

Review

An Assessment of Liquid Biofuel Value Chains from Heavy-Metal Contaminated Feedstock

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Abstract: The present work aims to identify alternative liquid biofuel value chain scenarios utilizing heavy metal (HM)-contaminated biomass feedstocks. The analysis is based on breaking down existing liquid biofuel value chains, focusing on the required adaptations needed for clean biofuel production. State-of-the-art and emerging liquid biofuel production options are reviewed. The potential implications caused by the HM load in the biomass feedstock are analyzed along the whole biofuel production chain, which includes pre-processing, conversion and post-processing stages. The fate of the most common HM species present in contaminated biomass is identified and graphically represented for advanced (second generation) biofuel conversion processes. This information synthesis leads to the description of alternative value chains, capable of producing HM-free biofuel. This work goes a step further than existing reviews of experiments and simulations regarding heavy metal-contaminated biomass (HMCB) valorization to biofuels since feasible value chains are described by synthesizing the findings of the several studies examined. By defining the adapted value chains, the “road is paved” toward establishing realistic process chains and determining system boundaries, which actually are essential methodological steps of various critical evaluation and optimization methodologies, such as Life Cycle Assessment, supply chain optimization and techno-economic assessment of the total value chain.

Keywords: liquid biofuels; heavy metals; contaminated biomass feedstock; value chains



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1. Introduction

The transport sector (including international aviation and shipping) is responsible for 32% of the total CO₂ emissions in the EU, and in 2017, 72% of these were attributed to road transport [1]. Given that the target of achieving carbon neutrality by 2050 [2] requires a reduction target of Greenhouse Gas (GHG) emissions of at least 55% by 2030 [3], a respective reduction of transport-related emissions is a priority issue.

Until newer technologies can be available at a large scale for the transport sector decarbonization (e.g., electrification or hydrogen), biofuels represent the most convenient and tangible short-term solution. Toward this direction, the EU, since 2009, has introduced Renewable Energy Directives (RED) [4,5], which mandate all country members to cover a significant part of their transport energy demand from renewable sources. In the latest amendment published in July 2021 [6], it is stated that the EU target of at least 32% of renewable energy sources in the overall energy mix must increase to 38–40% by 2030. In this direction, a 13% reduction in the transport fuels’ greenhouse gas intensity is proposed. According to [7], this target expressed in energy-based terms reaches up to a respective reduction of 28%, with an additional sub-target of 2.2% share for advanced biofuels (single counted), corresponding to a significant ambition increase considering that the previous

transport target (energy based) was 14%, with a 3.5% advanced biofuels sub-target (double-counted) in REDII [5].

The evolution of biofuels during the last decades is commonly distinguished into three generations. First-generation liquid biofuels were used commercially, as biodiesel (bio-esters) and bioethanol. They have been produced extensively, following standardized specifications [8,9] and well-established transformation processes. Vegetable oils, residual oils and fats produce biodiesel through transesterification, while bioethanol is derived from sugar and starch through fermentation. However, using commodities otherwise consumed in the food supply chain as raw materials for biofuels is considered to cause social and economic implications. Consequently, from a sustainability perspective, using food or feed crops for biofuel production is not considered an attractive option [10].

Lignocellulosic crops providing feedstocks to second-generation biofuels can solve this problem while being able to provide a sustainable supply of biofuel alongside affordable costs and lower environmental impacts. Various rapidly renewed sources of biomass are eligible feedstocks. Two categories of second-generation biofuels are distinguished. The first category is the residual non-food part of current crops that are considered waste flows after the extraction of the food crop (stems, leaves, husks). The second category is other non-food crops such as miscanthus, switch grass, reed canary grass, rye, wheat straw, cereals, etc. [11,12].

The superior capabilities of algae-derived biomass to produce an improved version of biofuels, considered third-generation biofuels, have been recently reported [13–15]. Algae could produce crude oil that can be processed into diesel and gasoline or be genetically modified to produce end-products, such as ethanol [16]. An additional emerging form of biofuels is electrofuels or e-fuels. These terms refer to advanced fuels produced from hydrogen obtained by water electrolysis and CO₂ from a biogenic source, such as biogas [17].

Soil contamination corresponds to reduced soil quality due to the presence of toxic substances resulting from human activity, and across the EU, the existence of 2.8 million potentially contaminated sites is estimated [18]. The main types of contaminants include inorganic (mostly heavy metals—HMs) and organic pollutants (petroleum, pesticides, polycyclic aromatic hydrocarbons—PAHs, etc.) [19]. Integrated approaches have been proposed combining the use of energy crops (such as miscanthus, *ricinus communis*, etc.) in phytoremediation campaigns with the potential of producing biofuels by implementing appropriate methods of treatment for the harvested contaminated biomass [20–22]. To demonstrate the scale of the problem, while 650,000 sites have been registered in the EU, only 10% of them have been remediated [18]. The annual cost of managing the contaminated sites in Europe is estimated at 6 billion EUR [23].

This paper proposes alternative value chain scenarios based on the analysis of existing liquid biofuel production value chains, identifying the adaptations required to be able to valorize HM-contaminated biomass feedstocks. It particularly refers to a future research direction identified by a relevant review [24], where the need for evaluating the economic, social, and environmental aspects of sustainable biofuel routes has been highlighted. The contribution of the present work focuses on describing clean biofuel value chains on being utilized by corresponding assessment and optimization methodologies (e.g., Life Cycle Assessment—LCA, supply chain optimization, techno-economic assessment of entire value chains). The absence of an LCA for assessing clean biofuel chains utilizing HM-contaminated feedstock was, in fact, one of the key findings of another relevant review [25]. Thus, an essential input for implementing critical economic and environmental viability assessment methodologies is herewith provided.

2. Value Chains of Producing Liquid Biofuels

According to the definition by the European Technology and Innovation Platform, “A value chain is a cluster of conversion pathways from a range of feedstocks to a range of products” [26]. Biofuel chains encompass several different stages, from feed-

stock production (agricultural phase), transport and processing to biofuel production, distribution, storage, dispensing and conversion [27]. As a first step to formulating liquid biofuel production value chains, all biomass treatment and biofuel production subprocesses have been grouped into three main stages: (a) pretreatment, which includes biomass collection, preparation and treatment processes prior to the conversion to biofuel, (b) conversion to liquid fuel, including biochemical and/or thermochemical processes implemented for the production of biofuel and (c) post-processing, which addresses distillation, upgrading and storage steps leading to the final biofuel product. Although the processes incorporated in the individual intermediate processes depend on the biomass feedstock specifications, conversion technology and biofuel form, the basic biofuel production stages are identical. Thus, the basic structure of a generalized biofuel production chain is presented in Figure 1.

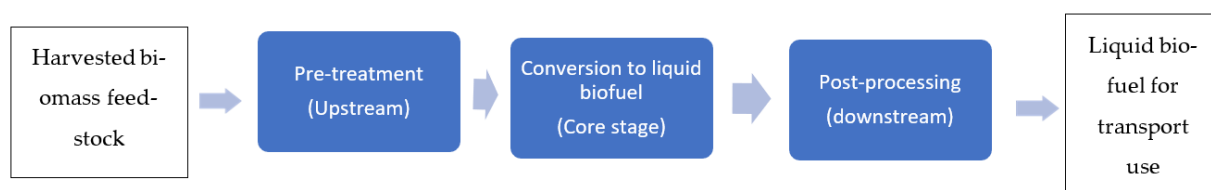


Figure 1. Basic structure of a generalized biofuel production value chain.

2.1. Pretreatment of Biomass Feedstock (Upstream Processes)

After the agricultural operations (ground preparation, planting, cultivation and harvesting, etc.), the biomass is moved to a point where it is accessible by road vehicles. This might include chipping or pelleting to perform the necessary size reduction of the material collected or baling for easier transportation. Then, the biomass is loaded onto trucks to go to the energy conversion facility [28].

The purpose of pretreatment methods is to reduce moisture, remove impurities, increase H/C ratios and energy content and improve the overall fuel property of biomass (such as heating value, moisture content, ash content, etc.) [29,30]. In the case of lignocellulosic feedstocks, additional pretreatment processes should also be applied toward changing the structure of the lignocellulose in order to make cellulose more accessible [31]. The general classification scheme of biomass pretreatment has been reported by Anukam et al. (Figure 2) [32]. As it can be seen, the reported pretreatment methods can be classified as: physical (targeted for thermochemical and biochemical conversion) and chemical and/or biological (targeted specifically for biochemical conversion). Physical pretreatment reduces the particle size to increase surface area and pore size, and chemical pretreatment is based on the use of compounds (organic and inorganic) to disrupt biomass structure and crystallinity [31]. Biological pretreatment involves fungi that produce enzymes that degrade, depolymerize and cleave the contents of biomass [32].

Following the harvest and collection of biomass, physical pretreatment focuses on the reduction of size. Starting from its as-received condition, biomass size is reduced according to the rough dimensions specified by the end user [12]. The biofuel heating rate heavily depends on the particle size of biomass when it comes to a thermochemical conversion process. It should have small dimensions in order to facilitate rapid heating and achieve high liquid yields [30]. The selection of optimum particle size may depend on several factors, such as the biomass's physical and material properties and the process–operational variables of the comminution system (e.g., shear forces). The most widespread technology for biomass comminution is hammer mills due to their high throughputs and flexible processing of many types of materials. According to Bridgewater [33], 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.

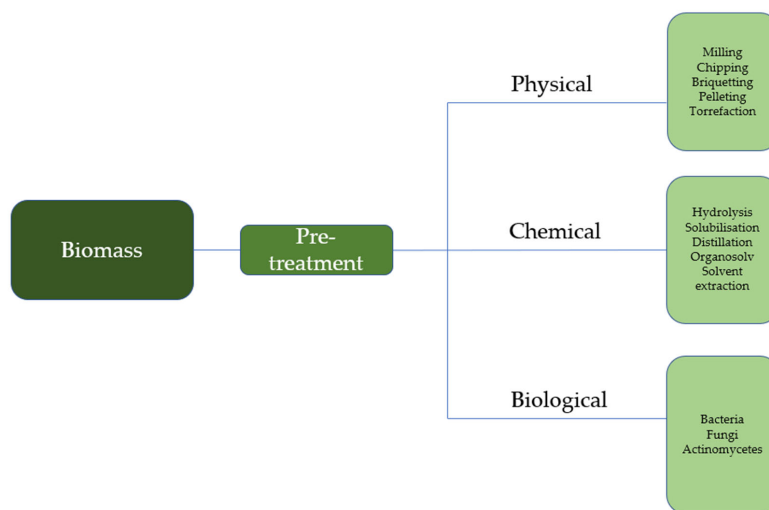


Figure 2. Classification of biomass pretreatment [32].

Once size reduction has been achieved, the next step is usually drying and densification of the biomass. This is performed in order to assure consistent properties (such as shape, bulk and unit density, size and durability), which determine the subsequent stages of storage, transportation and handling and have a significant influence on the feedstock cost and quality. Drying and densification is a process that produces pellets from raw biomass. The biomass is reduced in particle size, dried to 10–12% moisture content, steam conditioned and pelletized [12].

Other physical pretreatment methods include briquetting and torrefaction [32]. Torrefaction is a thermal degradation of biomass in mild conditions (250–300 °C). Contrary to pellet mills, briquetting machines can handle particles that are large in size and have higher moisture contents [34].

Common chemical pretreatment methods are hydrolysis, solubilization, distillation, organosolv and solvent extraction [32]. Another method is the acid treatment of biomass with H₂SO₄, which splits C-O bonds (present in connections between cellulose, hemicellulose and lignin). Like acid pretreatments, alkaline pretreatments with NaOH, Ca(OH)₂ and NH₄OH can improve the biomass structure by removing the lignin component and improving cellulose digestibility [29].

Biological pretreatment is considered advantageous because it does not generate toxic substances, can produce high yields of the product and has a low energy demand. However, the process is considered slow, and conditions need to be controlled carefully [32].

2.2. Conversion to Liquid Fuels

After the pretreatment stage is completed, a conversion process is needed to convert biomass into the desired liquid fuel. The most popular thermochemical conversion methods are (a) gasification followed by Fischer-Tropsch synthesis and (b) pyrolysis (Figure 3).

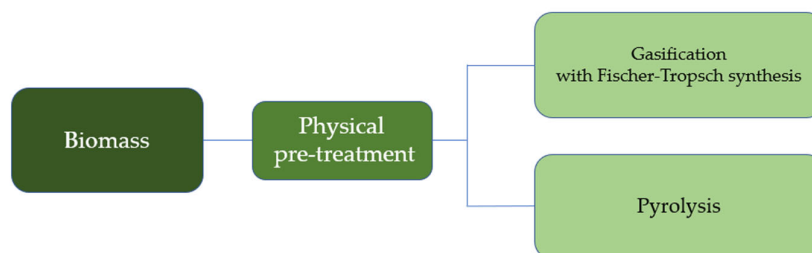


Figure 3. Classification of thermochemical methods.

On the other hand, the most common biochemical conversion methods are fermentation and transesterification.

2.2.1. Thermochemical Conversion

Gasification

One of the popular thermochemical methods applied to lignocellulosic biomass is gasification. Biomass reacts with air, oxygen or steam toward the production of a gaseous mixture of CO, H₂, CH₄, CO₂ or N₂ along with a variety of hydrocarbons. This mixture is widely known as synthesis gas, producer gas or syngas [35]. The main objective of gasification is to produce as much gaseous products as possible and simultaneously maximize the carbon conversion ratio by minimizing condensable hydrocarbons and unreacted char. Furthermore, different parameters affect the syngas composition, such as the type of feedstocks, their respective input ratios, process parameters and the reactor type used [36]. Gasifiers are capable of gasifying almost any kind of organic feedstock (agricultural residues, municipal solid waste, wood, etc.). If an atmospheric fluidized bed gasifier is used, then a mixture of feed with a bed material is “fluidized” (actually kept under constant motion) by air or oxygen and/or steam (the gasifying agents) introduced from the bed bottom. After that, direct or indirect heat is supplied to the gasifier in order to increase the gasification temperature in the range of 600–1000 °C [37]. Further, the typical residence time for the gasification reaction is 3–4 s [38]. 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 it is subsequently introduced to a gas–solid separator (e.g., a cyclone) in order to facilitate the separation of solid particles and the exhaust gas [39]. The produced syngas can be used as a typical gaseous fuel. In addition, syngas is also considered an intermediate step toward the final production of liquid fuels. The corresponding processes are presented in the next section, which presents post-processing steps.

Another alternative to conventional gasification is supercritical water gasification (SCWG). SCWG can effectively destroy cellular tissue and lead to the production of new compounds. The pressure ranges from 20 to 30 MPa, and a temperature within 400–700 °C [40]. Another alternative to SCWG is supercritical fluid extraction, which corresponds to the thermal disruption process of the lignocellulose in a temperature range of 250–400 °C under a pressure range of 4–5 MPa. This process is capable of effectively extracting and separating organic compounds from a matrix [41]. However, it is quite difficult to decompose lignocellulosic material in the production of biofuels due to its heterogeneous and recalcitrant structure [42]. Various studies have been performed focusing on biomass gasification with supercritical water, such as spent grain slurry [43] and microalgae [40].

Pyrolysis

Pyrolysis is defined as a thermochemical process in which lignocellulosic biomass is heated in the absence of oxygen and subsequently decomposed into a carbon-based solid product and volatile matter [44]. The most popular configurations used are fluidized beds (bubbling and circulating) since they are widely appreciated for their problem-free operation [45]. Depending on the residence time, pyrolysis can be characterized as slow or fast. Fast pyrolysis is accomplished by high heating rates, low vapor residence times and moderate temperature, which is constantly monitored and controlled. The liquid yield in fast pyrolysis is high compared to intermediate and slow pyrolysis, and the by-products, which are char and gas, can be utilized in the process (as providers of the required heat to eliminate all waste streams except for ash and flue gas), making fast pyrolysis a preferred option for liquid biofuel production [46]. Feedstock should be prepared in the form of small particle sizes and heat transfer rates to the particle range between 600 and 1000 W·cm⁻². Residence time should be limited to a few seconds to minimize char formation [30]. Moderate temperatures (in the range of 450–550 °C) are implemented depending on the species of crop and the end-product [47].

Pyrolysis provides three product phases: liquid pyrolysis oil, non-condensable gases and char. The ratios of each one of the three products are determined by operating conditions, reactor design and feedstock characteristics, including ash content as well as the relative amounts of cellulose and lignin. The fast pyrolysis liquid, also known as bio-oil, is obtained after the produced vapor is condensed. It is considered to be the main product of the process. Bio-oil yields can reach up to 80 wt% from dry feed. Furthermore, bio-oil contains water (<30% wt.) and various oxygenated compounds [48]. Char is a carbon-rich solid residue. It is usually separated from the fast pyrolysis vapors by cyclones. Fast pyrolysis has been the focus of many recent experiments for biomass feedstock, such as beech wood lignin [49], pitch pine [50] and date palm petiole/seed [51].

2.2.2. Biochemical Conversion

Fermentation

Fermentation is the metabolic process in which enzymes secreted by micro-organisms transform an organic substrate. Depending on the presence or not of oxygen, two basic types of fermentation are distinguished, respectively: aerobic and anaerobic. There are many micro-organisms in nature that provide fermentative transformation, and some produce ethanol from sugar or starch [52]. The ethanol-producing micro-organisms belong to three categories: yeast, bacteria and mold (mycelium).

Transesterification

Transesterification provides practically all of the biodiesel production currently. This process involves the reaction of a triglyceride (vegetable oils, animal fats, waste cooking oil [53]) with an alcohol (methanol) toward the formation of esters and glycerol.

During the esterification process, the triglyceride reacts with alcohol in the presence of a catalyst. The reaction of alcohol and fatty acids provided the monoalkyl ester (biodiesel) and crude glycerol. Usually, methanol or ethanol is used, producing methyl or ethyl esters, respectively. The base catalyst of KOH is considered more appropriate for producing ethyl ester biodiesel, but also NaOH can be used to obtain methyl ester. The products of the reaction are biodiesel and glycerol. The process is successfully finished when the methyl ester (biodiesel) and glycerol layers are distinctively separated after the reaction time. This crude light biodiesel phase requires some purification prior to use [54].

2.3. Post-Processing

Post-processing is an important part of the value chain because the output of the main conversion stages most probably needs additional treatment to assure compatibility with the existing infrastructure and comply with final fuel specifications.

Regarding the syngas produced by gasification, downstream processes are applied in order to obtain a liquid output. For acquiring liquid fuels from syngas, the following options are prominent: (a) H₂ by Water Gas Shift Reaction (WGSR), (b) hydrocarbons by Fischer–Tropsch (FT) synthesis or (c) methanol synthesis followed by further reaction to produce hydrocarbon or oxygenated liquid fuels [30,55]. Upgrading techniques are required to convert most of the syncrude (Fischer Tropsch product) phases into a single “biocrude oil”. These include various processes typical in crude oil refineries, such as cracking, hydrotreating, isomerization, aromatization, alkylation and oligomerization procedures. The goal is to produce a higher-quality oil end-product that can then be marketed as a synthetic crude oil to refiners [56].

Regarding bio-oil, stabilization is required in order to deal with the relatively high contents of water and oxygen [57]. Some common methods are herewith presented.

Catalytic cracking (CC) is a biofuel-producing process via the breakdown of bio-oil into low carbon aromatics and light olefins. The alkylation of aromatics with olefins produces C₈–C₁₅ hydrocarbons similar to diesel, while zeolite is considered the most highly effective catalyst. Hydrocracking, which is a variant of CC, uses supplemental H₂ in addition to a high temperature (400 °C) in order to achieve the catalytic decomposition of long

molecular chains and reach a conversion efficiency of up to 20% for gasoline fractions [57]. However, catalytic cracking has a few disadvantages, such as limited production of lighter hydrocarbons (aromatics) and a large deposition of coke [21].

Hydrotreatment refers to conventional oil industry processes, with an operating temperature range between 310 and 375 °C. H₂ is added in the presence of a 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 [57]. The main goal of hydrotreating is breaking the carbon-nitrogen, carbon-oxygen and carbon-sulfur bonds in reaction with H₂ [58]. In addition, hydrotreatment increases the calorific value of bio-oil [29].

Crude oil usually contains char particles that need to be removed with a filter to improve bio-oil properties. Filtration is divided into two categories: (a) liquid phase filtration and (b) hot vapor filtration. One major advantage of this method is that it prevents downstream corrosive and catalyst poisoning effects [29].

Solvent addition is another method that increases stability and decreases the viscosity of bio-oil. Common solvents such as acetone, isopropanol, ethanol, methanol and N,N-dimethylformamide have been observed to improve the physicochemical bio-properties of bio-oil. This method is considered a very simple approach to upgrading [29].

3. Effects of Heavy Metal (HM) Contaminated Input along the Liquid Biofuel Value Chains

In this section, the presence of contamination in the value chains examined is assessed in order to identify the corresponding effects and implications. Their effect is studied in each of the typical stages of the existing value chains, including pre-processing, conversion and post-processing steps. Special focus is assigned to the gasification and pyrolysis conversion processes, reviewing the fate of contaminants along each process. In the gasification process, parameters such as temperature, pressure, HM type and concentration are evaluated. At the same time, in pyrolysis, the major parameters considered were residence time and reactor temperature. Few relevant data were made available for the case of biodiesel production; therefore, this chain is partially addressed.

3.1. Pre-Processing of Contaminated Feedstocks

Regarding bioethanol feedstocks, Asad et al. [59] examined pretreatment options of lignocellulosic and woody HMxCB. Three widely used processes of chemical pretreatment (with dilute acid, alkali-catalyzed and ethanol organosolv) were investigated. The fractionation of phytoremediation biomasses for the production of bioethanol is also described. It was reported that in acidic conditions, pre-processing at a temperature of 170 °C with a sulfuric acid solution of 2% *w/w*, extracted up to 90% of metals (for Zn and Mn) recovered in the water effluent. As regards the intermediate product for the following process steps, a clean pulp was obtained. On the other hand, under alkaline conditions, low extraction of metals was observed. In a soda pretreatment of an HMxCB at temperatures over 170 °C, the metal recovery was high, while a clean liquid stream and lignin were obtained. For organosolv, metal concentrations were mainly in the pulp and to a lesser extent in the water effluent and lignin. Wu et al. [60] implemented three chemical pretreatments. As a result, two optimal chemical pretreatments were identified (12% H₂SO₄, 4.0% NaOH + 2.0% H₂SO₄) that could capture 99% (of the total in raw stalk) Cd from the mature stalks.

Concerning feedstocks for gasification, dry pretreatment methods can be utilized. However, there have been no reports on how HMs affect the yield and quality of the syngas [25]. On the other hand, according to a study by Yu et al. [61], the wet pretreatment method of leaching with distilled de-ionized 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.

The pretreatment of HM-contaminated feedstocks for pyrolysis has been intensively assessed. The relevant literature [25,62–74] distinguishes pre-processing methods in the dry

and wet. Dry pretreatment methods include processes such as preheating, crushing and torrefaction, while wet methods incorporate the utilization of acids or solvents. Various studies have examined the influence of both dry and wet pre-processing on the yield and H content of bio-oil acquired from Heavy Metal-Contaminated Biomasses (HMCBs).

Regarding dry pre-processing, two relevant studies [62,63] chose to reduce the contaminated feedstock to a particle size of below 2 mm before the introduction to the pyrolysis stage. Nevertheless, according to the findings of Wiinikka et al. [64], enhanced conversion is achieved with finer particles (less than 0.25 mm in size). Lower conversion rates were reported in [64] for larger particle sizes (between 0.5 and 1.0 mm).

Wet pretreatment aims to demineralize the biomass feedstock before further processing, thus promoting the enhancement of bio-oil yield and quality. Heavy metal presence in biomass has been found to favor gas and bio-char production at the expense of lower liquid yield [65–68]. Wigley et al. [69] followed a combined treatment approach by applying both wet (acid leaching) and dry (torrefaction) treatments. Acid leaching was performed for 4 h in a solution containing 1% acetic acid at a temperature of 30 °C, while torrefaction took place for 20 min at 270 °C.

Alternative treatments have also been reported, which can be applied as a supplement to the original “decontamination” attribute of pyrolysis itself (transformation of toxic HM ions to an amorphous state in the bio-char [70,71]). Phosphate-assisted pyrolysis contains HMs in phosphate minerals [72,73], and other materials can be used to stabilize the heavy metal load of the biomass feedstock, such as FeCl₃, Al₂O₃, NaOH and CaCO₃ [74]. Nevertheless, the application of these alternative treatments is mostly advised in order to safely dispose of HMCB, and not when bio-oil production is the first priority [25].

3.2. Conversion of HM-Contaminated Feedstocks to Liquid Biofuel

3.2.1. Fermentation

Regarding the production of bioethanol, Asad et al. [59] examined enzymatic hydrolyses of HM-enriched and HM-free pulps. The influence of the metal load on the enzymatic hydrolysis into monomeric sugars was investigated, and little or no effect on polysaccharide hydrolysability was observed for metals such as Zn, Fe and Mn. Sayago [75] concludes that various cases of Cr-doped biomass can be used for bioethanol production since the HM load had an insignificant influence.

Nevertheless, the chromium samples produced 33% less ethanol than the “clean” hydrolyzed biomass of *E. crassipes* (8000 mg/L vs. 12,100 mg/L after 25 h). On the contrary, Wu et al. [60] claim that the Cd accumulation in rapeseed stalks could improve biomass enzymatic saccharification and consequent bioethanol production under two-step (4.0% NaOH + 2.0% H₂SO₄) 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 Ko et al. [76], while Cr presence is also beneficial for the same process. On the other hand, negative impacts of biomass Zn and Cd contents on enzymatic hydrolysis were reported in the same paper, especially for lower enzyme dosages. In addition, the Cr contaminant in the biomass was shown to facilitate enzymatic hydrolysis at all three dosages. For Zn in biomass, a smaller impact was reported on bioethanol SSF processes.

3.2.2. Transesterification

Unfortunately, no papers examined biodiesel production from HM-contaminated feedstocks. Therefore, the content of HMs in biodiesel, obtained from vegetable oil derived from HMCB, remains an underexplored topic. In a study by Angelova et al. [77] on the deposition and allocation of HMs in oil crops, the content of Cd, Cu and Pb in plant organs and in the oil of rapeseed (*Brassica napus* L.) grown in a polluted area, is reported. HMs were distributed in the following order (in decreasing value): leaves > stems > roots > fruit shell > seeds. In the seeds, which contain pure plant oil, the concentration effect of HMs was the lowest. However, the quantities of Pb, Cu and Cd in the rapeseed oil were higher

than the accepted thresholds for human consumption. However, it has not been specified yet if the biodiesel exhaust fumes from rapeseed plants are associated with hazardous metal emissions [78].

3.2.3. Gasification

On the other hand, various studies have examined the fate and effect of HM through the gasification of contaminated biomass feedstocks. HMs can contribute to corrosion, fouling and erosion of the gasification facilities. Another common issue is catalyst deactivation [79,80]. Moreover, during the gasification process, many unwanted products are formed, such as ash and tar [81,82]. The tar, which sometimes contains HMs, can cause significant problems, such as plugging and corrosion and filter blockage [81].

Studies have heavily focused on the different parameters of the gasification process that contribute to the transfer and distribution of HM compounds into the gas phase. Many experiments and modeling simulations have been implemented that deduced different results. A simulation from Jiang et al. [79] concluded that temperature and HM content of the biomass are critical parameters that influence the fate of HMs in the gasification process. Some elements (As, Cd, Zn, Pb) volatilized at temperatures above 600 °C, others (Ni, Cu, Mn, Co) transferred to the syngas at temperatures 1000–1200 °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 HM transition temperature by 100–200 °C [79]. According to the bench scale experiments performed by Cui et al. [83], most HMs volatilized 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 [83]. Syc et al. [84] studied the distribution of HMs in the gasification system. The experiment focused on the gasification of energy crops (flax, mixed hardwood). The results showed that the HMs Cd, Zn, Pb, Ni and Cu were found in the bed ash, cyclone ash and downstream syngas. Further, the HM content in the syngas was found to be in the range of 0.37–4.2 mg/m³ [25].

In another experiment by Pudasainee et al. [80], which involved the introduction of a slurry composed of glycol and straw char in a gasifier reactor, it was deduced that the heavy metal load was allocated in many parts of the gasification systems, such as the cooler, boiler and the syngas cleaning section. Furthermore, Ni had the largest concentration in the syngas (53.2 µg/Nm³), followed by Cr, Pb, As, V and Cd. Hg has the lowest concentration (24 µg/Nm³) [80].

The volatilization temperatures of HMs in the gasification process, according to empirical and theoretical studies, can be categorized as follows:

1. Certain HMs (Mn) may be entirely condensed in gasification gas.
2. Others (Hg and Cd) are mostly expected to be present in the syngas.
3. Co can be totally or partially volatilized at hot gas cleaning systems temperatures ranging between 500 and 800 °C
4. A considerable group of HM species As, Cd, Zn, Cr, Pb, Cr, Sb and Ni will also be present in syngas, even at temperatures lower than 500 °C [25].

From the simulations and experiments that are mentioned above, it is apparent that the HMs that are contained in the contaminated biomass are volatilized. However, the type and amount of heavy metals that transfer to the gas phase are heavily dependent on temperature and pressure. The most common HMs that can be found in the syngas are Zn, Cu, Pb and Cd. Generally, a temperature lower than 1000 °C and a pressure of up to 30 atm are considered optimal conditions for gasification in terms of limiting the transfer of many volatile HMs [79].

It is important to note that when it comes to liquid biofuels (and bio-oil in particular), benchmark values have not been set for the maximum accepted level, as regards both inorganic compounds and heavy metal contents [25]. An upper limit <0.10 wt% for particles as well as for HMs has been recommended [85].

In addition, the distribution of HMs depends on [25]:

1. Chemical speciation of metals and dynamics of fluidization.

2. Reaction temperature and pressure.
3. Nature of the heavy metal-contaminated biomass.
4. Application of upstream or downstream treatment processes.
5. Reactor type (fluidized, fixed or entrained bed).
6. Effect of the materials contained in the fluidized bed.
7. What type of gas (air, oxygen, steam, etc.) is the 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 order of magnitude lower than those of a fluidized bed gasifier [86,87]. Additionally, the steam-fluidized is better than the air-fluidized bed gasification when it comes to the volatilization of HMs [88,89]. 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 H₂O, O₂, CO₂) is not the most important parameter that influences HM transfer to the syngas [90].

In order to acquire an overview of the HM load ratio that is carried from the feedstock to syngas after the completion of the conversion stage, Figures 4 and 5 have been elaborated. This ratio is important since syngas will be subsequently transformed to liquid biofuel through the Fischer–Tropsch process. For better distinguishing of the reported data points, Figures 4 and 5 cover the HM load ranges of 0–2570 and 0–7250 mgHM·kg⁻¹, respectively. The *x*-axis contains the feedstock HM loads, while the respective part that was carried by the syngas (also in mg of HM contained in syngas per kg of feedstock) is represented in the *y*-axis.

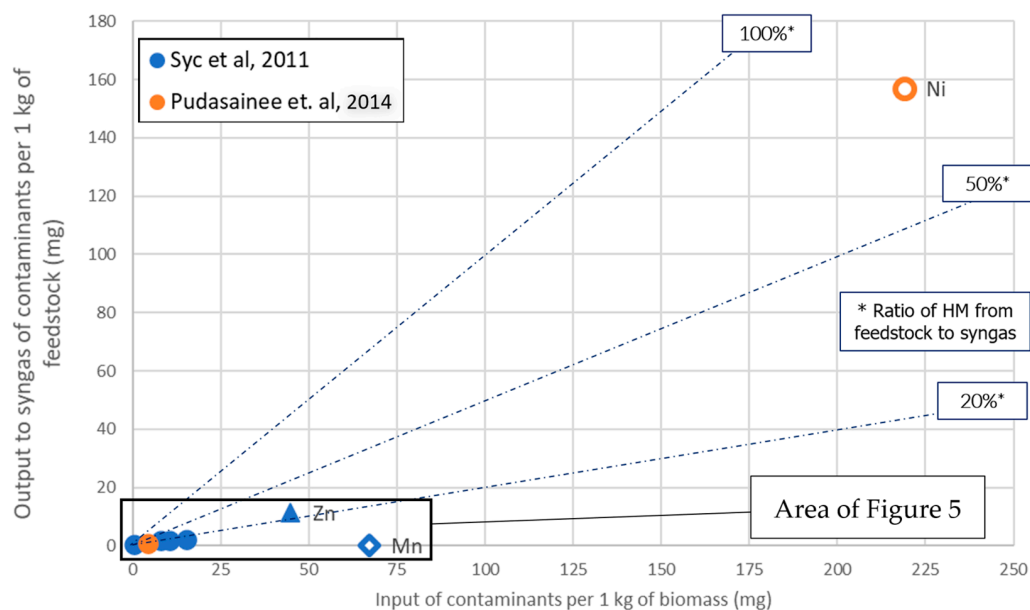


Figure 4. Gasification: Output to syngas vs. input with feedstock of HM species. All available input loads shown. Adapted from [80,84].

The data are distinguished in terms of the specific HM species and the source they have been retrieved from. In particular, Ni data are shown by a hollow circle, Pb by a triangle, while the rest of the HM species have a corresponding representing shape. Accordingly, the color of each point corresponds to the respective literature source. The diagonal lines with the indications “100%”, “50%” and “20%”, represent cases in which the produced syngas carries the corresponding ratio of the HM load. This means that the worst cases are closer to the “100%” line.

The abovementioned qualitative findings of the literature review are confirmed in Figures 4 and 5. A high risk of Cd presence in the syngas is demonstrated; nevertheless,

there is only one data point with a very low Cd load (~1 ppm). The relevant risk for Ni and Zn also seems higher than the rest of the HM species. All species examined show at least a 20% incorporation to syngas, except for Mn. Only two cases of syngas showed contamination levels higher than 10 ppm: Ni (~160 ppm) in [80] and Zn (11 ppm) in [84].

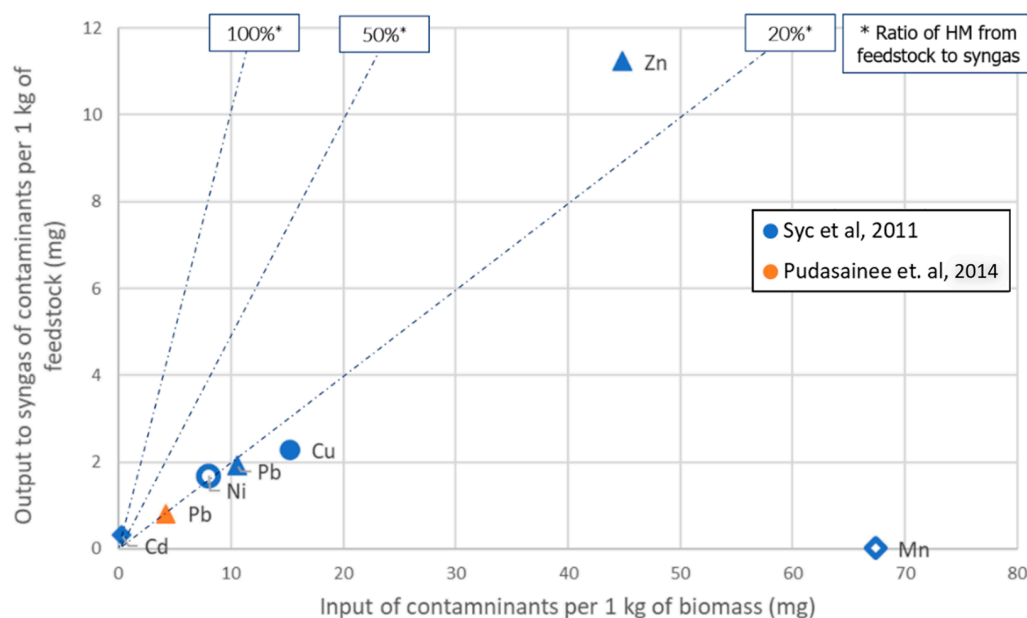


Figure 5. Gasification: Output to syngas vs. input with feedstock of HM species. Focus on low-input loads. Adapted from [80,84].

3.2.4. Pyrolysis

Flash pyrolysis generally meets the requirements of accomplishing the research goals of HMCB utilization: the rather low pyrolysis temperature (as opposed to combustion and gasification) inhibits metals from volatilization, and valuable bio-oil is obtained [91].

Mineral matter is typically carried by biomass. Generally, the major biomass minerals are composed of Ca, Si, K, Mg and Na, with smaller amounts of P, S, Mn, Al and Fe and trace amounts of heavy metals. Inorganic compounds are found in the form of silicates, oxides, sulfates, phosphates, carbonates and chlorides. The ash (mineral) content has an influence on the liquid, gaseous and solid fraction production rates and properties (adsorptive properties of char, heating value and the elemental composition) [66,92,93].

The most influential process parameters in terms of quantity and quality of the products obtained are: (a) reactor temperature, (b) residence time, (c) heating rate, (d) physico-chemical pretreatment, (e) particle size and (f) geometrical configuration of the reactor and solid heat carrier [44,93,94].

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

1. to acquire a final product (bio-oil) with zero (or negligible) heavy metal load,
2. to minimize the emission of any gaseous compound containing heavy metals (such as free ions, hydroxides or carbonates) and
3. to capture heavy metals in the structure of the bio-char.

A variety of factors (i.e., plant type, operating conditions [95], pretreatment [86,96], as well as downstream processes [86,91]) have been shown to affect the characteristics of both the liquid and the solid output in various ways. Zhong et al. [97] have pyrolyzed a hyperaccumulating plant carrying high HM loads, both under slow and fast conditions. The HM concentrations for 1 kg of biomass feedstock were reported to have the following values: Al: 13,976 mg; Zn: 9838 mg; Fe: 642 mg; Cd: 560 mg; Cu: 77.6 mg; Pb: 62.5 mg and Cr: 45.4 mg. It was shown that high reaction temperatures and heating rates favored the increase in HM concentration in the liquid product (e.g., Cd and Zn showed higher

concentrations in bio-oil produced at 750 °C than 650 °C). The temperature of 650 °C was actually optimal in terms of bio-oil quality (low HM concentrations) and yield.

Another experiment was performed by Lievens et al. [94], studying the lab-scale pyrolysis process of treating a sunflower feedstock with Cd, Cu, Zn and Pb. The volatilization of Cd and Zn was conveniently prevented due to non-favorable temperature levels of 623 K. Cu and Pb were correspondingly bound in the biochar within a temperature range between 623 and 873 K [94]. Moreover, a related study [98] showed that the pH of the liquid fraction increases with temperature raise, therefore, reducing the solubility of heavy metals.

The flash pyrolysis of HM-rich willow was the topic of [91]. It was thereby shown that a temperature rise from 350 to 550 °C facilitated Cd volatilization, while Zn remained in the bio-oil. Only traces of Pb were found in the bio-oil, even at the maximum temperatures examined. The study determined the optimal temperature range in terms of bio-oil yield and corresponding HM load, in the range of 350–450 °C. It was not advised to opt for lower operating temperatures, despite more intense HM incorporation in the biochar. The reason for that was the worse properties of the bio-oil obtained.

Leijenhurst et al. [86] applied fast pyrolysis on agricultural waste at a process temperature between 400 and 600 °C. The inorganic elements were almost entirely (>95% wt.) absent from the bio-oil, while heavy metals were contained in the bio-char in particular. Higher reaction temperatures and the respective volatilization of heavy metals under these conditions have also been identified by [91,97] to facilitate the gaseous phase transfer of heavy metals. Additional affecting parameters include the structural bond between HMs and biomass [67,99,100] and between HMs and the organic vapors produced [90].

HMCB pyrolysis was also the core process of the work by Dilks et al. [98]. The reactor was coupled with a downstream cyclone, achieving less HM loads in the bio-oil, while no upstream pretreatment was applied. The biochar obtained was reported as not suitable to be disposed of in the environment, as well as inappropriate to be used in terms of metal extraction/recovery. The same negative assessment regarding the biochar attributes was shared with [91].

Focusing on fluidized beds, Koppolu et al. [101] showed that it is possible to operate at higher temperatures (~600 °C) without any adverse effects regarding the incorporation rates of HM into biochar. However, Stals et al. [91] propose quite a lower temperature (around 350 °C) for a fluidized bed pyrolysis reactor coupled with a hot gas filter.

The issue of the influence of pyrolysis temperature is also assessed in [94,102–104], where higher oxygen bio-oil content and increased tar cracking were observed at 700 °C, leading to a decrease in terms of the bio-oil heating value (~16.8–19.0 MJ·kg⁻¹). On the other side, lower temperatures are assigned to less HM in the bio-oil [105,106] and higher biochar output [97,105]. A quite important side-effect of choosing a pyrolysis temperature on a scale of 350–450 °C is the minimum HM leachability of the biochar obtained. This finding has been confirmed in the cases of Cd and Pb contamination [91,107].

The optimum operating temperature for HMCBs pyrolysis is 350–450 °C in terms of the maximum HMs removal and acceptable bio-oil yield, which can be extended by 150–250 °C (i.e., threshold of 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. [108] 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 the pyrolysis of biomass [25].

Apart from the influence of temperature, the bio-oil yield and contents are heavily affected by the lignocellulosic composition of the contaminated feedstock [65]. As demonstrated by Lievens et al. [94], pyrolysis of two different contaminated biomass samples (sunflower and birch) provided a variety of outputs in terms of corresponding fraction yields, attributes and energy contents. In addition, heavy metals tend to show various concentrations and respective accumulating trends in different parts of the feedstocks harvested (e.g., leaves, branches, stems, etc.) [67,71,99,109]. As a consequence, a difference

may be observed regarding the yield, composition and heating value of the bio-oil obtained after pyrolyzing different parts of the contaminated biomass [94].

Similar to the previous gasification section, all of the literature cases that provided enough data to be represented in an HM input-output diagram were elaborated upon [62,64,86,97,110], and the corresponding figures (Figures 6 and 7) were obtained. In the pyrolysis case, the important ratio is how much of the HM load is contained in the bio-oil, since out of this intermediate product, the final biofuel will be eventually acquired. In parallel to the gasification process, fast pyrolysis is expected not only to provide a good yield of bio-oil but also to capture the HM load in the biochar. Due to the better distinguishing of data points, two figures are presented, covering the HM load ranges of 0–16,000 and 0–100 mgHM·kg⁻¹, respectively.

The high risk previously identified regarding the presence of Cd in the syngas is also demonstrated in the case of bio-oil. This risk is additionally observed for Pb, while Zn shows both very high and very low cases of incorporation in bio-oil. Cu also demonstrates a mixed behavior, in two cases with a very low incorporation ratio and one with a medium ratio. As an overview, at least 25% of most of the HM species examined ended up in the bio-oil, except Mn. A specific source [97] contained the cases featuring a high HM concentration in bio-oil: ~500 ppm of Cd, >400 ppm of Zn and ~40 ppm of Pb.

3.3. Post-Processing

3.3.1. Post-Processing of Bioethanol

Sayago [75] reported that there is no contamination present in the produced ethanol, but chromium remains in the waste and is, therefore, disposed of. In addition, a desorption process with chemical reagents (e.g., sodium hydroxide (NaOH)) for chromium recovery and reuse was proposed.

3.3.2. Post-Processing of Syngas

As it was mentioned above, by increasing the operating temperature of the gasification process, the volatilization rate of HMs and the ability of applied filters to capture elements with fine particulates in the syngas are negatively affected [83,109]. Many HMs (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 [25]. According to another report, cyclones were not effective in capturing some HMs such as Cd, Zn, Pb and Cu because of the high temperature of syngas and their high volatilization [82].

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 [86,111]. Stals et al. [91] reported that the reduction induced by gas filtration is observed for all three tested temperatures (623, 723, 823 K), and the volatilization increase with increasing temperature is only present for the case of cadmium.

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 of 0.3–20 µm. On the contrary, the electrostatic precipitators had lower efficiency (75%) for other particle sizes such as 4–400, 1.80–309 and 3.90–375 µm. HMs (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 [112]. Finally, the ash, which is a by-product of the gasification process, needs to be managed or disposed of. If the ash from the gasification of contaminated biomass from HMs cannot be reused, landfilling seems to be a promising disposal method [84].

3.3.3. Post-Processing of Bio-Oil

It is important to distinguish the downstream impact of the HM load from the positive catalytic effect of heavy metals in terms of bio-oil energy content and yield by enhancing thermo-decomposition and activation energy during the core process [62,113–116]. The post-processing stage expected to be the most affected by the HM load of the bio-oil is

catalytic upgrading [86]. Relevant problems focus on catalyst poisoning and deactivation, subsequently degrading the process efficiency. Additional detrimental impacts can be correspondingly expected from water content and coke presence, always depending on the attributes of the catalyst used [86,117–119]. In particular, the Fe and Cu from HMCB pyrolysis have been found to accumulate in the active areas of catalyst HZSM-5 [117], while coke is reported to have poisonous effects on catalysts thereby lowering useful product yields [120,121]. On the contrary, a situation of benefits caused by the presence of coke has also been reported by [122], where ZnO₂ poisoning by CO₂ and water is correspondingly impeded.

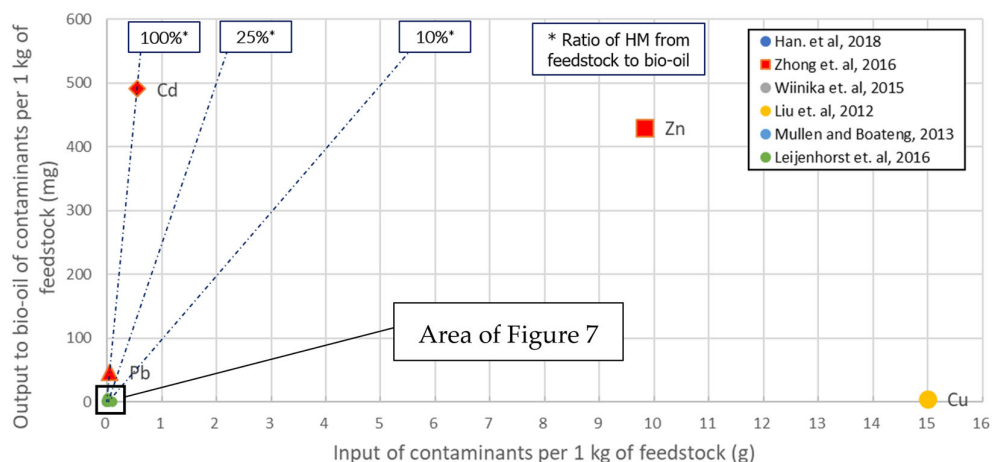


Figure 6. Pyrolysis: Output to bio-oil vs. input with feedstock of HM species. All available input loads are shown. Adapted from [62,64,86,97,110,117].

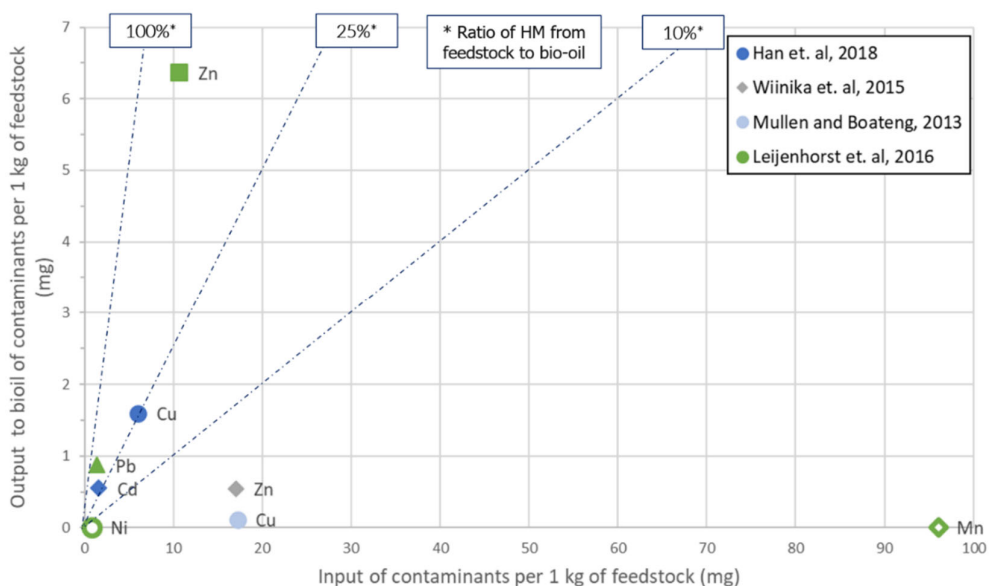


Figure 7. Pyrolysis: Output to bio-oil vs. input with feedstock of HM species. Focus on low input loads. Adapted from [64,86,110,117].

Nevertheless, various literature sources claim the primary production of HM-free bio-oil from contaminated biomass feedstocks [62,63,94,123]. In a pilot-scale experiment, Wiinikka et al. [64] demonstrated, on the one hand, the feasibility of HM-free bio-oil and, on the other hand, the concentration of heavy metals in the biochar.

It seems, however, that post-treatment processes should be eventually applied, at least for cases of high-HM concentrations in specific types of heavy metal hyperaccumulating

species. Relevant options would include separation methods before bio-oil condensation [64,86], or even considering cyclones, as recommended and tested by [97]. Moreover, as concluded by [25], downstream upgrading would be facilitated by adopting an additional treatment process, such as the adsorption or filtration of the bio-oil produced by fast pyrolysis.

4. Clean Liquid Biofuel Value Chains

This section combines the main points and findings of the literature reviews of the previous sections regarding biofuel value chains and implications/adaptations of utilizing HMCBs. It aims to provide a descriptive analysis of alternative value chains capable of providing HM-free liquid biofuel. In the present level of analysis, the identification and incorporation of adaptations relevant to the HM input are performed in qualitative terms. In other words, the chains proposed do not correspond to specific HM loads (both in terms of quantity and HM species carried).

The present study follows the value chain distinction by the European Technology and Innovation Platform (ETIP) [26], where first-generation biofuel chains are categorized as “established” and the second-generation as “priority”. Established value chains are value chains at Technology Readiness Level (TRL) 9, e.g., they are widely used in many industrial installations [26]. On the other hand, the priority value chains are developed beyond the research stage while not yet being established industrially, i.e., TRL5-8. Their technology will facilitate the utilization of sustainable feedstock sources, which are converted to biogas and biofuels, under the term “2nd generation” or “advanced” biofuels [26].

For the purpose of the present work, the term “clean biofuel chain” is assigned to a group of processes capable of producing a biofuel carrying a minimum load of contaminants. Nevertheless, no general benchmark values have been set for the maximum acceptable level of HM contents neither in bio-oils nor other biofuels. In fact, the only heavy metal present in the Directive 2009/30/EC, which determines the specifications of petrol, diesel and gasoil, is Pb with a limit of 5 mg/L and only in the case of petrol (not for diesel). In addition, there are no heavy fuel limits for biofuels in the current standards related to the production, storage, transportation and use of biofuels: EN590 (biodiesel); EN14214 (FAME); EN228, EN15736 (bioethanol). There is only one single reference in EN14214, but it is not relevant to heavy metals (it refers to limits for Na+K (combined) and Ca+Mg (combined), both sums being below 5 ppm). As a consequence, there is not a commonly accepted level of HM contamination below which a biofuel is considered “clean” or “HM-free”.

In order to overcome the absence of general benchmark values for the maximum acceptable level of heavy metals (with the sole exception of Pb in petrol), a measuring campaign of heavy metals in existing transportation fuels in Europe has been reviewed [124]. Fossil transport fuels have been reported to contain only traces of HMs (averaging between 5 and 33 ppb or $\mu\text{g}\cdot\text{kg}^{-1}$) [124]; 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. A rather strict benchmark is thus provided for the biofuels that wish to “claim” that do not contain more heavy metals than existing transportation fossil fuels.

4.1. Established and Clean Value Chain 1 (EVC1 and CVC1)—Sugar to Alcohols

In general, sugars obtained from sugar crops, starch crops and lignocellulose are fermented into alcohols (Figure 8). Bioethanol is the expected product, while biobutanol can be produced if engineered yeast with special bacteria is used. Lignin can be obtained as a co-product, which is useable as an energy carrier, animal feedstock, food ingredient, etc.

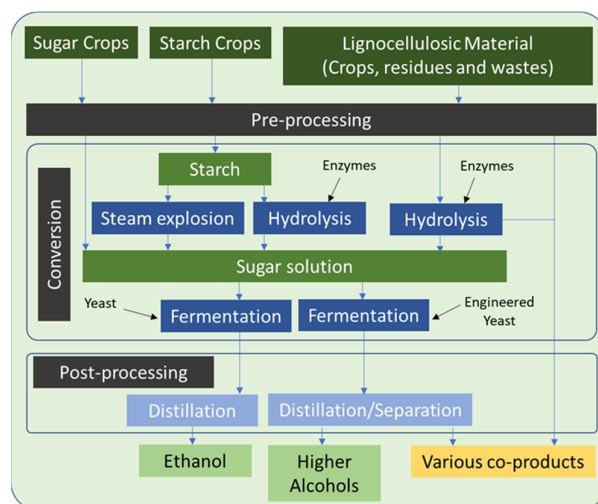


Figure 8. EVC1—Sugar to alcohols. Adapted from [26].

According to the information based on the previous experience of producing bioethanol from HM-contaminated feedstocks, a pre-processing stage is necessary to extract 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 9 summarizes the main features of clean value chain 1: sugar to alcohols.

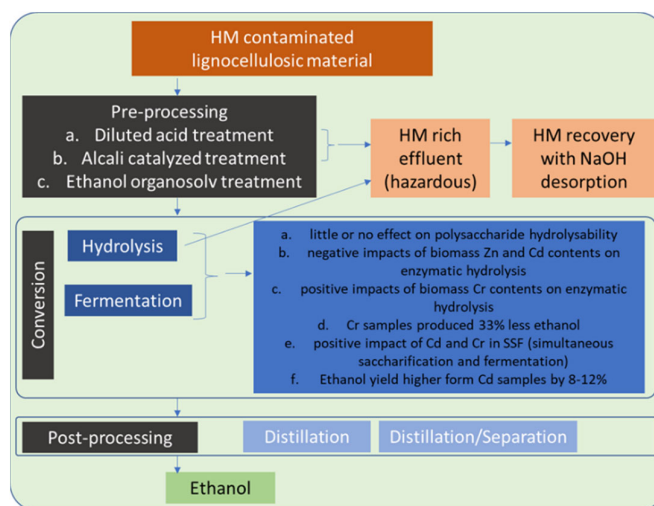


Figure 9. CVC1—Sugar to alcohols. Adapted clean value chain.

4.2. Established Value Chain 2: Oil Crops to Biodiesel

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

Unfortunately, there is no information retrieved regarding the effects or possible adaptations regarding the production of biodiesel from HM-contaminated feedstocks. Therefore, the unavailability of relevant literature prevents the representation of a corresponding clean value chain. There is, however, a main positive outcome from relevant papers: The

HMs 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.

4.3. Priority Value Chain 1 and Clean Value Chain 2 (PVC1 and CVC2)—Biomass to Liquid (BtL) via Gasification

Any lignocellulosic material, such as wood from forestry, short rotation coppice (SRC) or energy crops, is suitable for feedstock. Syngas is produced with gasification, while the Fischer–Tropsch (FT) process, combined with upgrading steps, can provide usable liquid fuels [26]. The Priority Value Chain 1 is presented in Figure 10.

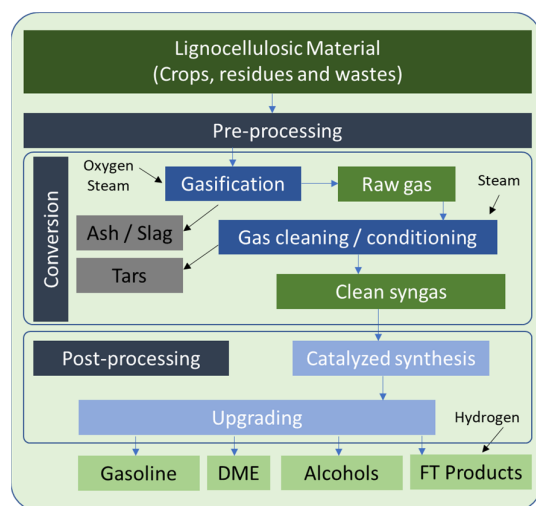


Figure 10. PVC1–BtL via gasification. Adapted from [26].

For the clean value chain, on top of the pretreatment options presented in Figure 9, de-ionized water is also proposed, as presented in Section 3.1. In a typical gasification process, HMs are expected to concentrate mostly in the bottom and fly ash; therefore, 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 above-mentioned measures are expected to provide an HM-free syngas for further processing (Figure 11).

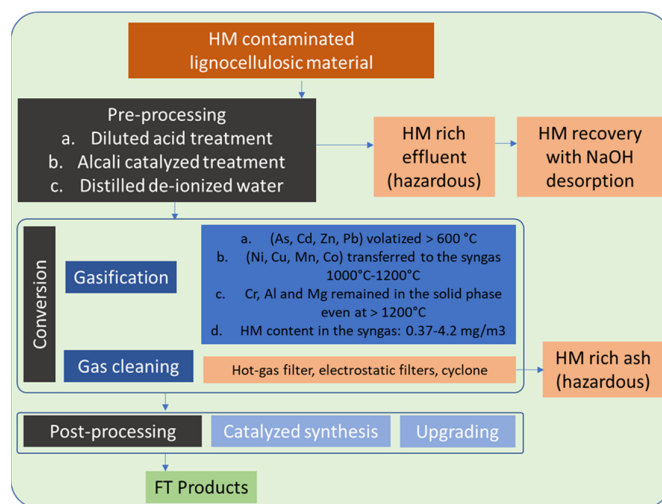


Figure 11. CVC2–BtL via gasification. Adapted clean value chain.

4.4. Priority Value Chain 2 and Clean Value Chain 3 (PVC2 and CVC3)—Biomass to Liquid (BtL) via Pyrolysis

In parallel to Section 4.3, 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 currently be used to replace heating oil. It may also be upgraded into advanced biofuels that have the same combustion properties as conventional fossil transport fuels [26]. The corresponding priority VC2 is presented in Figure 12.

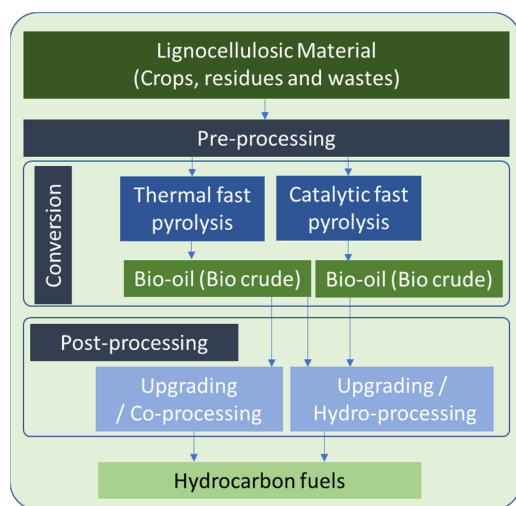


Figure 12. PVC2–BtL via pyrolysis. Adapted from [26].

Regarding CVC3 (Figure 13), all pre-processing treatments previously identified 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. As concluded from the corresponding literature review in the previous section, 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. Hot gas filtering is reported to be beneficial towards reducing the HMs in bio-oil, which can be further decontaminated with micro-filtration.

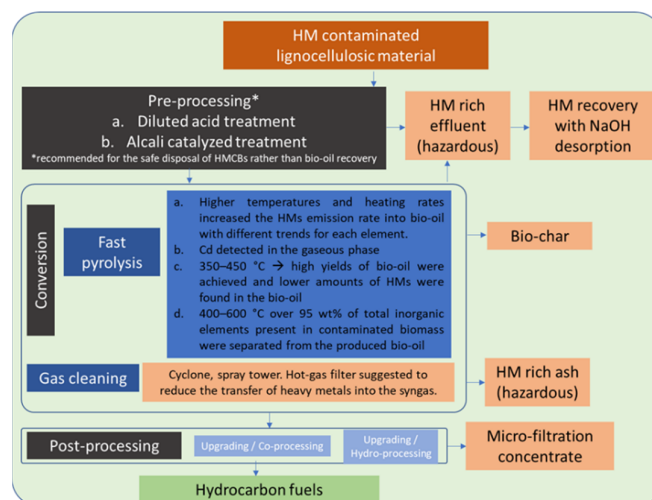


Figure 13. CVC3–BtL via pyrolysis. Adapted clean value chain.

5. Conclusions

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

Toward 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. The mechanisms affecting the fate of HM in the various process streams are quite complicated and are affected by various process parameters. An in-depth analysis was performed in Sections 3.2 and 3.3 for the conversion and post-processing stages, indicating the complexity of the matter. Nevertheless, the fate of the most common HM species present in contaminated biomass has been identified and graphically represented.

This work 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, so as to (potentially) provide a liquid fuel with a comparable HM load to existing fossil transport fuels.

This work goes a step further than existing reviews of experiments and simulations regarding HMCB valorization to biofuels since feasible value chains are described by synthesizing the findings of the several studies examined. By defining the adapted value chains, the “road is paved” toward establishing realistic process chains and determining system boundaries, which are actually essential methodological steps of a Life Cycle Assessment. Moreover, various critical evaluation and optimization methodologies (e.g., supply chain optimization, techno-economic assessment of the entire value chain) will benefit from the present work. The necessity of implementing LCA and optimization/evaluation methodologies and having a system boundary of a complete value chain has been stressed by both relevant literature reviews [24,25].

Further research needs to pursue a quantitative approach. The quantification of efficiencies regarding the processes considered and the capture of contaminants requires detailed mass/energy balances along the chain stages. The enhanced quality and quantity of data are thus necessary in order to achieve this goal and eventually compile the Life Cycle Inventories required. One issue that will need intensive data acquisition is the formulation of HM feedstock load scenarios since that will most probably have an effect on the configuration of specific process chains that can provide clean biofuels under variable HM input loads. Finally, options for managing or even valorizing the hazardous effluents or contaminated mass outflows for all alternative adapted chains should be further investigated and evaluated.

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