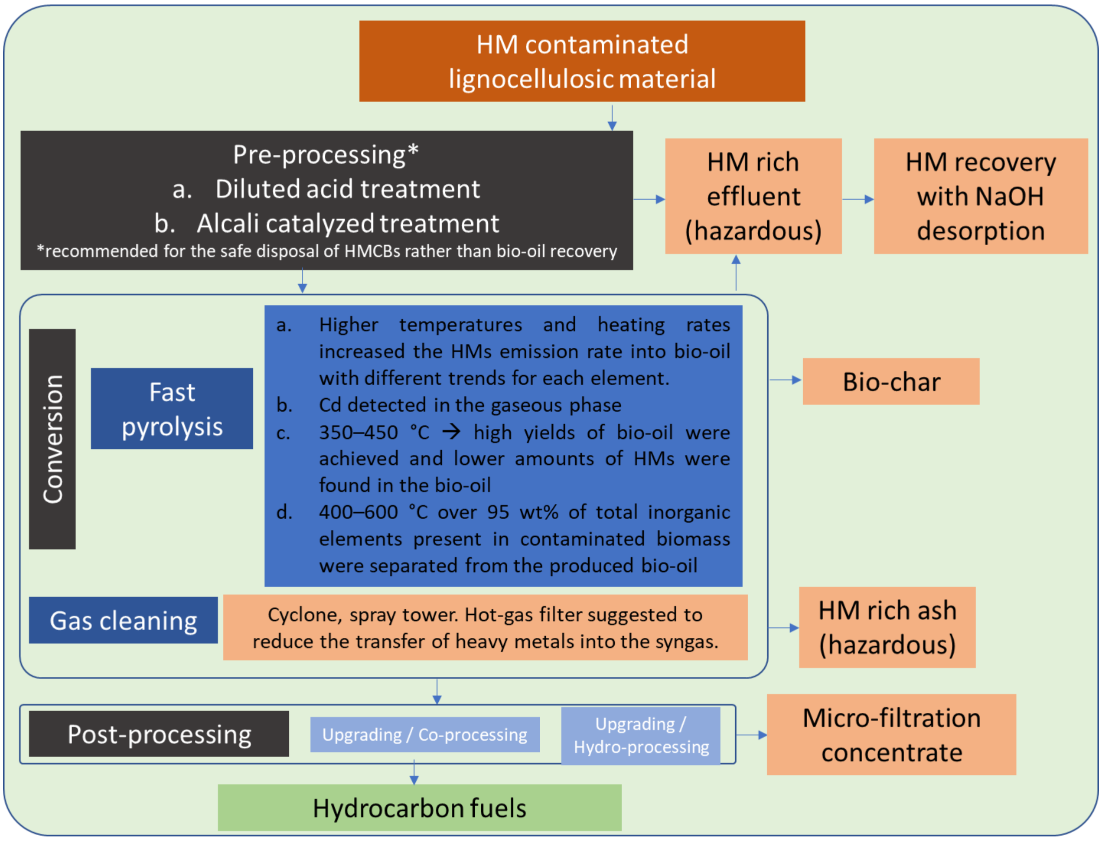


Figure 22 Alternative value chain scenario 4: BtL via pyrolysis

6 CONCLUSIONS

The objective of the present deliverable was to identify and examine the preliminary alternative liquid biofuel value chain scenarios, based on analysis of existing chains, focusing on the required adaptations needed for clean biofuel production. In this task, the incorporation of contaminated biomass was examined, to specify the requirements and constraints of integrated pathways.

Towards defining the clean biofuel chains, suitable pre-processing treatments have been described in section 3.1. As provided by the relevant literature, it is possible in some cases to capture the HM load before the main conversion stage, thus potentially addressing the issue of excessively contaminated feedstocks. However, options for managing the hazardous effluent should be further investigated in the forthcoming tasks and deliverables.

The mechanisms affecting the fate of HM in the various process streams are quite complicated and affected by various process parameters. An in-depth analysis was performed in sections 3.2 & 3.3 for the conversion and post-processing stages, indicating the complexity of the matter. Towards further addressing this issue, a quantitative approach will be pursued in the follow-up Task 1.7.

The quantification of efficiencies regarding the processes considered and the capture of contaminants requires detailed mass/energy balances along the chain stages. The quality and quantity of data available at this point of analysis was not sufficient, in order to achieve this goal. Nevertheless, mass and energy balances are a fundamental step of Life Cycle Analysis activities to be undertaken under WP4, therefore the quantification of efficiencies will be eventually completed in the forthcoming tasks of CERESiS workplan.

Unfortunately, there is very limited information available for mineral oil and aromatic hydrocarbon contaminated feedstocks. Relevant open literature sources are mostly dealing with the formation of PAH contaminants during thermochemical conversion of biomass or focusing on the effects of biomass yield of crops growing in correspondingly contaminated soils, while the subsequent stages towards liquid biofuels are not thoroughly examined. The main reason is because, due to their hydrophobic nature, hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in environmental matrices are rapidly adsorbed on particles and organic matter of soils. Consequently, soils are the ultimate repository for most hydrophobic organic contaminants that cannot be extracted by a plant since they cannot be dissolved in the aqueous phase moving from the soil to the vascular system of the plant. Moreover, several xenobiotic organic substances are degraded by soil microorganisms through both aerobic and anaerobic processes. However, biomass grown on soils with organics contamination presents this kind of contamination mainly due to soil particles adhering the external surface of the plant. Ultimately, the mechanisms through which the biofuel value chain is affected by the presence of aromatic hydrocarbons and chlorinated compounds in the soil is quite different than that of Heavy Metals. In the former case, biomass will not uptake contaminants – apart from soil particles transferred with the biomass -, but the contaminants may form during the conversion process. In the latter case (HM) contaminants will be uptaken by the biomass and moved downstream in the value chain. This issue will be also revisited in the follow-up task T1.7, where the final definition of the alternative biofuel chains is foreseen.

Nevertheless, T1.3 has successfully defined the preliminary alternative value chain scenarios in the case of heavy metal contamination, after processing and summarizing the information from a considerable number of relevant papers. The alternative biofuel value chains have been defined (and will be further refined in forthcoming deliverables), so as to (potentially) provide a liquid fuel with comparable HM load to existing fossil transport fuels. This is an important contribution, which will be the starting point of Task 1.7, in which the final definition of Annex I.

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8 ANNEX

EN & ASTM specifications for Biodiesel [1] [2]

<table>
<tr><th colspan="10">US and EU Biodiesel Specifications</th></tr>
<tr><th rowspan="2">Property</th><th colspan="2" rowspan="2">ASTM D975-08a</th><th colspan="3">ASTM D6751-12</th><th colspan="2" rowspan="2">EN 590:2004</th><th colspan="2" rowspan="2">EN 14214:2012</th></tr>
<tr><th>2-B</th><th>1-B</th><th>Test</th></tr>
<tr><td rowspan="2">Flash point, min</td><td>No 1D 38°C</td><td rowspan="2">D93</td><td rowspan="2">**93°C**</td><td colspan="2" rowspan="2">D93</td><td rowspan="2">55°C</td><td rowspan="2">EN 22719</td><td rowspan="2">**101°C**</td><td rowspan="2">EN ISO 2719</td></tr>
<tr><td>No 2D 52°C</td></tr>
<tr><td>Water & sediment, max</td><td>0.05% vol</td><td>D2709</td><td>**0.050% vol**</td><td colspan="2">D2709</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Water, max</td><td></td><td></td><td></td><td colspan="2"></td><td>200 mg/kg</td><td>EN ISO 12937</td><td>**500 mg/kg**</td><td>EN ISO 12937</td></tr>
<tr><td>Total contamination, max</td><td></td><td></td><td></td><td colspan="2"></td><td>24 mg/kg</td><td>EN 12662</td><td>**24 mg/kg**</td><td>EN 12662</td></tr>
<tr><td rowspan="2">Distillation temperature (% vol recovered)</td><td>90%:</td><td rowspan="2">D86</td><td rowspan="2">**90%: 360°C max**</td><td colspan="2" rowspan="2">D1160</td><td>65%: 250°C min</td><td rowspan="2">EN ISO 3405</td><td rowspan="2"></td><td rowspan="2"></td></tr>
<tr><td>1D 288°C max</td><td>85%: 350°C max</td></tr>
</table>

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[1] ACEA, 2009. “Biodiesel Guidelines”, European Automobile Manufacturers Association, Brussels, Belgium, March 2009, http://www.acea.be/uploads/publications/20090423_B100_Guideline.pdf

[2] ASTM, 2002. “Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels”, American Society for Testing and Materials, D6751-02

	2D 282-338°C							
Kinematic viscosity	1D 1.3-2.4 mm2/s 2D 1.9-4.1 mm2/s	D445	**1.9-6.0 mm2/s**	D445	2.0-4.5 mm2/s	EN ISO 3104	**3.5-5.0 mm2/s**	EN ISO 3104
Density					820-845 kg/m3	EN ISO 3675 EN ISO 12185	**860-900 kg/m3**	EN ISO 3675 EN ISO 12185
Ester content	5% vol. max	EN 14078			5% vol. max FAME	EN 14078	**96.5% min**	EN 14103
Ash, max	0.01% wt	D482			0.01% wt	EN ISO 6245		
Sulfated Ash, max			**0.020% mass**	D874			**0.02% mass**	ISO 3987
Sulfur, max (by mass)	1D and 2D:	D5453 D2622 D1292	**Two grades:**	D5453	Two grades:	EN ISO 14596	**10.0 mg/kg**	EN ISO 20846
	S15 15 mg/kg		**S15 15 ppm**		50 mg/kg	EN ISO 8754		EN ISO 20884
	S500 0.05%		**S500 0.05%**		10 mg/kg	EN ISO 24269		EN ISO 13032
	S5000 0.50%							
Copper strip corrosion, max	No 3	D130	**No 3**	D130	class 1	EN ISO 2160	**class 1**	EN ISO 2160
Cetane number, min	40	D613	**47**	D613	51.0	EN ISO 5165	**51.0**	EN ISO 5165
Cetane index, min					46.0	EN ISO 4264		
One of3:								
- cetane index	40 min	D976-80						
- aromaticity	35% vol max	D1319						
PAH, max					11% wt	IP 391 EN 12916		
Operability, one of:	Report	D2500 D4539 D6371						
- cloud point								
- LTFT/CFPP								

Cloud point			**Report**	D2500	Location & season dependant	EN 23015	**Location & season dependant**	EN 23015
CFPP					Location & season dependant	EN 116	**Location & season dependant**	EN 116
Carbon residue on 10% distillation residue, max	1D: 0.15% wt	D524	**0.050% wt5**	D4530	0.30% wt	EN ISO 10370		
	2D: 0.35% wt							
Acid number, max			**0.50 mg KOH/g**	D664			**0.50 mg KOH/g**	EN 14104
Oxidation stability			**3 hrs min**	EN 14112	25 g/m3 max	EN ISO 12205	**8 hrs min**	EN 14112
Iodine value, max							**1201 g Iod/100g**	EN 14111
								EN 16300
Linolenic acid methyl ester, max							**12.0% wt**	EN 14103
Polyunstatured methyl esters, max							**1.00% wt**	EN 15779
Alcohol control			**0.2% wt methanol max, or**	EN14110			**0.20% wt methanol max**	EN 14110
			130°C flash point min	D93				
				MG D6584			**MG 0.70% wt**	EN 14105

Monoglycerides, diglycerides & triglycerides, max				**0.40% wt**				**DG 0.20% wt** **TG 0.20% wt**	
Group I metals (Na + K), max			**5 mg/kg**	EN 14538				**5.0 mg/kg**	EN 14108 EN 14109 EN 14538
Group II metals (Ca + Mg), max			**5 mg/kg**	EN 14538				**5.0 mg/kg**	EN 14538
Free glycerin, max			**0.020% wt**	D6584				**0.02% wt**	EN 14105 EN 14106
Total glycerin, max			**0.240% wt**	D6584				**0.25% wt**	EN 14105
Phosphorous, max			**0.001% wt**	D4951				**4.0 mg/kg**	EN 14107 prEN 16294
Lubricity, max	520 µm	D6079				460 µm	ISO 12156-1		
Conductivity, min	25 pS/m	D2624 D4308							
Cold soak filtration time (CSFT), max			**360 s4**	**200 s**	D7501				

Ethanol specifications[3]

Properties	Units	Min.	Max.	Test methods
Density at 15°C	kg/m3	720	775	EN ISO 3675
Research octane number, RON	–	95	–	EN 25164
Motor octane number, MON	–	85	–	EN 25163
Vapour pressure, VP	kPa	45	60	EN 13016-1
summer	kPa	60	90	
winter				
Distillation (1013 mbar)	% vol.	20	48	ISO 3405
evaporated at 70°C, E70 (summer)	% vol.	22	50	
evaporated at 70°C, E70 (winter)	% vol.	46	71	
evaporated at 100°C	% vol.	75	–	
evaporated at 150°C				
Distillation residue	% vol.	–	2	ISO 3405
Final boiling point, FBP	°C	–	210	ISO 3405
Volatility, VLI (10 VP + 7 E70)	–	–	–	Calculation
summer	–	1000	1250	
winter				
Copper strip corrosion (3h at 50°C)	rating	Class 1		EN ISO 2160
Oxidation stability	hrs	6	–	EN ISO 7536
Hydrocarbons	% vol.	–	18	ASTM D 1319
Olefins	% vol.	–	35	

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[3] EN 228: Automotive fuels – Unleaded petrol – Requirements and test methods

Aromatics	% vol.	–	1	
Benzene				
Oxygen	% wt.	–	2.7	EN 1601, EN 13132
Oxygenates	% vol.	–	3	EN 1601, EN 13132
Methanol	% vol.	–	5	
Ethanol	% vol.	–	10	
Iso-propyl alcohol	% vol.	–	10	
Iso-butyl alcohol	% vol.	–	7	
Tert-butyl alcohol	% vol.	–	15	
Ethers (5 or more C atoms)	% vol.	–	10	
Other oxygenates				
Sulphur	mg/kg	–	10	EN ISO 20846
Lead	mg/l	–	5	EN 237
Gums	mg/100 ml	–	5	EN ISO 6246
Appearence	–	Clear and bright		Visual inspection