

Review

A Comprehensive Review of Biomass Pretreatment Technologies for High-Quality Fuel Production: Emphasis on Washing, Torrefaction, and Combined Approaches

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Abstract

Biomass is an abundant renewable feedstock for combustion, co-firing, gasification, and pyrolysis, but in its raw form, it is a low-grade fuel. Low energy density, high moisture, and high contents of alkali and alkaline earth metals (AAEMs) and chlorine drive slagging, fouling, and corrosion in thermal equipment. Pretreatment is therefore required to meet the fuel-quality specifications. This review critically examines biomass pretreatment technologies, including physical, chemical, and biological, and then focuses on the two routes most relevant to solid-fuel upgrading, namely water/solvent washing (leaching) and torrefaction (thermochemical). Washing removes water-soluble and organically bound AAEMs, directly reducing slagging and fouling propensity, but it adds moisture, requires a drying step, and does not increase energy density. Torrefaction raises the higher heating value and carbon contents, lowers oxygen and moisture contents, and improves grindability and hydrophobicity, but the accompanying mass loss concentrates the residual AAEMs, so the treated fuel can retain or worsen its slagging tendency. Because the two methods correct complementary deficiencies, deashing versus deoxygenation and energy densification, this review evaluates the combined washing-torrefaction route as an integrated strategy. The combined route delivers what neither single method achieves alone: high AAEMs removal, increased higher heating value (HHV) and carbon content, reduced oxygen and moisture, and balanced bio-oil and biochar yields in subsequent pyrolysis. The review further compares the methods against the fuel specifications of each end-use, summarises the limited pilot and demonstration-scale evidence, and techno-economic questions that currently keep combined pretreatment at the laboratory stage.

Keywords: biomass washing; torrefaction; combined pretreatment; AAEMs; slagging; fouling; biomass upgrading; pyrolysis



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1. Introduction

1.1. Background and Rationale

Fossil fuels are being depleted rapidly, necessitating the search for alternative energy sources to meet the world's energy needs. The utilisation of fossil fuels faces challenges,

including carbon dioxide emissions, limited fuel supply, and other environmental factors. Although technology has been developed to minimise these effects, there are still several factors that need attention [1–4]. Thus, there is a need to explore alternatives to fossil fuels and replace them with renewable energy resources that are cost-effective and energy-efficient [5]. In this scenario, biomass is an appreciable renewable energy resource.

Among renewable energy sources, solar and wind power are intermittent and weather-dependent, requiring storage or backup capacity to ensure a stable supply [6]. Moreover, solar, wind, and hydropower primarily generate electricity, whereas many end uses still rely on combustible fuels. Biomass is the only renewable resource that can be converted into liquid, gaseous, and solid fuels that are storable, transportable, and compatible with existing combustion engines and fuel infrastructure [2,7]. This makes biomass-derived fuels particularly relevant for hard-to-electrify sectors such as heavy-duty transport, agriculture, and marine applications [7]. Therefore, biomass is considered a complementary rather than competing option within the renewable energy mix. Among untreated biomass, energy crops and straw are viable alternatives to fossil fuels for large-scale heating and power production units [8,9]. It is estimated that in the year 2050, various developed countries will meet their energy requirements from renewable resources, with about 50% coming from biomass [10,11].

1.2. Biomass Availability and Utilisation

The history of biomass use dates back to ancient times, and the utilisation of agricultural biomass as an energy source is documented in the literature as early as 1830, in the production of biofuel from *Euphorbia abyssinica* in Ethiopia [1]. Biomass is produced worldwide in many forms, and some of these are wheat straw, rice straw, canary grass, and sugarcane bagasse. Wheat straw is a globally abundant biomass that is available in many countries. Different continents have their major biomass residues [1,12,13]. Wheat and rice residues are produced mainly in South Asia, maize residues in North America, and sugarcane bagasse in South America, where Brazil accounts for most of the production [14]. Figure 1 summarises the estimated global annual availability of lignocellulosic agricultural waste biomass, among which maize stover, wheat straw, and rice straw are the most abundant, each exceeding one billion tonnes per year [14].

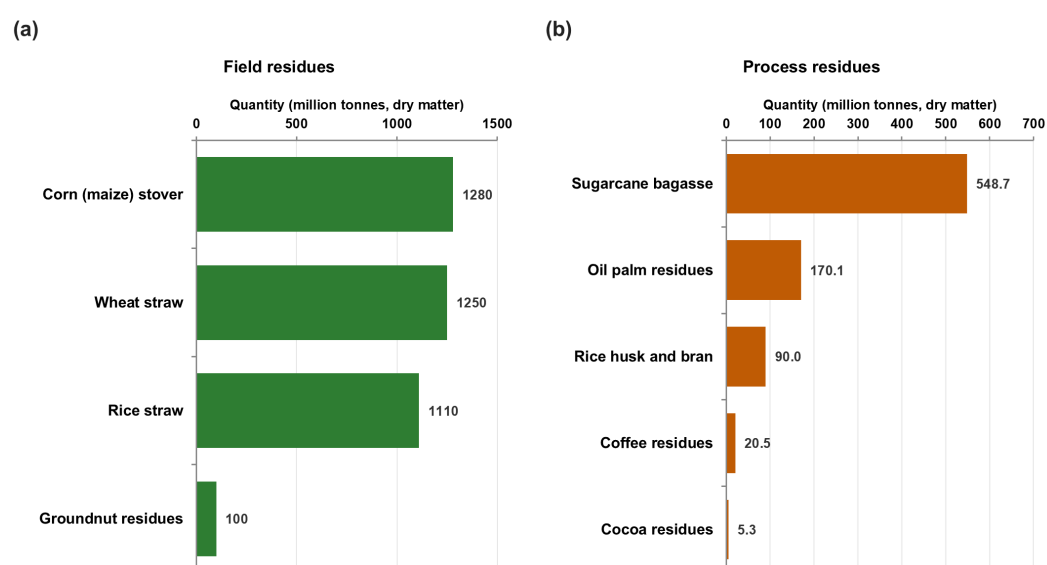


Figure 1. Estimated global annual availability of the main agricultural wastes (dry matter basis): (a) field residues; (b) process residues.

Biomass can be classified into different categories based on its origin and main sources. These can be agriculture, forestry, and organic wastes. These main sources have further classifications, as given in Figure 2.

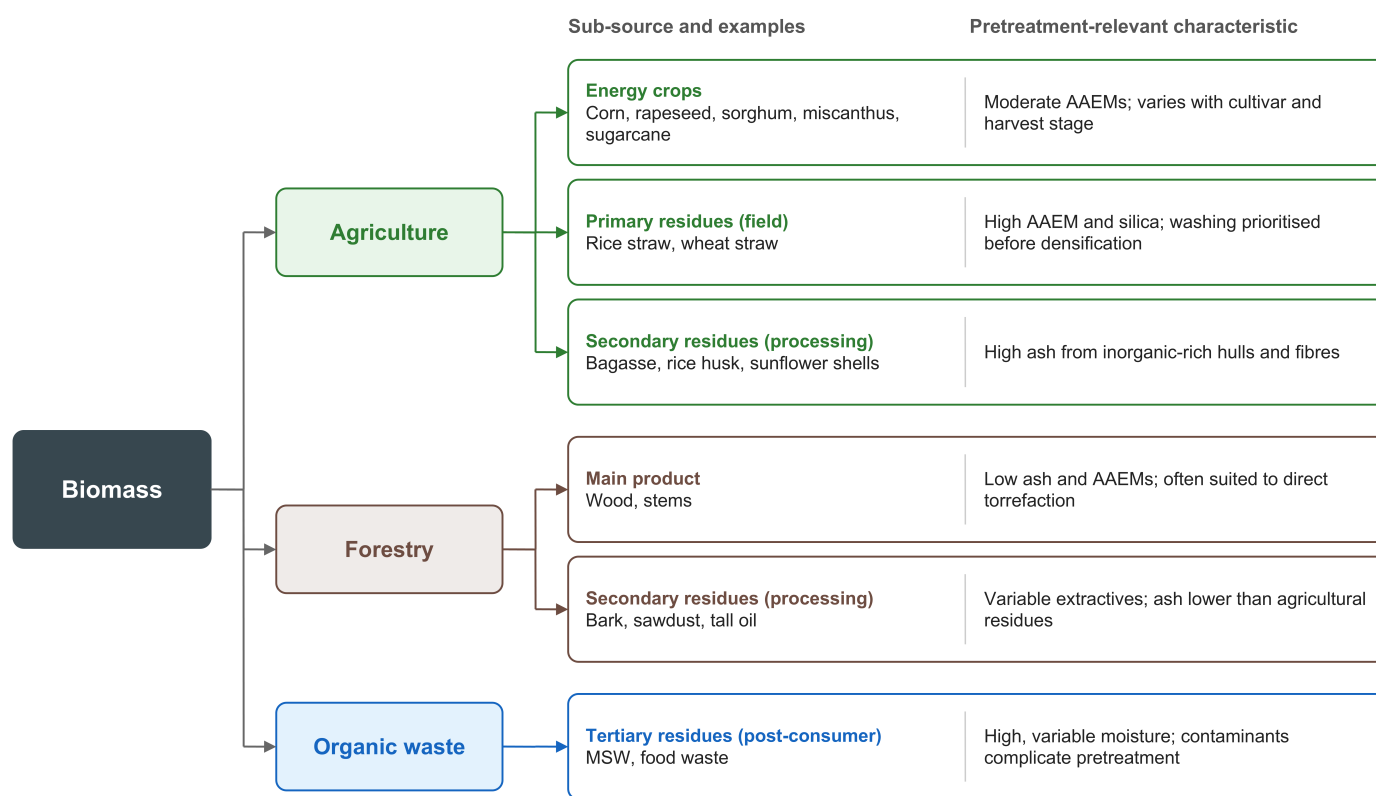


Figure 2. Classification of biomass by origin and its principal implications for pretreatment selection. Adapted from [15].

Bioenergy is already the largest renewable energy source, supplying about 56 EJ in 2023, equivalent to 9% of global primary energy supply and about 61% of all renewable energy, with solid biomass accounting for 83% of this supply [9]. Its future contribution depends strongly on land availability, crop yields, and the recovery of residues and wastes; recent projections place the global bioenergy potential in 2050 between 64 and 313 EJ, corresponding to 7.5–37% of global energy supply, with residues and bio-wastes expected to play a growing role [16]. Agricultural residues such as wheat and rice straw, corn stover, and sugarcane bagasse are among the most abundant of these resources (Figure 1).

1.3. Types of Biomasses

Based on the origin of biomass, it can be divided into primary, secondary, and tertiary residues, as well as energy crops (Figure 2). Primary residues are generated in the field (e.g., rice and wheat straw), secondary residues arise during processing (e.g., bagasse, rice husk, bark, and sawdust), and tertiary residues are post-consumer wastes (e.g., MSW and food waste). Biomass can also be classified based on its properties, as shown in Figure 3. These types are woody, herbaceous, aquatic, and waste-derived biomass. All the mentioned types of biomass have their distinct properties and structures [17].

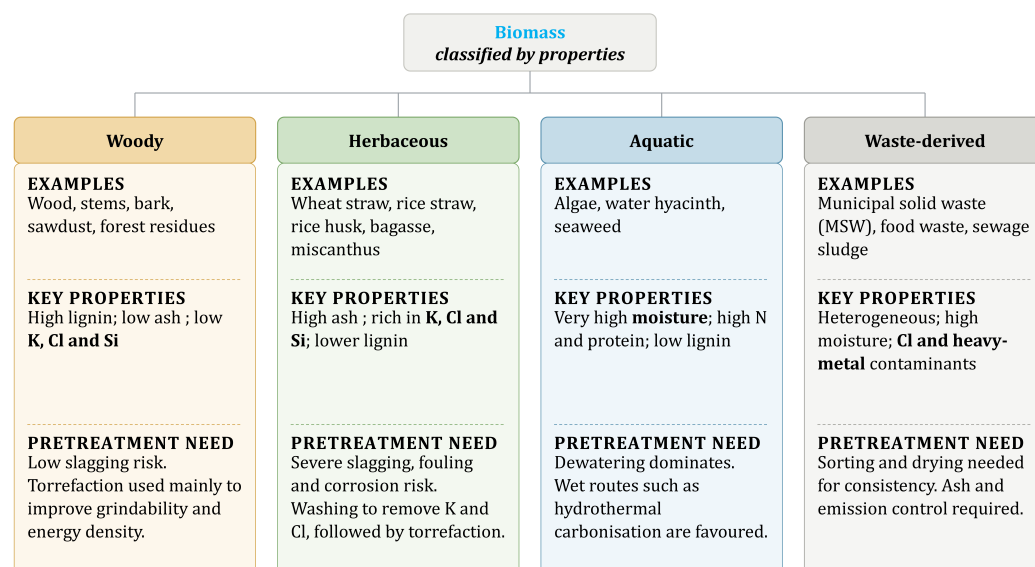


Figure 3. Classification of Biomass Based on Properties.

1.4. Properties of Biomass

Biomass properties are of vital importance in selecting the conversion method and other parameters that improve fuel quality. The choice of biomass depends on the energy requirement and the availability. The selection of conversion methods depends on the fuel properties [18,19]. Since these properties vary naturally with feedstock type, plant part, and growing conditions, their typical ranges for agricultural waste biomass are summarised in Table 1, together with the EN ISO 17225-6 limits for graded non-woody pellets [20,21]. Higher heating values favour energy recovery, whereas high ash, AAEMs, and chlorine contents, particularly potassium and chlorine, promote slagging, fouling, and corrosion during thermochemical conversion [22]. High moisture content reduces the net energy available, and the lignocellulosic composition, particularly the lignin content, governs the choice of pretreatment and conversion route [23].

Table 1. Typical ranges of key properties of agricultural waste biomass and EN ISO 17225-6 limits for graded non-woody pellets.

Property	Typical Range	ISO 17225-6 (A/B)	Ref.
Higher heating value (MJ/kg)	13.7–19.7	$\geq 14.5^2$	[20,21,24]
Ash content (wt%, dry basis)	0.3–16	$\leq 6/\leq 10$	[21,22,24]
Moisture content (wt%, air-dried)	≤ 10	$\leq 12/\leq 15$	[21,24]
Volatile matter (wt%)	71.5–90.8	–	[24]
Fixed carbon (wt%)	7.0–16.5	–	[24]
K ₂ O in ash (wt% of ash) ¹	6.95–50.2	–	[22]
CaO in ash (wt% of ash) ¹	2.41–20.95	–	[22]
MgO in ash (wt% of ash) ¹	1.54–7.59	–	[22]
Na ₂ O in ash (wt% of ash) ¹	0.16–4.62	–	[22]
Nitrogen (wt%)	–	$\leq 1.5/\leq 2.0$	[20,21]
Sulphur (wt%)	–	$\leq 0.2/\leq 0.3$	[20,21]
Chlorine (wt%)	–	$\leq 0.1/\leq 0.3$	[20,21]
Cellulose (wt%)	38–50	–	[25]
Hemicellulose (wt%)	20–35	–	[23,25]
Lignin (wt%)	15–30	–	[25]

¹ Alkali and alkaline earth metals (AAEMs), expressed as oxides. ² ISO value refers to net calorific value as received. A and B denote the two quality classes of EN ISO 17225-6; where a single value is given, it applies to both classes.

Proximate and ultimate analyses highlight the compositional contrast between raw biomass and fossil solid fuel. Wood shows the highest volatile matter content (82 wt.%) alongside low moisture (20 wt.%) and minimal ash (1 wt.%), yielding a lower heating value (LHV) of 18.6 MJ/kg, while wheat straw carries somewhat lower volatile matter (59 wt.%) and moisture (16 wt.%) but a higher ash content (4 wt.%), giving an LHV of 17.3 MJ/kg; lignite, included for comparison as a conventional solid fuel, shows the opposite profile, higher moisture (34 wt.%) and ash (6 wt.%) alongside lower volatile matter (29 wt.%), yet its greater fixed-carbon content (31 wt.%) drives a substantially higher LHV of 26.8 MJ/kg. This pattern is consistent with elemental composition: wood has the highest carbon content (51.5 wt.%) and lowest ash (1 wt.%), wheat straw shows slightly lower carbon (48.5 wt.%) with a higher ash content (4 wt.%), and rice straw shows the lowest carbon share (41.4 wt.%) because it is ash-rich, with ash typically 10–15 wt.% and dominated by silica, which dilutes the organic fraction [22,24,26,27]; hydrogen content ranges narrowly between 5.0–6.3 wt.% across all three, while nitrogen and sulphur remain low throughout (≤ 0.7 wt.% and ≤ 0.1 wt.%, respectively), reflecting the generally low heteroatom content typical of woody and herbaceous lignocellulosic biomass compared with fossil fuels [19,28].

Plants take up mineral nutrients from soil during growth, so the harvested biomass retains alkali and alkaline earth metals (AAEMs), namely K, Na, Ca, and Mg, together with other ash-forming elements, principally Cl, S, and Si, and to a lesser extent Fe and Al. Although Cl, S, Si, Fe, and Al are not AAEMs, they interact with the AAEMs and jointly govern the ash chemistry and the fuel behaviour towards slagging, fouling, and corrosion [29,30]. In this review, the term AAEMs is used strictly for K, Na, Ca, and Mg, and the other elements are named explicitly. The alkali metals are the principal issues; K and Na react with silica to form low-melting alkali silicate eutectics that soften and adhere to heat transfer surfaces, while in high-chlorine feedstocks such as straw they volatilise as KCl and NaCl, condensing downstream and degrading the protective oxide layers of boiler tubes [31,32]. Alkali chlorides further react with sulphur oxides in the flue gas to form sulphates (K_2SO_4 , Na_2SO_4), which deposit on convective surfaces and reduce heat-transfer rates [32,33]. Ca and Mg, by contrast, form refractory phases that raise the ash fusion temperature and partially suppress alkali silicate melting [29]. Since the alkali metals and chlorine are largely water-soluble, their removal from the fuel prior to combustion is an effective route to mitigate these ash-related problems [34,35].

1.5. Chemical Composition of Biomass

Biomass consists of two types of structures. The structural components are cellulose, hemicellulose, and lignin, while the non-structural components are extractives and other inorganic components that can be removed without altering the cell wall composition of the biomass [36]. The structural composition governs both biochemical and thermochemical conversion. For bioethanol production, a high cellulose content is preferred [18,19]. During thermal decomposition, the three polymers decompose over different temperature ranges: hemicellulose at about 220–315 °C, cellulose at about 315–400 °C, and lignin gradually over 160–900 °C [37]. Hemicellulose-rich feedstocks therefore lose more mass and release more volatiles within the torrefaction window, whereas lignin contributes most to char formation and the retained solid yield [38–40]. The structural components and the chemical composition of wheat straw, rice straw, sorghum straw, and barley straw are shown in Figure 4.

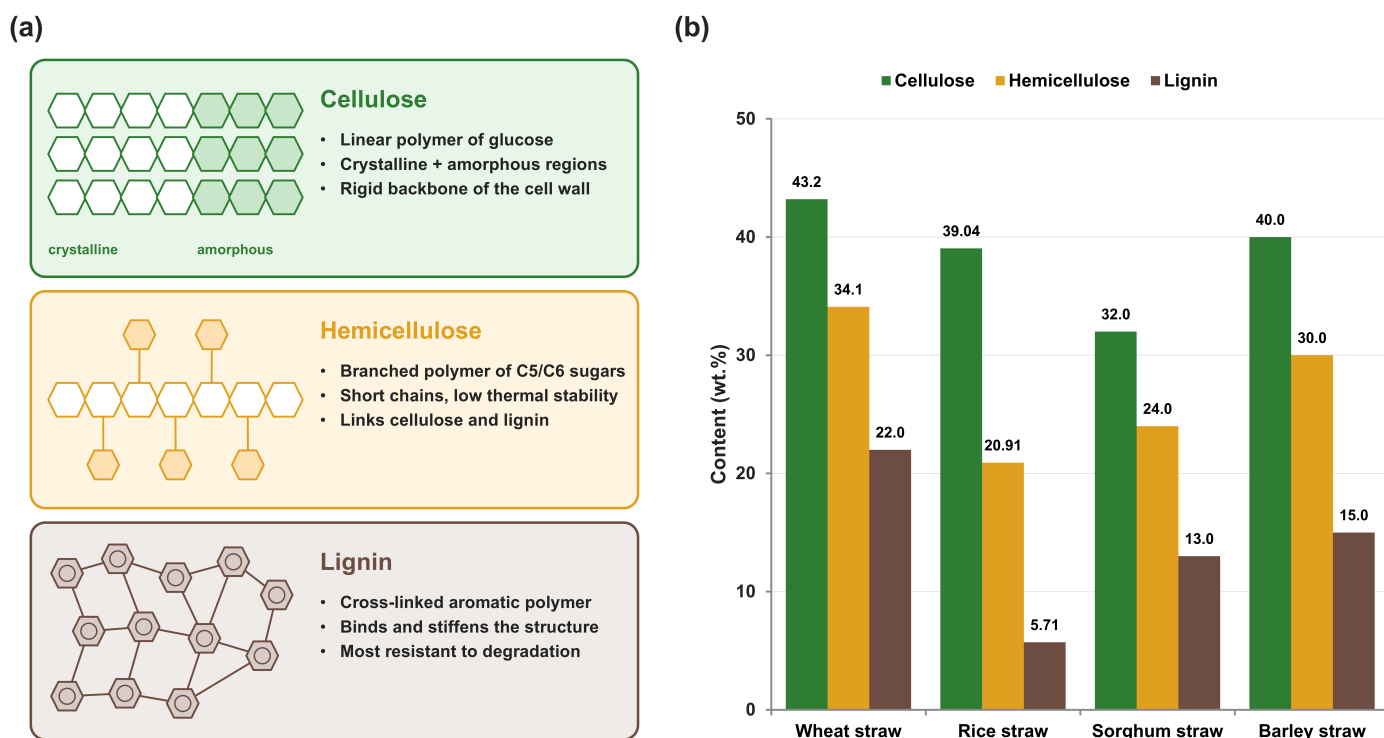


Figure 4. Chemical Composition of Biomass (a) Schematic of the structural components of lignocellulosic biomass; (b) chemical composition of wheat straw, rice straw, sorghum straw, and barley straw (wt.%). Data in (b) from Saleem [1].

1.6. Challenges Associated with Biomass

Biofuels produced from biomass are recognised for reducing greenhouse gas emissions and enhancing energy security [41]. Despite its potential, the widespread use of biomass as an energy source faces several challenges due to its inherent properties. These include the biomass composition, economic, and technological aspects [42]. Biomass composition varies significantly depending on its source, which includes energy crops, agricultural waste, forestry waste, and municipal solid waste (MSW). By nature, biomass has a lower energy density compared to fossil fuels, requiring larger volumes to produce the same amount of energy [43]. The higher heating values range between 17–21 MJ/kg for dry wood and 19–23 MJ/kg for bark. These are lower than those for coal 29–33 MJ/kg [36]. High moisture content further reduces energy density and efficiency during combustion or conversion processes, while AAEMs can cause slagging, fouling, and corrosion in combustion systems [19,28]. For efficient combustion of biomass, the optimal value of moisture content in biomass is suggested to be 8 to 10%, while the alkali content should be less than 0.5% for potassium and sodium combined [44].

1.7. Need for Biomass Pretreatment

AAEMs present in the biomass affect the combustion process and cause unwanted disruptions to boiler components. The main issues are slagging, fouling, and corrosion resulting from the AAEM and chlorine contents of biomass. Due to AAEMs' reactions, primary deposits form on the boiler tubes, containing high levels of sulphates and chlorides produced by the alkalis. It occurs due to the low melting points of these species, and these act as glue for the secondary deposits. During biomass combustion, gaseous KCl reacts with SO_2 and SO_3 to form K_2SO_4 and KHSO_4 . After combustion, as the temperature decreases, alkali sulphates condense to form a sticky material. The slagging formation is governed by the addition of fine particles in the form of KCl. These fine particles are deposited on the surface of the material and increase the amount of secondary deposits.

The practical severity of these mechanisms is confirmed by co-firing trials in a circulating fluidised bed, in which firing coal with rice straw, eucalyptus wood, or empty fruit bunch produced fouling deposits that grew in proportion to the biomass share, with potassium and chlorine identified as the principal deposit-forming species [29,45].

The slagging index predicts the boiler's tendency to form slag during combustion. The fouling index is used to predict the tendency of fuel ash (especially biomass ash) to cause fouling on convective heat-exchange surfaces in boilers, such as superheaters and economisers. Fouling leads to the formation of non-molten, sticky ash deposits that can significantly reduce heat-transfer efficiency and increase corrosion [29,46].

1.8. End-Use Applications and Target Fuel Specifications

Upgraded biomass is used in four principal thermochemical routes, each imposing a different fuel specification that the pretreatment must satisfy.

Direct combustion and co-firing with coal are the largest end-uses. Here, the binding constraints are ash-forming elements rather than calorific value, chlorine drives high-temperature corrosion, and potassium and sodium drive alkali-induced slagging and convective-pass fouling [29]. The international solid-biofuel standard ISO 17225 codifies these limits into graded classes for pellets and briquettes, specifying maxima for ash, Cl, S, and N and reporting ash-melting behaviour, precisely because herbaceous and agricultural fuels have low ash-fusion temperatures and cause fouling and corrosion in boilers [47,48]. Washing addresses these constraints directly by removing K and Cl, while torrefaction alone does not, and can raise the relative alkali content.

Entrained-flow and fluidised-bed gasification additionally require good grindability and low moisture so that fine, free-flowing particles can be fed and converted; AAEMs again govern agglomeration and downstream corrosion [38]. Torrefaction is well suited to the grindability and moisture requirements, which is why torrefied fuels are covered by their own standard (ISO 17225-8) for commercial and industrial use [48].

Densification (pelletisation/briquetting) is not an end-use in itself, but the logistics step that makes the others economic, setting requirements on durability, bulk density, and for torrefied material binder behaviour.

Fast pyrolysis targets a liquid product; here AAEMs act catalytically to promote ring-opening and cross-linking that suppress bio-oil yield and raise water and acid content, so demineralisation by washing is the decisive pretreatment for oil quality [26,49].

To address the challenges with biomass utilisation, various pretreatment technologies have been developed, including physical, chemical, physicochemical, biological, and thermochemical methods, and each carries distinct advantages and limitations. Physical methods reduce particle size at an industrial scale but do not improve fuel quality or AAEMs content [50,51]. Chemical and physicochemical methods achieve high delignification efficiency but generate corrosive or inhibitory waste streams and entail high solvent-recovery costs, which have so far confined them to laboratory and pilot scales [50,51]. Biological methods are the most environmentally benign option but are limited by slow kinetics, typically requiring residence times of a month or more [52]. Leaching (washing) and thermochemical (torrefaction) methods, instead, target the two deficiencies that disqualify raw biomass as a solid fuel directly. Washing removes the water-soluble and ion-exchangeable AAEMs and chlorine responsible for slagging, fouling, and corrosion, while torrefaction raises energy density, carbon content, and grindability, their weaknesses are complementary, since washing does not densify energy and torrefaction does not remove AAEMs. Combined pretreatment methods, discussed later in this review, build on these two routes to target liquid and solid product quality, respectively.

Several reviews already address LCB pretreatment, but their scope is almost exclusively biochemical. Acid, alkali, organosolv, ionic-liquid, deep-eutectic-solvent, and supercritical-fluid routes are evaluated for delignification and enzyme accessibility, ahead of enzymatic hydrolysis and fermentation to liquid biofuels. Very few benchmarks pretreatment performance against the fuel specifications that govern the largest-volume solid-fuel end-uses, direct combustion, co-firing, and gasification, where ash, chlorine, potassium, and higher heating value (HHV) are the binding constraints, nor do they treat washing and torrefaction as a complementary pair rather than as isolated techniques. It is this complementarity, together with their proximity to industrial deployment relative to the biochemical routes above, that motivates the present review's focus on washing, torrefaction, and their combination.

The objective of this review is to analyse and compare state-of-the-art pretreatment methods to enhance fuel quality. It seeks to evaluate the effectiveness, efficiency, and sustainability of various pretreatment techniques, highlighting their impact on fuel properties, conversion efficiency, and environmental benefits. Additionally, the review aims to identify current challenges and future research directions to optimise biomass processing for high-quality fuel production. Various pretreatment methods are studied in detail and compared. The focus of this study is on the washing and torrefaction pretreatment methods due to their ability to remove AAEMs, reduce ash content, increase heating value and energy density, improve the quality of pyrolytic products, and ease of operation. Case studies are included for the washing, torrefaction, and combined washing-torrefaction.

2. Biomass Pretreatment Technologies

Pretreatment of LCB is essential to improve its fuel quality, in particular its energy density, homogeneity, and ash chemistry. Pretreatment of LCB affects the subsequent processes of pyrolysis and combustion to achieve premium quality fuel. Figure 5 summarises the different pretreatment methods.

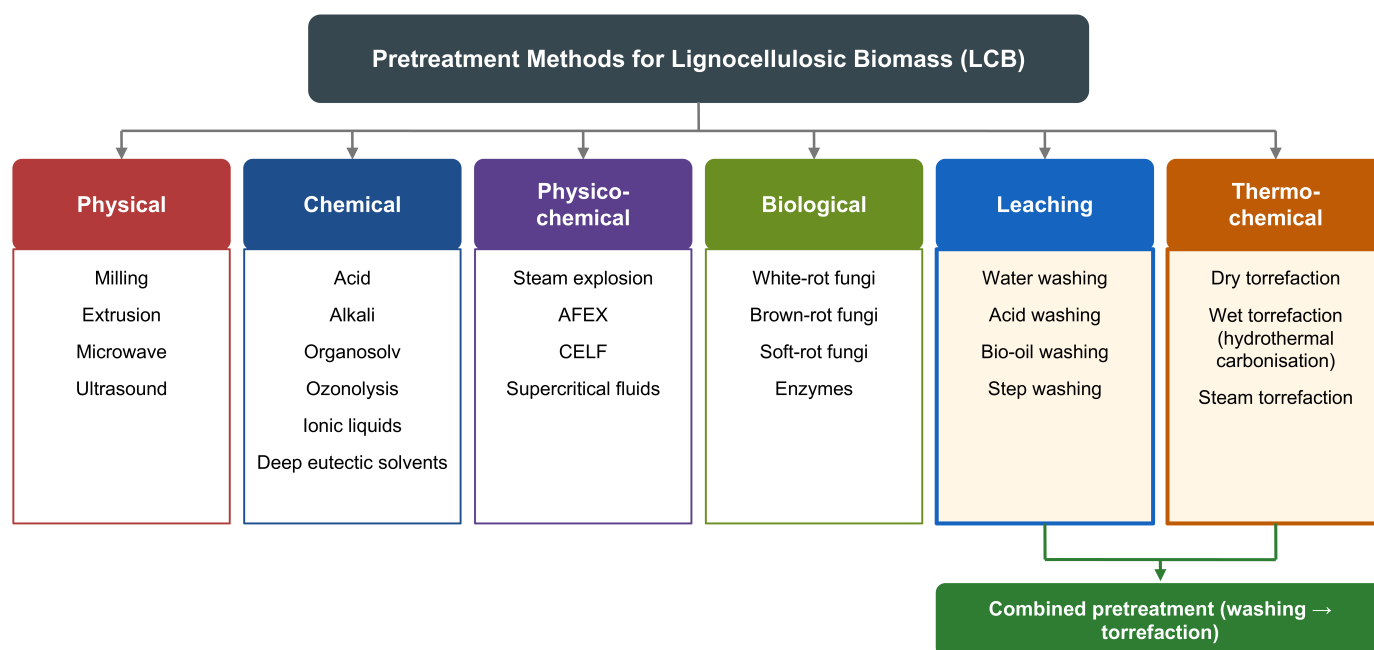


Figure 5. Pretreatment Methods for LCB.

2.1. Physical Pretreatment Methods

2.1.1. Milling Pretreatment

Milling is the most common technique for reducing the particle size of biomass. The method includes milling, grinding, chipping, and shredding of the biomass. The desired biomass size depends on the pretreatment method. Milling and grinding can provide a size between 0.2 and 2 mm. But if the desired size exceeds 10 mm, only chipping is performed. This method can provide biomass up to 30 mm in size [53]. Ball milling is an effective process for improving digestibility and crystallinity. Wet disk milling is preferred over ball milling because it enhances biomass hydrolysis [54]. Hiden et al. [55] performed wet disc milling and ball milling on rice straw. They observed that the energy required for ball milling was much higher than that of wet disc milling.

2.1.2. Mechanical Extrusion

In this pretreatment, screws reduce biomass size through shear force generated by moving blades. The biomass is compressed between the blades and the barrel, thereby increasing temperature and pressure, enhancing fibre cutting and enzyme accessibility. Key factors affecting output include screw type, moisture content, and temperature. For soybean hulls, glucose yield increased as extruder speed increased from 280 to 350 RPM, but decreased as temperature increased from 80 °C to 140 °C [50].

2.1.3. Microwave Pretreatment

There are many advantages of this method. These include easy handling, high heating capacity, small process time, and low energy requirements. This method was implemented by the scientist in Japan at Kyoto University in 1984 [56]. Sugarcane bagasse, rice straw, and rice hulls were pretreated using microwave irradiation [54]. Microwave irradiation encounters the surface of biomass materials and generates an explosion inside the particles. With continuous microwave exposure, the internal structure of biomass changes significantly [57].

Nowadays, microwave pretreatment methods are used in combination with other methods [56]. This method is also effective for bioethanol production [58]. Microwave pretreatment is gaining attention from researchers nowadays due to its many advantages, but due to emerging technology, there are also some drawbacks to this treatment. The initial setup cost is high compared to other techniques. As technology is in the developing stages, it is crucial to understand the dielectric specifications of various biomasses before implementing this technique.

2.1.4. Ultrasonic Pretreatment

This pretreatment method is used to accelerate chemical and physical processes in biomass. The typical range of frequency varies from 20 kHz to 1000 kHz [59]. Due to these high-energy shock waves, the crystalline structure of biomass is disintegrated. High-energy acoustic vibrations generated during ultrasonic pretreatment produce hydrogen and hydroxyl radicals through the decomposition of water molecules. These factors contribute to the collapse of LCB structures. Velmurugan et al. [60] experimented on sugarcane bagasse using the ultrasonic method assisted by alkaline pretreatment. The recovered values for cellulose were 99%, and for hemicellulose, 79%. The lignin removal rate was 75.44%. The sugar yield was 26.01 g/L, corresponding to 95% and equivalent to the theoretical yield. The use of ultrasound techniques has provided a much simpler disintegration of biomass in a shorter period. But multiple factors govern the efficiency of the process, including residence time, type of biomass used, composition of the biomass, and type of solvent

used in the experiment [60,61]. A comparison of physical pretreatment methods is given in Table 2.

Table 2. Summary and comparison of physical pretreatment methods for lignocellulosic biomass (LCB).

Method	Mechanism	Typical Conditions	Advantages	Disadvantages/Limitations
Milling/ Grinding/ Chipping	Mechanical size reduction (milling, grinding, chipping, shredding) to increase surface area	Milling/grinding: 0.2–2 mm; chipping: up to 30 mm, used when target size exceeds 10 mm [53]	Ball milling improves digestibility and crystallinity; wet disk milling is preferred over ball milling as it enhances biomass hydrolysis [54]	Energy required for ball milling is much higher than for wet disk milling [55]
Mechanical Extrusion	Extruder screws reduce biomass size via shear force; compression between blades and barrel raises temperature and pressure, enhancing fibre cutting and enzyme accessibility [50]	Screw speed 280–350 rpm; barrel temperature 80–140 °C (soybean hulls) [50]	Glucose yield increased as extruder speed increased from 280 to 350 RPM [50]	Output depends strongly on screw type, moisture content, and temperature; glucose yield decreased as temperature increased from 80 to 140 °C [50]
Microwave Pretreatment	Microwave irradiation strikes the biomass surface and generates an explosion inside particles; continuous application significantly alters internal biomass structure [57]	Applied to sugarcane bagasse, rice straw, and rice hulls [54]; first used on rice straw and bagasse in 1984 [56]; increasingly used in combination with other pretreatments	Easy handling, high heating capacity, small process time, low energy requirement [54]; effective for bioethanol production [58]	High initial setup cost compared to other techniques; technology is still developing, so dielectric specifications of each biomass must be understood before implementation
Ultrasonic Pretreatment	High-energy shock waves disintegrate the crystalline structure of biomass; acoustic vibrations generate hydrogen and hydroxyl radicals through decomposition of water molecules, contributing to the collapse of LCB structure [59]	Frequency 20–1000 kHz [59]; often combined with alkaline pretreatment [60]	Simpler, faster disintegration of biomass; alkaline-assisted ultrasound on sugarcane bagasse recovered 99% cellulose and 79% hemicellulose, removed 75.44% lignin, and gave a sugar yield of 26.01 g/L (~95% of theoretical yield) [60]	Efficiency is governed by multiple factors: residence time, biomass type, biomass composition, and solvent type [60,61]

2.2. Chemical and Physicochemical Pretreatment Methods

These methods destroy the structure of LCB and enhance its properties for the enzymatic hydrolysis [62]. Different chemical pretreatment methods are described below. This section covers chemical pretreatments, which rely mainly on reagents such as acids, alkalis, and solvents, and physicochemical pretreatments, namely ammonia fibre explosion (AFEX), supercritical fluids, co-solvent-enhanced lignocellulosic fractionation (CELf), and steam explosion, which combine chemical action with elevated temperatures and pressures.

2.2.1. Ozonolysis

This method is used to reduce the lignin content in LCB. The other two proportions of LCB, i.e., hemicellulose and cellulose, are less affected by this pretreatment. Ozonolysis can be performed under atmospheric conditions. This method is also environmentally friendly and does not leave any toxic residue. Ozonolysis is not widely adopted at the industrial scale, as it is more costly than the other chemical pretreatment methods. This is because a large amount of ozone is required to use this method. Many of the ozonolysis experiments are carried out in a hydrated fixed bed. Research is underway to find less expensive ways for ozonolysis [63–66].

2.2.2. Alkali Pretreatment

This process is performed to weaken the bonds between the lignin and hemicellulose. In this process, the final products are hemicellulose and cellulose, which are suitable for subsequent conversion procedures [51]. Sodium hydroxide is the most effective reagent for this pretreatment [67]. Sun et al. [68] studied the efficiency of various hydroxide solutions for wheat straw. It was reported that the optimal condition was 1.5% NaOH at 20 °C for about 144 h duration. In this experiment, it was found that 60% of lignin was released, and the removal proportion of hemicellulose was 80% [68]. Li et al. [69] performed the ammonia pretreatment for the sugar beet pulp (SBP) and found that pores had occurred on the surface of raw SBP after the experiment. The sugar yield from enzymatic hydrolysis was increased, and it was 2.42 times higher than the original raw sample of SBP [69]. Lime is also used to pretreat the biomass. In an experiment, wheat straw, poplar wood, switch grass, and corn stover were pretreated using lime. It resulted in the enzymatic hydrolysis of corn stover being increased by 9 times as compared to the raw material. The optimal conditions were found to be 0.075 g lime-loading calcium hydroxide, 5-g water loading of dry material, with a heating duration of 240 min at a temperature of 120 °C [70,71]. The advantage of lime pretreatment is its lower cost compared with other methods [72].

2.2.3. Organosolv Pretreatment

This pretreatment achieves a high lignin removal rate without altering biomass composition or structure, but the solvent left after the process creates inhibitory effects in enzymes [73]. It is carried out in organic solvents such as methanol, ethanol, glycol, or acetone, often with a catalyst to accelerate the reaction [50]. Tang et al. [74] treated corn stover with 60% ethanol and n-propylamine at 140 °C for 40 min, removing 81.7% of lignin at an 83.2% sugar yield. Comparing MgSO_4 , H_2SO_4 , and NaOH catalysts on pine, Park et al. [75] found H_2SO_4 most effective for ethanol yield and 2% NaOH best for digestibility; high solvent cost and slow recovery remain the principal constraints. For wheat straw, the highest acid concentration removed hemicellulose and cellulose almost completely, while ethanol concentration reduced xylan hydrolysis from 36.3% to 6.7% [76]. Using 75% ethanol with 1% (w/w) H_2SO_4 at 150–180 °C, 37.7%, 21%, and 27% of lignin were removed from rice straw, pinewood, and elmwood, respectively [77]. Organosolv with hydrothermal pretreatment outperforms organosolv alone: 150 min of organosolv at 190 °C following 60 min of hydrothermal treatment at 160 °C reduced lignin to 13% and raised cellulose to 76% [78], while 190 °C for 180 min gave 70.1% delignification [79].

2.2.4. Ionic Liquids (ILs)

This pretreatment is performed at room temperature and pressure. ILs have been recognised as an effective means of pretreating the LCB. These liquids have special properties, such as low vapour pressure, low melting points, and high polarity. The ILs are composed of only ions. These are generally cations and anions [80]. Several salts are used as ILs. But imidazolium is the most commonly used one of all. ILs weaken the hydrogen bonding in LCB, thereby altering its composition. There are some limitations that need to be addressed before this method can be adapted for large-scale industrial use. These are given as follows.

1. The cost of ILs is high.
2. There is a regeneration requirement.
3. There is a lack of basic physicochemical characteristics.
4. Inhibitors are produced during the process.

Further detailed research is necessary to minimise the above-mentioned challenges regarding the utilisation of ILs [81].

2.2.5. Ammonia Fiber Explosion (AFEX)

In AFEX, LCB is exposed to liquid ammonia at high temperature and pressure for a set period, after which the pressure is suddenly released [71]. Typical conditions are ammonia at 1:1 *w/w*, 60–170 °C, 15–30 bar, and process times up to 60 min [82]. Its main advantages are low residence time, cellulose remains largely intact, minimal inhibitor production, and high glucan and xylan yields under optimised parameters; the treatment also rearranges hydrogen bonding, increasing inter- and reducing intra-hydrogen bonds to give an amorphous biomass [83]. Applying AFEX to corn stover at a lower temperature of 40 °C for 8 h, followed by 72 h of hydrolysis, Bals et al. [84] obtained glucose and xylose yields of 90% and 60%, respectively, indicating that longer residence times can offset milder conditions. Zhao et al. [85] later modified the method as liquid ammonia pretreatment (LAT), in which ammonia is released gradually rather than explosively; applied to giant reed, this avoided the explosion step and reduced both cost and hazard. The process nevertheless requires expensive pressure-rated equipment, raising processing costs, and is unsuitable for biomass with high lignin content [85,86].

2.2.6. Deep Eutectic Solvents (DESs)

Deep eutectic solvents are a modified form of ILs and share many of their properties [87]. As conventional industrial solvents are toxic and hazardous to the ecosystem, DESs have attracted both industrial and research interest as a greener alternative: first composed by Abbot et al. [88] in 2003 from hydrogen-bond acceptors and donors, they are cheaper, less toxic, and biodegradable relative to other available solvents [50,88,89]. Lynam et al. [90] attributed their high delignification effectiveness to strong hydrogen bonding between cellulose and the DES. Treating willow biomass with urea, lactic acid, and glycerol DESs for 6 h at 120 °C, Li et al. [91] obtained a maximum lignin yield of 52.4% with lactic acid, against less than 10% for the other two. In the first reported use of DESs for biomass pretreatment, Francisco et al. [92] found that lignin was effectively solubilised but cellulose was not, and Zhang et al. [93] recorded a fivefold improvement in lignin yield from corncob when the temperature was raised from 70 °C to 110 °C with lactic acid. DESs are therefore low-cost and readily available, but not all of them dissolve lignin effectively, so the DES type must be matched to the specific biomass [51].

2.2.7. Supercritical Fluids (SCFs)

SCFs behave as intermediate gases and liquids and are considered eco-friendly and sustainable for LCB pretreatment. Their low viscosity, high diffusivity, non-toxicity, and low cost give them a high tendency to penetrate solid biomass and higher mass transfer rates than other chemical solvents. The commonly used media are supercritical CO₂ (ScCO₂) and supercritical water (SCW), both non-flammable, non-toxic, and highly stable, and have been used to delignify switchgrass, corn stover, wheat straw, and bagasse [94,95]. Narayanaswamy et al. [96] obtained a maximum glucose yield from corn stover using ScCO₂ at 3500 psi and 150 °C over 60 min, the fluid enhancing mass transfer by lowering viscosity and raising diffusivity. Applying SCW to sugar beet pulp at 250 bar and 390 °C with reaction times of 0.11–0.15 s, Martinez et al. [97] minimised dehydration products while achieving C₆ and C₅ sugar yields of 61% and 71%, respectively; a later study by the same group showed that longer reaction times reduce sugar yield [98]. SCFs remain at an evolutionary stage, with inhibitor formation and short residence times being the key challenges limiting its use at large industrial scale [50,97,98].

2.2.8. Co-Solvent Enhanced Lignocellulosic Fractionation (CELf)

First developed by Cai et al. [99], CELf removes lignin from LCB and simplifies downstream conversion using tetrahydrofuran (THF), which readily forms an azeotrope with water, in a THF–water mixture; the one-pot reaction was performed on maple wood at 5 wt.% with 1% sulphuric acid at 170 °C. Applying CELf to maple wood and corn stover, Cai et al. [100] achieved high yields of 5-hydroxymethyl furfural and compared FeCl₃, CuCl₂, ZrOCl₂, and CrCl₃ against sulphuric acid. At 170 °C with 1 wt.% metal halide, furfural yields ranged from 38% to 85% and 5-HMF from 12% to 18%, the maximum of 85% being obtained with FeCl₃ and approaching the 87% given by sulphuric acid; apart from ZrOCl₂, all halides extracted about 90% of the lignin. Coupling simultaneous saccharification and fermentation (SSF) with CELf for ethanol production from corn stover, Nguyen et al. [101] reported an ethanol yield of about 90% in four days, against 50% in six days for dilute acid pretreatment, confirming CELf as the faster and higher-yielding route [102].

2.2.9. Acid Pretreatment

Acid pretreatment is the earliest and most researched LCB pretreatment method. It is classified by acid type into organic (acetic, oxalic) and inorganic (sulphuric, nitric, phosphoric, hydrochloric) routes, and by concentration into concentrated and dilute pretreatment, with dilute sulphuric acid the most widely used [51]. Its main objective is the removal of hemicellulose, which improves enzyme accessibility to cellulose [50]. Concentrated pretreatment (>10% *w/v* sulphuric acid) operates at room temperature and pressure with a high reaction rate and enhanced sugar production: pretreating cotton waste for 30 min with concentrated sulphuric acid followed by microwave treatment at 180 °C for 3 min gave a glucose yield of 74.2% [103].

Reported dilute-acid results span a range of feedstocks: 2% sulphuric acid on wheat straw at 180 °C for 10 min recovered 43.1% of the sugar at a 5.2% ethanol yield [104]; 1% sulphuric acid on rapeseed straw (20% *w/v*) under the same conditions gave an 84.6% sugar yield after enzymatic hydrolysis [105]; wheat straw reached an ethanol yield of 0.20 g/g [106]; and rice straw treated with 0.35 wt.% acid at 160 °C for 10 min yielded 83.3 g/L glucose and 31.9 g/L xylose [107]. For corn stover, removal of up to 19.3% of the lignin raised the glucose yield by 58.6% in enzymatic hydrolysis [108]. The principal limitation is that the low acid concentration requires high operating temperature and pressure.

These limitations have prompted interest in phosphoric acid, which reacts with the hydroxyl groups of cellulose to form water-soluble cellulose phosphate and thereby separates the components of LCB. On *Sida acuta*, it removed most of the xylan and a small part of the lignin while leaving glucan largely intact [109]; wheat straw reached enzymatic hydrolysis of up to 90% [110]; and for brewers' grains, 63% of the sugar was dissolved at 155 °C, giving 69% sugar production in ethanol fermentation at an enzymatic hydrolysis efficiency of 68.61% [111]. Combining phosphoric acid with hydrogen peroxide on wheat straw further improved hydrolysis efficiency over phosphoric acid alone. Phosphoric acid is comparatively low-cost, less corrosive, and safer, and causes less environmental pollution [112].

2.2.10. Steam Explosion

Steam explosion is a physicochemical pretreatment in which biomass is exposed to saturated steam at 160–280 °C and 0.7–4.8 MPa, followed by rapid decompression to atmospheric pressure [113]. The high temperature promotes autohydrolysis of hemicellulose by acetic acid released from acetyl groups, while the explosive decompression disrupts the fibre structure and increases cellulose accessibility [114]. It requires little or no chemical

addition and has a comparatively low energy demand, which is why it is among the most widely applied pretreatments at an industrial scale for second-generation bioethanol production [113,114]. Its main drawback for biochemical routes is the formation of furfurals and phenolic compounds that inhibit fermentation. Steam explosion is also relevant to solid-fuel upgrading. The partial degradation of hemicellulose and redistribution of lignin produce a more homogeneous material with higher binding ability, so steam-exploded “black pellets” show higher durability, tensile strength, and water resistance than conventional white pellets and can be co-fired in existing coal-fired plants [114,115]. However, like dry torrefaction, steam explosion does not remove AAEMs on its own. Integrating water leaching with steam explosion removed 44–62% of the ash and substantially reduced Cl and K in wheat straw, spruce bark, and empty fruit bunches, producing pellets with an HHV of 18.6–20.8 MJ/kg and a durability of 98.4–99.5% that met ISO and ENplus requirements [116]. This mirrors the complementarity of washing and torrefaction discussed in Section 5. Steam explosion is closely related to steam torrefaction (Section 4.2.3), which uses similar temperatures but is directed at fuel upgrading rather than fibre disruption.

A comparison of chemical and physicochemical pretreatment methods is given in Table 3.

Table 3. Summary and comparison of chemical and physicochemical pretreatment methods for lignocellulosic biomass (LCB).

Method	Mechanism	Typical Conditions	Advantages	Disadvantages/Limitations
Ozonolysis	Ozone selectively degrades lignin; cellulose and hemicellulose are minimally affected [63–66]	Atmospheric pressure, ambient temperature; typically carried out in a hydrated fixed bed; used on wheat straw, pine, and bagasse [63–66]	No high operating conditions required; environmentally friendly; leaves no toxic residue [63–66]	Not widely adopted industrially; large ozone requirement makes it costlier than other chemical methods [63–66]
Alkali Pretreatment (NaOH/ammonia/lime)	Saponification weakens lignin–hemicellulose bonds [51]; NaOH is the most effective reagent [67]; aqueous ammonia and lime weaken/break lignin bonds [69,71]	Wheat straw: 1.5% NaOH, 20 °C, 144 h [68]; barley straw: 2% NaOH, 105 °C, 10 min [50]; lime: 0.075 g Ca(OH) ₂ , 5 g water per g dry material, 120 °C, 240 min [71]	60% lignin release, 80% hemicellulose removal for wheat straw [68]; 84.4% lignin removal and crystallinity index rise from 45.1% to 71.5% for barley straw [50]; ammonia raised SBP enzymatic-hydrolysis sugar 2.42-fold [69,70]; lime increased corn stover hydrolysis 9-fold and is lower-cost than other methods [71,72]	Optimal NaOH conditions require long duration (up to 144 h) [68]; efficiency is strongly reagent- and biomass-specific
Organosolv Pretreatment	Organic solvents (methanol, ethanol, glycol, acetone), often with a catalyst, remove lignin with minimal disruption to biomass composition and structure [50,73]	Corn stover: 60% ethanol, n-propylamine catalyst, 140 °C, 40 min [74]; pine: MgSO ₄ /H ₂ SO ₄ /NaOH catalysts [75]; wheat straw: varying ethanol/acid concentration [76]; rice straw/pinewood/elmwood: 75% ethanol + 1% H ₂ SO ₄ , 150–180 °C [77]; combined with hydrothermal step: 160–190 °C [78,79]	High lignin removal without altering biomass structure [73]; 81.7% lignin removal, 83.2% sugar yield for corn stover [74]; combined organosolv–hydrothermal reached 76% cellulose concentration and 70.1% delignification [78,79]	Incomplete solvent removal creates enzyme-inhibitory effects [73]; high operational cost; slow, costly solvent recovery [75]
Ionic Liquids (ILs)	Cation–anion (mostly imidazolium-based) solvents weaken hydrogen bonding in LCB, altering its composition [80]	Room temperature and pressure; IL choice is biomass-specific [81]	Low vapour pressure, low melting point, high polarity; highly efficient delignification [80,81]	Very high cost; regeneration required; lack of basic physicochemical characterisation; inhibitor production during processing [81]

Table 3. Cont.

Method	Mechanism	Typical Conditions	Advantages	Disadvantages/Limitations
Ammonia Fibre Explosion (AFEX)	LCB exposed to liquid ammonia under high pressure, then suddenly decompressed; rearranges hydrogen bonding, increasing inter-hydrogen and reducing intra-hydrogen bonds [71,83]	Ammonia:biomass 1:1 <i>w/w</i> ; 60–170 °C; 15–30 bar; up to 60 min [82]; low-temperature AFEX: 40 °C, 8 h [84]	Low residence time; cellulose largely intact; minimal inhibitor production; high glucan/xylan yields [83]; 90% glucose and 60% xylose yields [84]; LAT variant lowers cost and hazard by avoiding explosive decompression [85]	High-pressure equipment raises processing cost; unsuitable for high-lignin biomass [85,86]
Deep Eutectic Solvents (DESs)	Modified ionic liquids formed from hydrogen-bond acceptors and donors; strong hydrogen bonding with cellulose promotes delignification [87,88,90]	e.g., willow biomass with urea/lactic acid/glycerol DESs, 120 °C, 6 h [91]; corncob with lactic acid, 70–110 °C [93]	Lower cost, less toxic, and biodegradable relative to other solvents [50,88,89]; 52.4% lignin yield for willow with lactic acid [91]; fivefold lignin yield increase for corncob at 110 °C vs. 70 °C [93]	Not all DESs dissolve lignin effectively; some solubilise lignin but not cellulose [92]; suitable DES types must be matched to the specific biomass [51]
Supercritical Fluids (SCFs)	ScCO ₂ or supercritical water (SCW) behave as intermediate gas/liquid phases; high diffusivity and mass transfer break LCB bonds under high pressure [94,95]	Corn stover with ScCO ₂ : 3500 psi, 150 °C, 60 min [96]; sugar beet pulp with SCW: 250 bar, 390 °C, 0.11–0.15 s [97]	Low viscosity, high diffusivity, non-toxic, low cost [94,95]; C ₆ /C ₅ sugar yields of 61%/71% for sugar beet pulp [97]	Technology still evolving; inhibitor formation; short residence time; longer reaction time reduces sugar yield [50,98]
Co-solvent Enhanced Lignocellulosic Fractionation (CELf)	THF–water co-solvent (forms an azeotrope with water) removes lignin and simplifies downstream conversion [99]	Maple wood/corn stover: 1% H ₂ SO ₄ or 1 wt.% metal halide (FeCl ₃ , CuCl ₂ , ZrOCl ₂ , CrCl ₃), 170 °C [100]	Furfural yield 38–85%, 5-HMF 12–18%; FeCl ₃ yield (85%) close to sulphuric acid (87%); most halides extract ~90% of lignin [100]; coupled with SSF, ethanol yield ~90% in 4 days vs. 50% in 6 days for dilute acid [101,102]	Requires acid or metal-halide catalysts; solvent/catalyst recovery cost not fully established
Acid Pretreatment (sulphuric/phosphoric)	Concentrated (>10% <i>w/v</i>) or dilute (0.1–1.5% <i>w/v</i>) sulphuric acid degrades hemicellulose to xylose; phosphoric acid reacts with cellulose hydroxyl groups to form water-soluble cellulose phosphate [50,51]	Concentrated: room temperature/pressure, e.g., cotton waste 30 min + microwave 180 °C/3 min [103]; dilute: 120–200 °C, e.g., wheat straw 2% H ₂ SO ₄ , 180 °C, 10 min [104]; rapeseed straw 1% H ₂ SO ₄ , 180 °C, 10 min [105]; rice straw 0.35 wt.% acid, 160 °C, 10 min [107]; phosphoric acid on <i>Sida acuta</i> [109], wheat straw [110], brewers' grains at 155 °C [111]	Most researched, earliest LCB pretreatment; improves enzyme accessibility to cellulose [50]; 74.2% glucose yield (cotton waste) [103]; 43.1% sugar recovery, 5.2% ethanol yield (wheat straw) [104]; 84.6% sugar yield (rapeseed straw) [105]; 58.6% glucose increase via 19.3% lignin removal (corn stover) [108]; phosphoric acid is lower-cost, less corrosive, safer, and low-pollution, with waste usable as fertiliser [112]	Dilute acid needs high operating temperature/pressure despite low acid concentration [108]; phosphoric acid alone requires combination with H ₂ O ₂ to match higher hydrolysis efficiencies [112]

2.3. Biological Pretreatment Technologies

These methods are considered safe, consume less energy, and are eco-friendly. Cellulolytic and hemicellulolytic microorganisms present in the environment, such as white-, brown-, and soft-rot fungi, can be used for biological pretreatment. These microbes mainly disrupt the lignin and hemicellulose, and a small part of the cellulose in the LCB. Peroxidases and laccases are known as lignin removal enzymes [66].

The biological pretreatment method alters the composition of LCB and makes it more suitable for enzymatic digestion. Hwang et al. [52] performed the biological pretreatment on wood chips for 30 days by using the white rot fungi of four different types. The results showed that the yield of glucose from the pretreated wood by *Trametes versicolor* MrP 1 reached 45% by the enzymatic hydrolysis, and 35% of the solid wood was converted into glucose after the fungal incubation.

Despite these advantages, biological pretreatment is much less widely applied than chemical and physicochemical methods, for four main reasons. First, its kinetics are slow: fungal pretreatment typically requires residence times of several weeks, as in the 30-day incubation above, compared with minutes to hours for chemical and physicochemical routes [52,66]. Second, the microorganisms consume part of the cellulose and hemicellulose as a carbon source, reducing the carbohydrate and energy yield of the treated biomass [50,66]. Third, the process requires controlled conditions of temperature, moisture, and sterility, together with large reactor or storage volumes to support long residence times, which makes it difficult and costly to scale up [50,51]. Finally, its effectiveness is limited because delignification is often incomplete, and, for solid-fuel applications, it neither removes AAEMs nor increases energy density. For these reasons, biological pretreatment has so far remained largely at laboratory scale, and fewer studies are available for review than for chemical and physicochemical pretreatments.

2.4. Rationale for Focusing on Washing and Torrefaction

The pretreatment methods surveyed above were largely developed for biochemical objectives: delignification and increased enzyme accessibility for hydrolysis and fermentation into liquid biofuels. Acid, alkali, organosolv, ILs, AFEX, DESs, and biological routes are all optimised to fractionate the lignocellulosic matrix rather than to correct the two deficiencies that disqualify raw biomass as a solid fuel, namely its low energy density and its high AAEMs/ash content [50,51]. They also carry limitations that make them unattractive for solid-fuel upgrading at scale: chemical routes generate corrosive or inhibitory waste streams and incur high solvent-recovery costs, whereas biological routes require residence times of the order of thirty days and remain confined to the laboratory [51,52]. Washing and torrefaction are singled out in this review because they target the two solid-fuel deficiencies directly and are the closest to industrial deployment: washing is a cost-effective route for removing the AAEMs and chlorine responsible for slagging, fouling, and corrosion, while torrefaction is established for raising energy density, carbon content, and grindability so that biomass can be handled and co-fired with coal [38,117]. Crucially, their respective weaknesses are complementary; washing does not densify energy, and torrefaction does not remove AAEMs, which is the physical basis for combining them, developed in Section 5. Other thermochemical processes, such as pyrolysis and gasification, are not considered as pretreatments in this review, since they are the downstream conversion routes whose performance pretreatment is intended to improve. Hydrothermal carbonisation is included under wet torrefaction, as both terms describe the treatment of biomass in subcritical water to produce hydrochar. Steam explosion, although developed mainly for bioethanol production, is also relevant to solid-fuel upgrading and is therefore linked to steam torrefaction.

3. Biomass Washing Pretreatment

3.1. Biomass Washing

Water washing is an effective pretreatment method to enhance the biomass properties and its composition for the agricultural biomass [118]. Water washing can be used to decrease the slagging and fouling issues related to LCB combustion. Detailed research on the washing conditions for the effective removal of alkalis and increasing the fuel properties is still limited. Various aspects of washing, like stirring time, temperature, and liquid/solid ratio, still need to be investigated for the different types of biomasses for efficient and maximum removal of undesired species from LCB to increase the fuel properties [117]. Ash and metallic AAEMs present in biomass reduce bio-oil yield and lower carbon content. These AAEMs work as the catalyst in pyrolysis and increase the yield of water and acids

in the bio oil. Therefore, it is desired to remove these alkalis from the biomass before subsequent pyrolysis and combustion and to improve the quality of biomass.

3.2. Experimental and Case Studies

Choice of washing agent. Cen et al. [26] washed rice straw with water, dilute hydrochloric acid (HCl), and aqueous phase bio-oil (APBO), while Zhang et al. [119] washed rice husk with light bio-oil and compared the results with raw and acid-washed samples. Water washing removed most of the K (about 80%) but little Ca and Mg (about 10–20%), and it lowered the ash content of rice straw only from 13.3 to 12.8%, against 9.2% for HCl and 8.2% for APBO [26]. The other two solutions removed more than 90% of the alkalis: about 99.7% of K was removed by APBO, while Na, Mg, and Ca were removed at 91.7, 96.6, and 95.2%, respectively [26]. Light bio-oil removed 98.5, 95.1, and 93.9% of K, Mg, and Na from rice husk, but only 66.7, 73.5, and 72.5% of Ca, Fe, and Al [119]. The high efficiency of bio-oil is attributed to the acetic acid and phenols it contains, the acid mobilising the AAEMs while the phenolic compounds promote the ease of access to AAEMs for the acetic acid, thereby increasing the removal rate [26,119]. Water dissolves the free ionic species alone, whereas acid and bio-oil additionally attack the organically bound and ion-exchangeable complexes in which Ca and Mg reside.

Washing time. Singhal et al. [120] washed empty fruit bunches (EFB), a residue generated at about 50 million tonnes annually by the palm oil industry [121,122], and removed Cl, K, S, N, Fe, and Mg by about 98, 77, 81, 64, 62, and 40%, respectively, together with 67% of the ash and a gain of about 0.9 MJ/kg in HHV. Up to 90% of the chlorine was removed in just 5 min, and removal reached 97% with longer washing, with a negligible further rise after 30 min. In wheat straw, by contrast, about 81% of K but only 53% of Cl was removed within the first 10 min, and 20 h were required to reach 93, 92, and 100% of K, Na, and Cl [123]. The high removal rate was the result of the migration of water-soluble elements during leaching, while the slow removal rate resulted from the weakly bound inorganic matter held by ion exchange [123]. The two elements that matter most for ash chemistry are thus not removed on the same timescale, a distinction with direct consequences for wash design that is developed below.

Temperature, solid-to-liquid ratio, and feedstock. Deng et al. [124] washed six biomasses, wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood, and rice hull at 303, 333, and 363 K. About 80% of K was removed from all of them except candlenut wood, and more than 90% of Cl from rice straw. The removal efficiency of K increased with temperature, because more of the K^+ ions bound in complexes with organic acid anions are released from the biomass matrix at higher water temperature. The removal efficiency of Cl, however, did not increase with temperature for rice straw, wheat straw, or corn stalk, since the water was already sufficient at low temperature to remove Cl^- , which competes with SO_4^{2-} , CO_3^{2-} , and HCO_3^- to enter the water [124]. This competitive leaching was, in turn, suppressed by raising the dilution ratio, so that Cl removal improved at higher S/L [125]. Temperature and dilution are therefore not general intensifiers of washing; each acts on a different element through a different mechanism.

Process configuration. Singhal et al. [126] introduced step washing of wheat straw and EFB using fresh water and recirculated wastewater. Three freshwater steps of 10 min outperformed a single wash of 3–24 h for N and S removal from wheat straw and achieved 64–68% K and 97–99% Cl removal, the fresh water used at each step being the main cause of the high Cl removal rate. A continuous reduction in the B/A ratio was observed as steps were added, lowering the slagging and fouling tendency in the operational parts.

Effect on the pyrolysis product slate. Washing with water had little effect on the yield of pyrolytic products, but acid and APBO had a great effect, biochar yield fell from 37.9

to 36.4, 28.3, and 26.5% with water, acid, and APBO washing, while bio-oil yield rose to a maximum with APBO [26]. Washing rice husk with bio-oil likewise produced a higher bio-oil yield than acid washing, since Na, K, Ca, and Mg increase the gas yield and depress the bio-oil yield when present [119]. The alkali metals act as a catalyst on the pyrolysis vapours, promoting the ring-opening of carbohydrates towards low-molecular-weight, non-condensable species and the cross-linking reactions that build char [26]; the gas and water yields during pyrolysis rise with K content, so its removal is necessary to lower the water content of the oil [127].

Table 4 consolidates the findings of all washing pretreatment studies reviewed in this work. The studies span a range of biomass types, washing agents, temperatures, and contact times, yet several consistent trends emerge. Bio-oil (APBO/light bio-oil) consistently outperformed water and dilute acid for alkali removal, achieving K removal of up to 99.7% and raising the bio-oil yield to 55.2% for rice straw [26]. Water washing, while less effective for Ca and Mg removal, achieved near-complete Cl removal (97–100%) across multiple biomasses due to the high water-solubility of Cl[−] ions [120,123]. Step washing with fresh water in three stages of 10 min each proved competitive with single-batch washing of several hours, offering a practical route to industrial scale-up [126]. These results collectively confirm that washing is a highly effective and low-cost method for deashing and AAEMs removal, but requires a post-washing drying step to restore fuel quality.

Table 4. Summary of biomass washing pretreatment studies reviewed in this work.

Ref.	Biomass	Washing Agent	T (°C)	Time	K Removal	Cl Removal	Key Outcomes
[26]	Rice straw	Water	50	120 min	High	–	Ash: 13.3% → 12.8%;
[26]	Rice straw	HCl (dilute)	50	120 min	>90%	–	Ash: 13.3% → 9.2%; Bio-oil: 40.6% → 51.8%
[26]	Rice straw	APBO	50	120 min	99.7%	–	Ash: 13.3% → 8.2%; Bio-oil: 40.6% → 55.2%; Na 91.7%, Mg 96.6%, Ca 95.2%
[119]	Rice husk	Light bio-oil	30	4 h	98.5%	–	Mg 95.1%, Na 93.9%; bio-oil yield > acid washing
[120]	EFB	Water	20–80	2–180 min	77%	98%	Ash removed 67%; HHV +0.9 MJ/kg; S 81%
[123]	Wheat straw	Water	RT	10 min–20 h	81% (10 min); 93% (20 h)	53% (10 min); 100% (20 h)	HHV ↑; slagging/fouling index ↓
[124]	WS, RS, CS, CTS, CW, RH	Water	30–90	3 h	~80%	>90% (RS)	S > 70% most biomasses; K removal ↑ with temperature
[126]	WS + EFB	Step washing (3×)	20–40	3×10 min	64–68%	97–99%	B/A ratio ↓; comparable to 24 h single-batch washing

APBO = Aqueous Phase Bio-Oil; WS = wheat straw; RS = rice straw; CS = corn stalk; CTS = cotton stalk; CW = candlenut wood; RH = rice hull; EFB = empty fruit bunches; RT = room temperature; B/A = base-to-acid ratio (slagging index). ↑ = increase; ↓ = decrease; – = not reported.

The choice of washing agent critically determines both the AAEMs removal efficiency and the quality of the resulting pyrolytic products. Table 5 presents a side-by-side critical comparison of the three principal washing agents reported in the literature: water, dilute acid (primarily HCl), and bio-oil (APBO or light bio-oil). Water is the most accessible and lowest-cost option and is highly effective for K⁺ and Cl[−] removal owing to their high water solubility, but shows limited removal of Ca and Mg, which are organically bound. Dilute acid breaks organically-bound AAEM complexes through acid dissolution, achieving removal rates exceeding 90% for all major species [26]. Bio-oil (APBO) achieves the highest removal efficiencies across all species, K removal of 99.7%, Na of 91.7%, and bio-oil yield improvement because acetic acid and phenolic compounds act synergistically to mobilise both water-soluble and organically-bound AAEMs [26,119]. Despite its superior perfor-

mance, bio-oil washing remains at an early pilot-scale stage, and its economic feasibility for industrial applications requires further investigation.

Table 5. Critical comparison of washing agents for biomass pretreatment.

Parameter	Water	Dilute Acid (HCl)	Bio-Oil (APBO/Light)
K removal	High (K^+ highly water-soluble)	>90% [26]	99.7% [26] (acetic acid + phenols)
Na removal	≈70% [26]	>90% [26]	91.7% [26]
Mg removal	≈20% (organically bound)	>90% [26]	96.6% [26]
Ca removal	≈10%	>90% [26]	95.2% [26]
Cl removal	97–100% [120,123]	–	–
Bio-oil yield (rice straw)	–	40.6% → 51.8% [26]	40.6% → 55.2% [26]
Ash (rice straw)	13.3% → 12.8% [26]	13.3% → 9.2% [26]	13.3% → 8.2% [26]
HHV improvement	+0.9 MJ/kg (EFB) [120]	–	–
Cost	Low	Moderate	Moderate–High
Environmental impact	Low	High (acid waste)	Moderate (process liquor)
Scale-up status	High (industrial)	Medium (pilot–industrial)	Emerging (lab–pilot)
Key mechanism	Ion exchange; dissolution of K^+ , Cl^-	Acid dissolution of organically-bound AAEMs	Acetic acid + phenols mobilise all AAEM forms

APBO = aqueous phase bio-oil; EFB = empty fruit bunches; – = not reported.

4. Torrefaction Pretreatment

4.1. Background

In recent years, torrefaction has become an effective pretreatment technique for improving biomass fuel quality. The focus of researchers was on the effects of torrefaction on the biomass fuel properties, char yield, biomass composition, and environmental impacts of torrefied biomass combustion. Then, later, several studies investigated the mechanism of chemical reaction and thermal degradation of biomass [38]. Torrefaction is a thermochemical process in which biomass is converted into different products. The main torrefaction product is solid char. Torrefaction increases the gravimetric energy density of the solid product, but the loss of volatiles and the resulting porous, brittle structure generally reduce its bulk density. Bulk density is subsequently restored or substantially increased by pelletisation or briquetting, so torrefaction is usually combined with densification to reduce storage and transportation costs [38,128].

4.2. Types of Torrefaction

The classification of the torrefaction process is given in Figure 6.

4.2.1. Dry Torrefaction

Dry torrefaction is performed in a non-oxidative environment. In this type, nitrogen and carbon dioxide are used as carrier gases. Apart from nitrogen, air and flue gases have also been employed as carrier gases for biomass thermal conversion processes. Due to the presence of oxygen and the exothermic nature of the process, oxidative torrefaction has higher chemical reaction rates than non-oxidative torrefaction. The operational cost of using air or flue gases, compared to nitrogen, is cheaper. Oxidative torrefaction provides a lower yield of solid as compared to the non-oxidative torrefaction. HHV of torrefied biomass decreased with the increase in oxygen concentration when torrefaction is performed below the temperature of 300 °C [129–133].

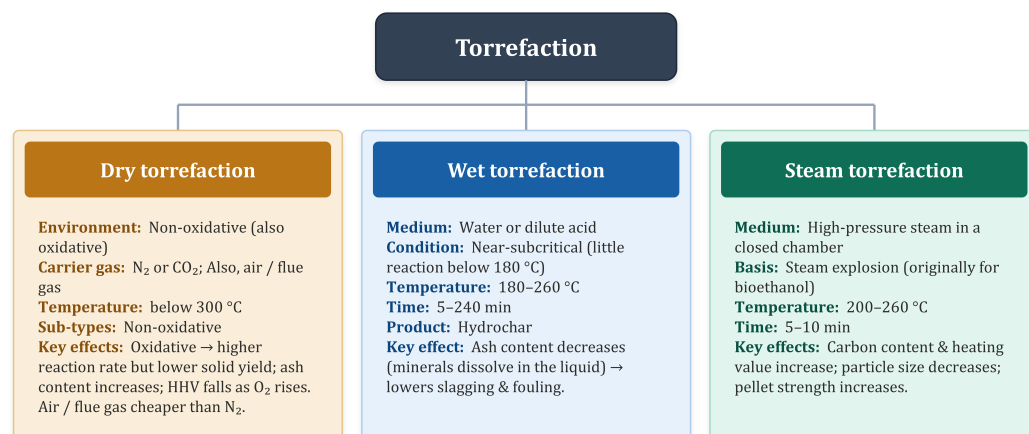


Figure 6. Classification and Types of Torrefaction Process.

4.2.2. Wet Torrefaction

In wet torrefaction, also referred to as hydrothermal pretreatment or hydrothermal carbonisation, biomass is treated in hot compressed (subcritical) water in a closed vessel instead of an inert gas, and the solid product is known as hydrochar [25,38]. No appreciable reaction of biomass takes place with hot water if the temperature is below 180 °C; therefore, wet torrefaction is generally carried out between 180 and 260 °C with a residence time of 5 to 240 min. In dry torrefaction, the ash content of biomass generally increases, whereas in wet torrefaction it decreases, because minerals present in the biomass dissolve in the liquid phase, which also lowers the slagging and fouling impacts [38]. A further advantage of the hydrothermal route is that it can process wet biomass without pre-drying and can yield a valuable liquid co-product in addition to the solid fuel [25,134].

4.2.3. Steam Torrefaction

Steam torrefaction is performed under high-temperature and pressure conditions. The process of steam torrefaction was initially started to produce bioethanol. In this process, high pressure steam is injected into a closed chamber containing the LCB at temperatures of 200 to 260 °C and for 5 to 10 min. In this process, carbon content and heating value are increased while particle size decreases. The strength of pellets after steam torrefaction is also increased [38]. The comparison of types of torrefaction is given in Table 6. Steam torrefaction shares its operating principle with steam explosion, the two differ mainly in whether rapid decompression is applied to disrupt the fibre structure.

Table 6. Comparison of Dry, Wet, and Steam Torrefactions. Adapted from Chen et al. [38].

	Dry Torrefaction	Wet Torrefaction	Steam Torrefaction
Conditions	• 200 to 300 °C • 10 to 240 min • 1 atm	• 180 to 260 °C • 5 to 240 min • 1 to 200 atm	• 200 to 400 °C • 5 to 120 min • 1 to 40 atm
Advantages	• Easy process • No need for post-drying • Batch production	• Low temperature • Can handle wet biomass	• No pre-drying • Good for wet biomass • High solid products
Disadvantages	• Pre-drying is needed • High ash content	• Post-drying is needed • Corrosion generation in the reactor	• Requires high energy • High pressure needed

4.2.4. Principle of Torrefaction

Biomass is degraded during torrefaction, releasing char and volatiles. These volatiles are compounds and non-condensable gases. Char produced by torrefaction contains compounds derived from the degradation of sugars and lignin. The first phase is drying the

biomass and evaporating moisture. Some extractives, such as terpenes, are also evaporated along with moisture. At about 200–220 °C, hemicellulose degradation begins, followed by cellulose, while lignin degrades slowly over a wide range [37]. In the final stage, the bonds between carbon, oxygen, and hydrogen break, yielding thermally stable torrefied biomass [135]. The torrefaction process is shown in Figure 7.

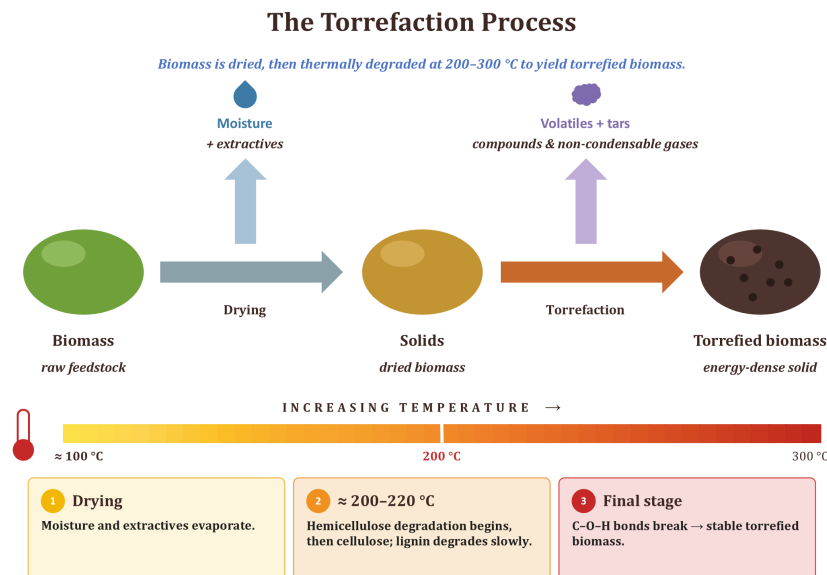


Figure 7. Steps in the Torrefaction Process.

It is important to distinguish an increase in energy density from an increase in the total recoverable energy. Torrefaction raises the HHV of the solid by removing oxygen-rich volatiles, but this is achieved through a loss of mass, so the weight and energy yields decrease under severe torrefaction even though the energy density of the fuel is enhanced [38]. The performance of torrefaction is therefore described by three related quantities [136].

$$\text{Mass yield (\%)} = \frac{m_{\text{torrefied}}}{m_{\text{raw}}} \times 100, \quad (1)$$

$$\text{Energy densification ratio} = \frac{\text{HHV}_{\text{torrefied}}}{\text{HHV}_{\text{raw}}}, \quad (2)$$

$$\text{Energy yield (\%)} = \text{Mass yield} \times \text{Energy densification ratio}, \quad (3)$$

where $m_{\text{torrefied}}$ and m_{raw} are the dry masses of the torrefied and raw biomass, and $\text{HHV}_{\text{torrefied}}$ and HHV_{raw} are their higher heating values. Since the mass yield decreases faster than the HHV increases under severe conditions, the energy yield decreases with increasing torrefaction temperature and time. The energy lost from the solid is carried by the volatiles, which can be recovered by combustion to supply process heat. Torrefaction conditions must therefore be selected to balance the gain in energy density against the loss in energy yield, rather than to maximise HHV alone.

There are five stages in the torrefaction process. In the first stage, biomass is heated up to the drying temperature so that the moisture in the biomass is evaporated gradually. The temperature in the initial heating stage is up to 90 °C. In the drying stage, the temperature of the biomass is kept constant at 100 °C, and all moisture is evaporated. The third stage, called the post-drying and intermediate stage, involves mass loss due to the complete removal of water. The temperature of this stage is 200 °C. The fourth stage is called torrefaction. In this stage, the temperature rises to 270 °C, the torrefaction temperature, from 200 °C, then gradually returns to 200 °C after a constant torrefaction temperature for

a set time. In the final stage, the biomass is cooled down to the room temperature or the desired temperature. The properties of raw and torrefied biomass are shown in Figure 8.

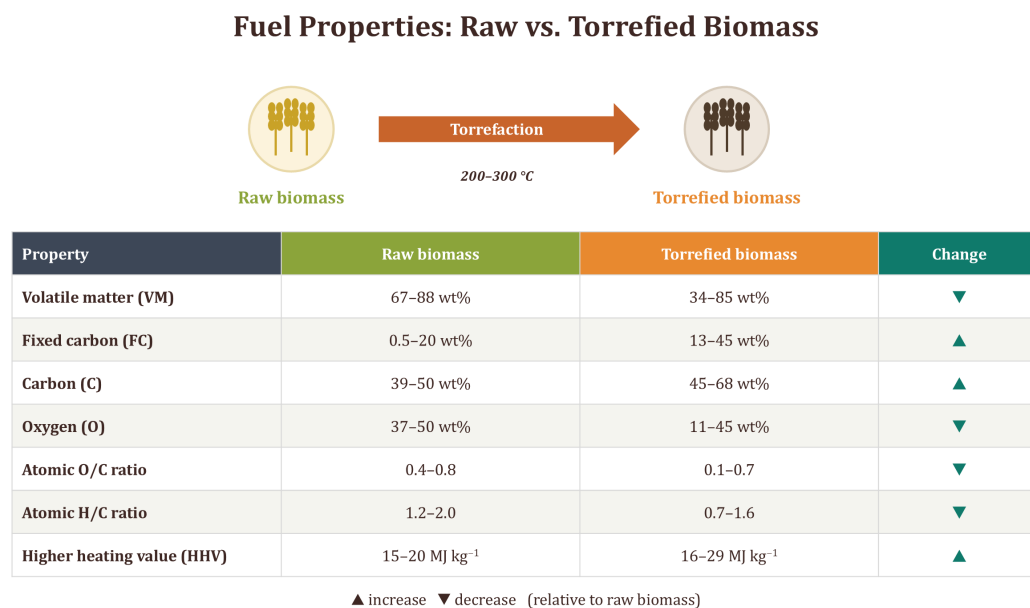


Figure 8. Comparison of the fuel properties of raw and torrefied biomass, Adapted from Chen et al. [38].

4.3. Applications of Torrefaction

Torrefaction finds application in co-firing, combustion, gasification, pyrolysis, and ironmaking. Conventional co-firing requires a separate biomass feed system because of the large particle size of raw biomass, whereas torrefied biomass has a small particle size, low moisture, excellent grindability and combustion characteristics, making it well suited to co-firing with coal; its reduced dimensions also allow much shorter gasification times at reactor temperatures of 1400 °C [38]. Torrefaction affects the pyrolytic product slate, yielding bio-oil of lower water content and a solid of higher carbon content than raw biomass [137]. In ironmaking, where the steel and iron industry accounts for about 20% of total industrial energy demand and 6.7% of CO₂ emissions [138], energy efficiency and emissions reduction have received growing attention [139]. Biomass has been proposed as a substitute for coal in pulverised coal injection for iron production [140], and simulation of biomass substitution in a blast furnace estimated an energy saving potential of 115.7 GWh/year and a 6.4% reduction in CO₂ using torrefied biomass [141]. Torrefied biomass therefore serves as a coal replacement that lowers CO₂ emissions.

4.4. Torrefaction—Experimental and Case Studies

Pentananunt et al. [142] torrefied wood and briquettes, and found moisture content to fall with increasing temperature and time. After 3 h at 270 °C, moisture dropped from 11.25 to 3.20%, VM and ash from 69.80% and 0.74% to 65.71 and 0.65%, and FC increased from 18.20% to 30.24%. Ultimate analysis showed carbon increasing from 51.91 to 64.37%, hydrogen falling from 6.1% to 5%, and oxygen from 41 to 29.80%.

Torrefying poplar at 200, 225, 250, 275, and 300 °C, Ru et al. [143] observed that both the pyrolysis char yield and the initial decomposition temperature T_i increased with torrefaction temperature, the pyrolysis char yield reaching 29.7% for poplar torrefied at 300 °C for 30 min, as condensation reactions enhanced solid yield.

T_i increased through the breakage of weak branches and ether linkages during high-temperature torrefaction, raising the thermal stability of the samples.

Bajcar et al. [144] torrefied miscanthus, wheat straw, and white willow at 220, 240, 260, 280, and 300 °C. Wheat straw held the largest chlorine fraction at 0.78% in raw biomass, followed by miscanthus and willow at 0.55% and 0.12%; after torrefaction, these fell to 0.24%, 0.18%, and 0.05%, respectively. For both miscanthus and wheat straw, the rapid decrease in Cl occurred at 220 °C with no significant change beyond 260 °C. Cl removal increased with temperature owing to the breakage of Cl volatile compounds.

Rubberwood is abundantly available in southern Thailand and has high potential for biofuel production. Kongto et al. [39] torrefied rubberwood sawdust (RWS) at 200, 250, and 300 °C, and found temperature to affect liquid and solid yields significantly, while time had only a small effect. Solid yield was above 85% at 200 °C for all times, indicating that the low temperature did not decompose the LCB and that mass loss arose solely from evaporation of moisture and VM; it fell to 70–75% at 250 °C through thermal degradation of cellulose and hemicellulose, and to 39.07–41.09% at 300 °C, where decomposition of most hemicellulose increased liquid and gas yields. The trade-off between energy and solid yield after torrefaction may be taken into account. After torrefaction, solid and energy yields are 70% and 90%, typically [39].

Bridgeman et al. [145] torrefied willow, wheat straw, and reed canary grass (RCG) at 503, 523, 543, and 563 K. At 563 K, RCG calorific value (CV) rose from 19,500 to 21,800 kJ/kg, moisture fell from 4.7 to 1.2%, and carbon rose from 48.6% to 54.3%; wheat straw CV rose from 18,900 to 22,600 kJ/kg, moisture fell from 4.1% to 0.8%, and carbon rose from 47.3% to 56.4%; willow CV rose from 20,000 to 21,900 kJ/kg, moisture fell from 2.8% to 0.0%, and carbon rose from 49.9% to 54.7%.

Studying the yield and quality of rice husk (RH) pyrolysis char at 220, 250, and 280 °C, Zhang et al. [146] recorded carbon rising from 39.4% to 45.5% and HHV from 16.24 to 17.57 MJ/kg at 280 °C, together with an increase in ash content from 15.3% to 18.7%. Solid char yield increased and liquid decreased with temperature. Interactions among lignin, cellulose, and hemicellulose negatively affect char formation through the matrix effect; in the pyrolysis of torrefied RH, these effects were eliminated during torrefaction, resulting in greater char.

Trubetskaya et al. [40] examined the effects of particle size, temperature, and residence time on olive stone torrefaction. The torrefied product contained high concentrations of K, Ca, and Si, and the char fraction exceeded both the gas and liquid yields. Below 270 °C, the degree of torrefaction was low, char yield being not significantly different; at 300 °C, char yield decreased while gas and bio-oil increased, and particles larger than 2 mm gave rise to vapour-char interaction that increased the tar fraction. Extending residence time from 30 to 60 min at 270 °C produced no significant change, but from 60 to 120 min, char yield fell from 80% to 45% with increased water and tar yield. Olive stone below 2 mm torrefied at 270 °C for 30 min was found suited to briquetting with coal, owing to high solid char yield and low reactivity.

Benavente et al. [147] converted two phases of olive mill waste (TPOMW) into carbon-rich solids at 150, 200, 250, and 300 °C. At 300 °C, carbon rose from 56.1% to 67.7%, oxygen fell from 29.9% to 10.1%, and HHV rose from 26.4 to 30.0 MJ/kg. Energy density fell from 12397 to 9366 MJ/m³ after torrefaction but rose sharply to 29,994 MJ/m³ once the sample torrefied at 300 °C was briquetted, showing that torrefaction and briquetting are promising routes for converting olive mill waste into a useful feedstock.

Zhang et al. [148] applied wet torrefaction to rice husk at 150, 180, 210, and 240 °C. Between 60–90% of AAEMs were removed, the rate increasing with reaction temperature as the pH of the reaction liquid fell; organic acids induced by wet torrefaction caused the removal, and removal efficiency for the ion-exchangeable AAEMs held in extractives and hemicellulose depends on the decomposition of these elements. Raw rice husk gave solid

char, bio-oil, and gas yields of 29.8%, 38.2%, and 32%. At 150 °C bio-oil rose to 45.4% while char and gas fell to 27.4% and 27.2%, reflecting reduced AAEMs and their effect on pyrolytic products; at 240 °C biochar rose to 42.7% and bio-oil fell to 30.2%, due to increased lignin and decreased hemicellulose and cellulose content. Wet torrefaction thus improved fuel quality by combining the advantages of dry torrefaction and demineralisation. However, the same acidic liquid phase that drives AAEMs removal also creates a significant metallurgical challenge for wet torrefaction reactors. The organic acids released from hemicellulose, mainly acetic and formic acid, lower the pH of the process water, and together with the chloride leached from the biomass they attack the passive oxide film of stainless steel, promoting pitting and localised corrosion; this attack intensifies with increasing temperature and acid concentration [149]. In biomass hydrothermal conversion, acetic acid was found to noticeably accelerate the corrosion of candidate reactor steels, and an austenitic stainless steel (SS310) performed much better than a ferritic–martensitic steel (P91) [150]. This produces a direct trade-off: in the study by Zhang et al. [148], AAEM removal increased as the pH of the liquid fell with rising temperature, but so did the corrosion risk. The deashing benefit of wet torrefaction must therefore be balanced against the higher capital cost of corrosion-resistant alloys or linings, the need for corrosion allowances and inspection of pressurised vessels, and the treatment of the acidic process water, which remain key barriers to its scale-up.

Kai et al. [27] torrefied rice straw (RS) at 200, 225, 250, 275, and 300 °C, improving its physiochemical properties. Moisture fell from 4.35 wt.% in raw RS to 1.89 wt.% at 200 °C and 1.73 wt.% at 300 °C, volatiles from 74.86 to 66.42 wt.% at 300 °C, while FC rose from 11.56 to 19.16 wt.%. Initial concentrations of K, Na, Cl, Ca, Mg, and Si were 1.131, 0.540, 0.630, 0.120, 0.068, and 2.082 wt.%; after torrefaction at 300 °C, K and Na decreased to 1.117 and 0.099 wt.% while Cl, Ca, Mg, and Si increased to 0.662, 0.159, 0.084, and 2.693 wt.%. K changed little (1.10–1.15 wt.%) at all temperatures, whereas Na fell gradually to 0.447 wt.% at 250 °C and then sharply to 0.099 wt.% at 300 °C.

Comparing wet and dry torrefaction of corncobs, Zheng et al. [151] found that carbon content increased in both cases, with dry torrefaction yielding more. Raw ash content of 5.80% fell to 2.38% in WTC-175 and rose to 3.59% and 4.42% at WTC-185 and WTC-195, still below the initial value, whereas dry torrefaction raised it to 6.59% and 8.25% at DTC-245 and DTC-265, above the original. Na fell from 72.85 mg/kg to 21.07–27.10 mg/kg by WTC but only to 35.45–41.80 mg/kg by DTC. WTC significantly removed K, while DTC increased it. Dry torrefaction raises ash through concentration effects; in wet torrefaction, ash increased with temperature but remained below the original value, indicating that deashing is achievable by this route. AAEMs were therefore lower in wet- than dry-torrefied corncobs, and wet torrefaction was judged more effective for corncobs [151]. Since a small amount of AAEMs can alter the pyrolysis reaction mechanism and the properties of products, their removal reduces catalytic reactions in fast pyrolysis and increases the liquid product [49,152].

Pimchuai et al. [153] torrefied rice husk, sawdust, peanut husk, bagasse, and water hyacinth at 250, 270, and 300 °C. Moisture content and VM decreased with increasing temperature and residence time for rice husk, and ash content and FC increased with temperature but fell with residence time. Moisture loss reached 88% and 89% for bagasse and hyacinth, against 84%, 82%, and 79% for rice husk, sawdust, and peanut husk, the lowest moisture content being observed at 300 °C and 1.5 h.

The reviewed studies demonstrate that torrefaction enhances biomass fuel quality through moisture reduction, carbon enrichment, and increased heating value. Across feedstocks such as wood, rubberwood, rice straw, rice husk, wheat straw, willow, and olive waste, higher torrefaction temperature generally reduced moisture and VM while

increasing FC [27,39,142,145,147], giving higher calorific values and improved thermal stability that indicate the suitability of torrefied biomass as a coal substitute. Several studies, however, reported a substantial decline in solid yield above 280–300 °C from extensive decomposition of hemicellulose and cellulose [39,40], so torrefaction conditions must be optimised to balance energy densification against acceptable mass retention.

A critical comparison further reveals that conventional dry torrefaction alone may not effectively remove AAEMs. While some reduction in Cl and certain minerals was achieved [144], several studies reported concentration effects that increased ash and mineral contents in the torrefied product [146,151]. Wet torrefaction, by contrast, demonstrated superior demineralisation, removing up to 90% of AAEMs and significantly reducing ash-forming elements [148,151]. These findings highlight an important research gap, although torrefaction improves fuel properties, its effectiveness in mitigating slagging, fouling, and corrosion risks remains feedstock-dependent, so integrating biomass washing or wet torrefaction with conventional torrefaction may offer a more effective pathway to high-quality solid fuel with reduced inorganic contaminants.

4.5. Challenges and Limitations of Torrefaction

Despite its effectiveness at upgrading solid fuel, torrefaction faces three categories of limitations that constrain its deployment.

The first is intrinsic to the process chemistry. Because upgrading is achieved through the loss of volatile mass, the residual non-volatile AAEMs are concentrated in the solid, so dry torrefaction improves calorific value and grindability while simultaneously raising the AAEMs that govern slagging and fouling [38,146], the central argument for coupling torrefaction with washing. The devolatilised organics also leave the reactor as tar and condensable vapours, typically 10–40 wt.%, which can foul and plug reactors and downstream lines unless off-gas handling and catalytic tar reduction are provided [154].

The second concerns reactor engineering and product consistency at scale. Heterogeneous feedstock with variable particle size and moisture produces non-uniform heat and mass transfer, and hence a non-uniform torrefied product, and demonstration plants have struggled to deliver a consistent, specification-grade fuel at a commercial level [155]. Defined and reproducible product quality is, in turn, a prerequisite for transparent solid-biofuel classes that meet standards such as ISO 17225-8 [48].

The third category is downstream. Torrefaction removes the lignin-derived and volatile components that act as natural binders, so the material is harder to densify and its pelletisation demands higher die temperature and pressure or added binders, increasing die wear and densification cost [129]. This is treated as a densification-and-logistics constraint rather than a torrefaction problem. Torrefied biomass is also prone to self-heating during storage, a handling-safety issue managed by controlling gas flow and oxygen exposure and by adequate post-production cooling [154]. Taken together, these limitations, not calorific performance, are what currently keep torrefaction financing and market maturity uncertain.

Table 7 summarises the key outcomes of all torrefaction pretreatment studies covered in Section 4. Regardless of biomass type, dry torrefaction consistently increased carbon content and HHV while reducing moisture and oxygen content. The largest HHV gain was observed for rubberwood, from 19.8 to 27.2 MJ/kg at 300 °C [39], followed by wheat straw (18.9 to 22.6 MJ/kg at 563 K) [145] and olive mill waste (26.4 to 30.0 MJ/kg at 300 °C) [147]. Carbon content increases ranged from 4.8 pp (willow: 49.9% to 54.7% at 563 K [145]) to 20.7 pp (rubberwood: 48.7% to 69.4% at 300 °C [39]), reflecting the significant role of temperature in driving devolatilisation. A critical finding common to all dry torrefaction studies is that AAEM concentration increases after treatment due to mass loss of volatiles, which concentrates the inorganic fraction, a limitation that wet

torrefaction partially addresses by achieving 60–90% AAEM removal simultaneously with fuel upgrading [148]. Cl removal by dry torrefaction was confirmed by Bajcar et al. [144], who reported Cl reduction from 0.78% to 0.24% in wheat straw at 300 °C, providing a route to reduced corrosion risk without the need for aqueous washing.

Table 7. Summary of torrefaction pretreatment studies reviewed in this work.

Ref.	Biomass	Type	Temp. (°C)	Time	Carbon (%)	HHV	Moisture	AAEM/Other Key Finding
[142]	Wood	Dry	270	3 h	51.91 → 64.37	↑↑	11.25 → 3.20%	FC: 18.20 → 30.24%; O: 41 → 29.8%
[145]	Reed canary grass	Dry	290	–	48.6 → 54.3	19,500 → 21,800 kJ/kg	4.7 → 1.2%	Oxygen decreased
[145]	Wheat straw	Dry	290	–	47.3 → 56.4	18,900 → 22,600 kJ/kg	4.1 → 0.8%	Oxygen decreased
[145]	Willow	Dry	290	–	49.9 → 54.7	20,000 → 21,900 kJ/kg	2.8 → 0.0%	Oxygen decreased
[146]	Rice husk	Dry	280	30 min	39.4 → 45.5	16.24 → 17.57 MJ/kg	–	
[144]	Wheat straw	Dry	220–300	60 min	–	–	–	Cl: 0.78 → 0.24%
[144]	Miscanthus	Dry	220–300	60 min	–	–	–	Cl: 0.55 → 0.18%
[144]	Willow	Dry	220–300	60 min	–	–	–	Cl: 0.12 → 0.05%
[39]	Rubberwood	Dry	200–300	20–60 min	48.67 → 69.40	19.78 → 27.15 MJ/kg	–	Ash increased: 1.61 → 3.93%
[147]	Olive mill waste	Dry	300	2 h	56.1 → 67.7	26.4 → 30.0 MJ/kg	–	Oxygen decreased
[148]	Rice husk	Wet	150–240	60 min	40.8 → 45.8	16.22 → 18.1 MJ/kg	–	AAEM removal 60–90%
[27]	Rice straw	Dry	200–300	10–70 min	–	–	4.35 → 1.73%	VM: 74.86 → 66.42%
[153]	Rice husk, residues	Dry	250–300	1–2 h	–	–	Loss 79–89%	Moisture loss max. at 300 °C, 1.5 h

FC = fixed carbon; VM = volatile matter; O = oxygen content. ↑↑ = significant increase; – = not reported. Temperatures are converted from Kelvin for Bridgeman et al. [145].

4.6. From Laboratory to Demonstration Scale

Most of the studies reviewed above were conducted at gram-to-kilogram laboratory scale, and this is itself the principal barrier to deployment. Torrefaction is the more mature of the two routes: a survey of global initiatives classified installations as pilot (0.05–0.50 t h^{−1}), demonstration (0.5–2 t h^{−1}), and commercial (>2 t h^{−1}), with a number of demonstration and commercial plants commissioned between 2010 and 2014, for example, Torr-Coal (4 t h^{−1}; 30 kt yr^{−1}) and Topell (60 kt yr^{−1}), several of which have since been mothballed, dismantled, or shut down owing to weak market pull for torrefied fuel [156]. Representative demonstration data illustrate the transition: a semi-mobile pilot torrefaction-and-briquetting plant processing forest residuals at 510–680 kg h^{−1} produced torrefied biomass with a HHV of 21.2–23.0 MJ kg^{−1} (from 19.6 MJ kg^{−1} raw) at 79–84% dry-mass yield, with briquettes requiring on average only 37% of the grinding energy of raw material [157]. A pilot-scale vibrating torrefaction system treating rubber-wood and corn-waste pellets at 220–300 °C raised the heating value by about 20% (to 22.4 MJ kg^{−1}) with improved grindability and hydrophobicity, although mass and energy yields fell as torrefaction severity increased [158]. The recurring scale-up problems are reactor design for uniform heat and mass transfer across heterogeneous feedstock, off-gas (VOC/tar) handling, and product-quality consistency for a defined end-use, all identified as the outstanding demonstration-scale challenges [155].

Washing is comparatively closer to industrial practice for specific streams: the pilot-scale studies of empty fruit bunches and wheat straw reviewed in Section 3 were explicitly

designed around industrial washing parameters and step-washing with water recirculation to limit water consumption [120,126]. A pilot-scale test reinforces this: a continuous hydrothermal (hot-water) treatment unit of $15 \text{ ton-EFB}_{\text{wet}} \text{ h}^{-1}$, installed in the process line of a palm-oil mill, removed at least 78% of the potassium from empty fruit bunch at $\geq 60^\circ\text{C}$, and in fixed-bed combustion tests the treated EFB gave less than half the fouling deposit of untreated EFB, showing that laboratory washing results can be reproduced at pilot scale in an operating mill [159]. Combined washing–torrefaction, however, has been demonstrated only at lab-to-pilot scale, where combustion testing has confirmed reduced chlorine corrosion and aerosol formation but also exposed the water and effluent-management burden of the washing step [160]. No integrated, continuous washing–torrefaction demonstration plant with heat and water integration has yet been reported.

5. Combined Washing and Torrefaction Pretreatment

5.1. Rationale for Combining Washing and Torrefaction

The case for combining the two methods is not additive but complementary, and it follows directly from their individual limitations established in Sections 3 and 4. Washing removes the water-soluble and ion-exchangeable AAEMs (chiefly K), together with Cl, that cause slagging, fouling, and corrosion, and because these same species catalyse secondary cracking of pyrolysis volatiles, it also raises bio-oil yield, however, it leaves the oxygen content and energy density essentially unchanged and adds moisture [26,120]. Torrefaction does the opposite, it removes oxygen-containing volatiles, raising carbon content, HHV, and grindability, but the associated mass loss concentrates the residual AAEMs, so the torrefied solid can retain or worsen its slagging propensity [38,146]. Combining them therefore corrects both deficiencies in one processing chain deashing by washing, and deoxygenation plus energy densification by torrefaction.

The synergy is order-dependent. Washing before torrefaction removes free ions while they are still mobile, performing torrefaction first alters the inorganic speciation and binds free ions to the organic matrix, reducing the AAEMs removal achievable in a subsequent wash [161]. Reported outcomes confirm genuine, more-than-additive benefits for wheat straw, coupled with aqueous-phase-bio-oil washing and torrefaction, which removed up to 98.8% of K while simultaneously lowering the O/C ratio and shifting the pyrolysis product slate toward sugars and phenols and away from acids and ketones [162]. On a larger scale, combined pre-washing and torrefaction of low-grade biomass has been shown to reduce fine-particulate (aerosol) formation and mitigate high-temperature Cl corrosion during combustion, although its effect on bulk slagging can be modest, an important qualification that a purely additive view would miss [160].

5.2. Experimental and Case Studies

Cen et al. [161] conducted the combined pretreatment (CP) of rice husk, pinewood sawdust, and cotton stalk to observe the effects on AAEMs removal, deoxygenation, and the products of pyrolysis. Results showed that single washing with acetic acid removed more ash than washing with hydrochloric acid, and both washing pretreatments slightly increased the volatile content and HHV. After single torrefaction pretreatment, HHV and ash contents both increased, and lowered VM and oxygen content. It was observed that washing efficiently removed the AAEMs species, but the removal rate was not the same for all the species. The removal rate of K was about 95% for all three biomasses, as K was present in the water-soluble forms of KCl and K_2CO_3 in the intercellular spaces of biomass. The removal rates of Na and Mg were greater than 70%. After torrefaction, the amount of AAEMs increased due to some gas molecules of water, carbon dioxide, and carbon monoxide being released, which reduced the total mass and increased the AAEMs

proportion. AAEMs decreased significantly after the CP. Instead of the torrefaction-washing sequence, washing-torrefaction reduced the large amount of AAEMs, since torrefaction altered the composition of inorganic matters in biomass and resulted in better binding of free ions with organic compounds, which made the removal of AAEMs difficult in washing after torrefaction.

Zhang et al. [163] performed CP on rice husk to observe the effects on the distribution of pyrolysis products. It was observed that water washing removed about 95% of K and 54% of Cl from rice husk, but had little effect on Mg, Ca, and Fe. Water washing increased the yield of bio-oil from 35.90% to 41.25% and decreased the solid and gas yield, because AAEMs removed by washing contributed to char formation. Torrefaction increased the solid yield from 37% to 56.37%, but liquid yield decreased from 35.90% to 25.65%, and gas yield dropped from 27.10% to 17.98%. CP increased the biochar yield from 37.00% to 45.90% and decreased the gas yield from 27.10% to 21.20%, with no significant change in the liquid yield. Therefore, CP was better for the target generation of biochar and bio-oil [163].

Cen et al. [164] conducted the single and CP treatments of the corn stalk (CS). Washing decreased the K amount to a high level. During torrefaction, AAEMs were not removed but rather remained intact. CP was better than single washing or torrefaction because it improved the fuel qualities by reducing the AAEMs, increasing the HHV, and retaining the high energy yield. CP gave bio-oil and biochar yields between those of single washing and single torrefaction. The water content after CP in bio-oil produced from pyrolysis was reduced from 56.18% to 39.41%, while single washing and torrefaction reduced this value to 54.34% and 40.32%, respectively. CP increased the HHV of bio-oil from 10.61 to 14.91 MJ/kg, thus not only improving the quality of bio-oil but also maintaining the balance between the yield of bio-oil and biochar [164].

Chen et al. [136] performed the CP of cotton stalk (CTS) to upgrade the pyrolysis products and reduce the AAEMs. Washing improved the fuel properties by removing the K, with a removal rate of 82.30%. The removal rates of the other AAEMs (Na, Mg, and Ca) and of Fe were between 15 and 79 %. The amount of AAEMs increased after torrefaction but then decreased after CP. The carbon increased after CP from 45.16% to 52.27%, which was greater than the single washing and torrefaction pretreatment. CP indicated that HHV was greater than all other pretreatments. As compared with torrefaction, the CP increased the bio-oil yield from about 30.1 to 34.9 wt.% and the biochar yield from about 35.5 to 38.9 wt.% (relative increases of 16.1% and 9.58%), while the non-condensable gas yield decreased from about 34.1 to 26.2 wt.%. CP was better than the single one, because it gave higher yields of both bio-oil and biochar and decreased the yield of non-condensable gases [136].

Cen et al. [165] performed the CP of rice straw using three washing agents, namely acid, phenol, and simulated light bio-oil (SBO). K was removed 90.51%, 99.49%, and 99.53% by phenol, acid, and SBO, respectively. SBO showed the highest AAEM removal rates during washing. The increase in AAEMs in rice straw after torrefaction is due to the release of a small portion of the volatile content. The amount of AAEMs in the torrefied-washed biomass was more than that of the washed ones, but still lower than the single torrefaction of the sample. CP was more effective for demineralisation and deoxygenation than any single pretreatment [165].

From the above experimental and case studies, it is evident that CP is an effective way to increase the biomass fuel properties, reducing AAEMs, increasing HHV, lowering the oxygen content, increasing the bio-oil yield, reducing the gas yield, and increasing the quality of pyrolytic products. Table 8 presents a comparison of CP outcomes against single washing or single torrefaction across all five studies reviewed in Section 5. The data demonstrate unambiguously that CP provides outcomes that neither single method can achieve independently. Washing alone maximises AAEM removal but reduces biochar

yield; torrefaction alone maximises biochar yield and energy density but increases residual AAEM content, whereas CP balances both objectives. The most compelling quantitative evidence comes from Cen et al. [164], who reported that CP reduced water content in bio-oil from 56.18% to 39.41%, compared to 54.34% for single washing and 40.32% for single torrefaction. Chen et al. [136] showed that CP increased bio-oil yield from about 30.1 to 34.9 wt.% and biochar from about 35.5 to 38.9 wt.% relative to torrefaction alone for cotton stalk. These results confirm CP as the most effective approach for producing premium pyrolytic products from LCB, though the optimal sequence (washing-then-torrefaction) must be respected, as torrefaction prior to washing reduces subsequent AAEM removal efficiency [161].

Table 8. Quantitative outcomes of combined washing and torrefaction pretreatment versus single pretreatments.

Ref.	Biomass	Washing Conditions	Torrefaction Conditions	K Removal	Bio-Oil/Biochar Yield	Bio-Oil HHV/Water Content
[161]	RH, Pinewood, Cotton stalk	50 °C, 2 h, HCl or AcOH	260 °C, 30 min, N ₂	>95%	CP > single pretreatment	CP > single pretreatment
[163]	Rice husk	60 °C, 6 h, DI water	280 °C, 10 min, N ₂	≈95%	Washing: bio-oil 35.90 → 41.25%; Torr: liquid 35.90 → 25.65%; CP: biochar 37.0 → 45.9%, gas 27.1 → 21.2%; liquid unchanged	–
[164]	Corn stalk	60 °C, 6 h, DI water	250 °C, 30 min, N ₂	K removal: >85%	–	Water in bio-oil: Raw 56.18%, Wash 54.34%, Torr 40.32%, CP 39.41%; HHV: 10.61 → 14.91 MJ/kg
[136]	Cotton stalk	60 °C, 2 h, torr. liquid	250 °C, 30 min, N ₂	82.3%	CP vs. Torr: bio-oil 30.1 → 34.9%, biochar 35.5 → 38.9%, gas 34.1 → 26.2%	C: 45.16 → 52.27%; HHV CP > all pretreatments
[165]	Rice straw	50 °C, 2 h, SBO/acid/phenol	250 °C, N ₂	SBO: 99.53%; Acid: 99.49%; Phenol: 90.51%	–	CP > single pretreatment for demineralisation + deoxygenation

CP = Combined Pretreatment; RH = rice husk; AcOH = acetic acid; SBO = simulated bio-oil; DI = deionised; N₂ = nitrogen atmosphere; Torr = torrefaction alone.

6. Critical Comparison of All Pretreatment Methods

The pretreatment methods reviewed in this work are compared using twelve criteria, and the process-based definitions applied to the qualitative grades are given in Table 9. Table 10 provides a critical comparison of all biomass pretreatment methods discussed in this review. The criteria were defined by the authors rather than adopted from a previously published comparison, and follow directly from the requirements established earlier in this work. Criteria 1–4 (AAEM removal, HHV, carbon content, deoxygenation) correspond to the biomass properties of concern and the ash, Cl, and calorific limits that solid-biofuel standards impose on combustion and co-firing (Section 1.8) [29,47,48]. Criteria 5–7 (bio-oil yield, biochar yield, post-treatment moisture) follow from the downstream end-uses of Section 1.8, since AAEMs govern the pyrolytic product slate while gasification and densification demand a low, stable moisture content [26,38,49]. Criteria 8–12 (energy consumption, capital cost, environmental impact, scale-up status, and the governing limitation) are the deployment dimensions on which the demonstration-scale and techno-economic literature evaluates these technologies (Sections 4.6 and 6.2) [155,156,166,167]. A criterion was re-

tained only where the reviewed studies report comparable evidence for at least two of the seven method classes; the cellulose/lignin ratio and grindability were therefore excluded, the former being decisive only for the biochemical routes set aside in Section 2.4 and the latter reported quantitatively for torrefaction alone. Quantitative values from the reviewed studies are reported wherever the literature allows; where only a qualitative grade can be given, it is defined by explicit process-based criteria (Table 9; footnote b of Table 10) rather than by relative ranking.

Physical methods such as milling and extrusion are effective for particle size reduction and are well-established at an industrial scale, but impart no improvement in fuel quality or AAEM content, and ball milling carries a heavy energy penalty [50,55]. Chemical methods (acid, alkali, ionic liquids) offer high delignification efficiency suitable for biochemical conversion pathways, but generate chemical waste streams and present high scale-up costs [50,51]. Biological pretreatment is the most environmentally benign option but is limited by slow kinetics (typically 30+ days) and remains confined to laboratory scale [52]. Among the thermochemical options, dry torrefaction provides the largest gain in heating value, raising HHV by 1.3–7.4 MJ/kg and carbon content by up to 20.7 pp, but consistently increases AAEM concentration as a consequence of mass loss during devolatilisation [38,144,146]. Wet torrefaction uniquely combines fuel upgrading with AAEMs removal (60–90%), but requires post-treatment drying and is susceptible to reactor corrosion [148,151]. Washing alone is highly effective for AAEMs removal and is the most cost-efficient single pretreatment, but does not improve energy density and requires drying [26,120]. The CP addresses the limitations of each individual method and gives the most complete improvement in fuel quality and pyrolytic product distribution; it has been validated at pilot scale for combustion performance [160] and assessed techno-economically for grasses and straw [167], but no integrated continuous plant has yet been demonstrated, and its operating conditions remain unoptimised for most feedstocks. The advantages and limitations of washing, torrefaction, and their combination are summarised in Figure 9, which illustrates the complementary nature of the two methods; the principal limitation of each is offset by the principal advantage of the other.

Table 9. Process-based criteria used for the qualitative grades in Table 10.

Criterion	Low	Moderate	High
Energy consumption	Ambient operation; no thermal step	One thermal step at ≤ 300 °C and atmospheric pressure, or drying of a wet product	Pressurised operation, solvent recovery, or sequential thermal steps
Capital cost	Atmospheric vessels in standard materials	Heated reactor, or two units with a dryer	Pressure vessels, corrosion-resistant alloys, or solvent-recovery plant
Environmental impact	Benign reagents; recirculated or negligible effluent	Off-gas (VOC/tar) or process liquor requiring treatment	Acid, alkali, or solvent waste streams requiring neutralisation or recovery

Table 10. Critical comparison of biomass pretreatment methods across technical, economic, and environmental criteria.

Criterion	Physical	Chemical & Physicochemical ^a	Biological	Washing	Dry Torrefaction	Wet Torrefaction	Combined (Wash → Torrefy)
AAEMs and Cl removal	None; particle-size reduction only [50,53]	Not targeted; not reported for solid-fuel metrics [50,51]	None [52]	K up to 99.7%; Cl up to 100%; ash 13.3 → 8.2% [26,119,120,124–126]	None; AAEMs concentrated by mass loss [38,146,151]; Cl only: 0.78 → 0.24% [144]	60–90%; ash 5.80 → 2.38% [148,151]	K 82.3–99.5% [136,161,165]; up to 98.8% [162]
HHV improvement	None [50]	Not reported [50,51]	None [52]	+0.9 MJ/kg (EFB) [120]	+1.3–7.4 MJ/kg (16.2 → 17.6 [146]; 26.4 → 30.0 [147]; 19.8 → 27.2 [39])	16.2 → 18.1 MJ/kg (240 °C) [148]	Bio-oil HHV 10.61 → 14.91 [164]; 11.34 → 15.56 MJ/kg [136]
Carbon content	None [50]	Not reported (structural fractionation) [51]	None [52]	Slight ↑ via ash removal [125]	+4.8–20.7 pp (49.9 → 54.7 [145]; 39.4 → 45.5 [146]; 51.9 → 64.4 [142]; 48.7 → 69.4 [39])	↑, below dry torrefaction [151]	45.2 → 52.3% (cotton stalk) [136]
Deoxygenation	None [50]	Partial [50,51]	None [52]	Negligible [26,120]	O ↓ 11–20 pp (41 → 29.8 [142]; 29.9 → 10.1 [147])	Partial [148,151]	O/C ratio ↓ [161,162,165]
Bio-oil yield (pyrolysis)	No effect	Not reported	No effect	↑ 40.6 → 55.2% [26]; 35.9 → 41.3% [163]	↓ 35.9 → 25.7% [163]	T-dependent: 38.2 → 45.4% (150 °C); 30.2% (240 °C) [148]	34.9 vs. 30.1% (torrefaction alone) [136]
Biochar yield	No effect	Not reported	No effect	↓ 37.9 → 26.5% [26]	↑ 37 → 56.4% [163]; ↑ with T [143]	↑ with T: 29.8 → 42.7% [148]	38.9 vs. 35.5% (torrefaction alone); gas 34.1 → 26.2% [136]
Post-treatment moisture	Unchanged [50]	Increased; solvent removal needed [50,73]	Unchanged [52]	Increased; drying mandatory [117,120]	↓ (11.25 → 3.20% [142]; 4.35 → 1.73% [27]); hydrophobic [38]	Wet product; post-drying required [38]	↓ after torrefaction; interstage drying required [161,167]
Energy consumption ^b	5.4 (wet-disk) to 54 (ball) MJ/kg; mill-dependent [55]	Route-dependent; solvent recovery dominant for ILs, DESs, and organosolv [50,73]	Low (ambient) [52]	Moderate (ambient–60 °C wash + drying) [117,167]	Moderate (≤300 °C, atmospheric); electricity dominant cost [158]	High (pressurised + post-drying) [38]	High (interstage drying + torrefaction); sequence-dependent drying duty [167]

Table 10. Cont.

Criterion	Physical	Chemical & Physicochemical ^a	Biological	Washing	Dry Torrefaction	Wet Torrefaction	Combined (Wash → Torrefy)
Capital/production cost ^b	Low [50]	Route-dependent; high with solvent recovery or corrosion-resistant equipment [50,51]	Low [52]	Low; water and effluent handling [126,160]	Moderate; pellets US\$100–110/t [166]; +14% capex if torrefaction precedes pelletisation [128]	High (pressure vessel; corrosion-resistant alloys) [38]	Moderate (two units + dryer); biocoal 1.4–7.7 € GJ ^{−1} [167]
Environmental impact ^b	Low [50]	Route-dependent; high for acid/alkali/IL waste, lower for supercritical CO ₂ [50,51]	Low [52]	Low if effluent recirculated (step washing), else moderate [126]	Moderate (VOC/tar off-gas, 10–40 wt.%) [154]	Moderate (process liquor requires treatment) [38,148]	Moderate (effluent + off-gas); ↓ Cl corrosion, aerosols [160,167,168]
Scale-up status	Industrial [50]	Route-dependent: acid/alkali pilot–industrial [107]; ILs, DESs, SCFs lab–pilot [50,81]	Lab only [52]	Pilot–industrial; 15 t-EBF _{wet} h ^{−1} continuous unit, ≥78% K removal [159]; pilot rigs [120,126]	Demonstration–early commercial (pilot 0.05–0.50; demo 0.5–2; commercial > 2 t h ^{−1}) [156]; pilot plants [157,158]	Lab–pilot [148,151]	Lab–pilot; combustion validated at pilot scale [160]; no integrated continuous plant [167]
Main limitation	No fuel-quality gain; high milling energy [50,55]	Inhibitors; waste streams; solvent-recovery cost [50,51,73]	Very slow (≈30 d); lab scale [52]	Adds moisture (drying); no energy densification [117,120]	AAEMs concentrated; tar/VOC; poor pelletability [129]; self-heating <100 °C [154]	Reactor corrosion; pressurised; post-drying [38]	Complexity; effluent burden; conditions unoptimised; TEA limited to grasses and straw (see Section 6.3) [160,167]

^a Routes of Section 2.2 (ozonolysis, acid, alkali, organosolv, ILs, DESs, AFEX, SCFs, CELF, steam explosion), grouped for conceptual comparison only; they differ widely in cost, solvent recovery, toxicity, and pressure, so no single cost or environmental rating applies to all of them. Dilute acid used as a *leaching agent* is treated under “Washing”. ^b Qualitative grades (Low/Moderate/High) are defined by the process-based criteria in Table 9, not by relative ranking. AAEMs = alkali and alkaline earth metals; HHV = higher heating value; pp = percentage points; VOC = volatile organic compounds; EFB = empty fruit bunches; TEA = techno-economic assessment; ILs = ionic liquids; DESs = deep eutectic solvents; AFEX = ammonia fibre explosion; SCFs = supercritical fluids; CELF = co-solvent enhanced lignocellulosic fractionation; *T* = temperature. ↑ = increase; ↓ = decrease.

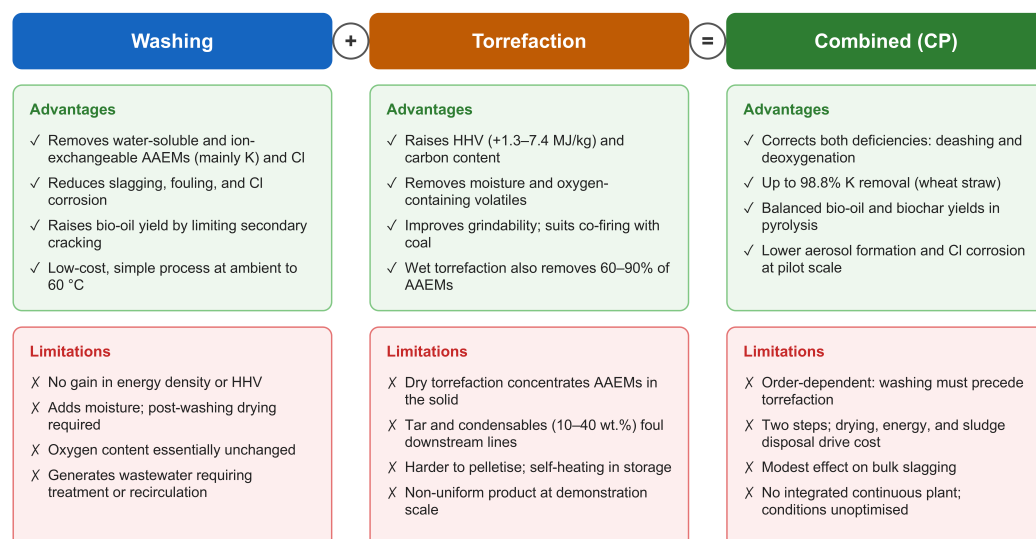


Figure 9. Advantages and limitations of washing, torrefaction and combined pretreatments.

6.1. Synthesis and a Pretreatment-Selection Framework

Read together, the tabulated data presented in this study do not identify a single “best” pretreatment; they identify a best pretreatment for a given feedstock and a given end-use, and the choice is governed by the target products. Three conclusions follow directly from the tabulated data.

First, for feedstocks whose limiting problem is ash chemistry (high-Cl, high-alkali herbaceous residues such as wheat and rice straw and empty fruit bunches), washing is both necessary and sufficient to meet combustion and co-firing specifications, achieving up to 99.7% K removal and near-complete Cl removal at the lowest cost of any single method, at the price of a mandatory drying step. Second, for feedstocks whose limiting problem is energy density and handling (woody residues already low in ash), dry torrefaction is the appropriate single method, raising HHV by roughly $1.3\text{--}7.4\text{ MJ kg}^{-1}$ and carbon content by up to 20.7 pp, but it must not be used where alkali is the constraint because it concentrates AAEMs. Third, for the common case of agricultural residues that suffer both deficiencies, and wherever a high-quality pyrolysis oil or gasification feed is the target, the combined washing-then-torrefaction route is superior to either single method: across the five studies in Table 8 it improved AAEM removal and fuel quality, balanced bio-oil and biochar yields, and, where reported, lowered bio-oil water content (e.g., from 56.2% to 39.4% with a 40.5% rise in oil HHV for corn stalk), subject to respecting the washing-before-torrefaction sequence.

These conclusions can be organised into the selection logic of Figure 10, which maps feedstock character and target end-use to a recommended pretreatment. The framework is offered as a decision aid rather than a rigid prescription, because the optimum still depends on operating parameters (wash time, temperature, solid/liquid ratio, torrefaction temperature and residence time).

6.2. Technical and Economic Feasibility

Fuel quality gains are only meaningful if the upgraded fuel remains economic against untreated biomass and coal. Techno-economic analyses of torrefaction, almost always coupled with pelletisation, place the plant-gate minimum selling price of torrefied pellets in the region of US \$100–110 per tonne for agricultural-residue feedstock, with the torrefaction reactor identified as the single largest capital item and feedstock and labour costs dominating operating expenditure [166]. Whether torrefaction precedes or follows densification materially changes the economics: torrefaction-before-pelletisation configurations

were reported to need roughly 14% higher total capital investment than the alternative sequence at $\sim 100 \text{ kt yr}^{-1}$ capacity [128]. For steam-based upgrading, the premium is larger, pretreated pellets cost 146–156 US $\text{\$ t}^{-1}$ against 95–105 US $\text{\$ t}^{-1}$ for conventional pellets, i.e., an added 2–3 US $\text{\$ GJ}^{-1}$ [169]. A recent pilot-scale study placed the production cost of torrefied rubber-wood and corn-waste pellets at 8000–11,000 THB per tonne, with the electricity demand of the torrefaction step rather than feedstock as the dominant and most scale-sensitive cost component [158]. These figures show that torrefaction can be profitable but is sensitive to feedstock cost and scale, which is consistent with the thin population of surviving commercial plants noted in Section 4.6.

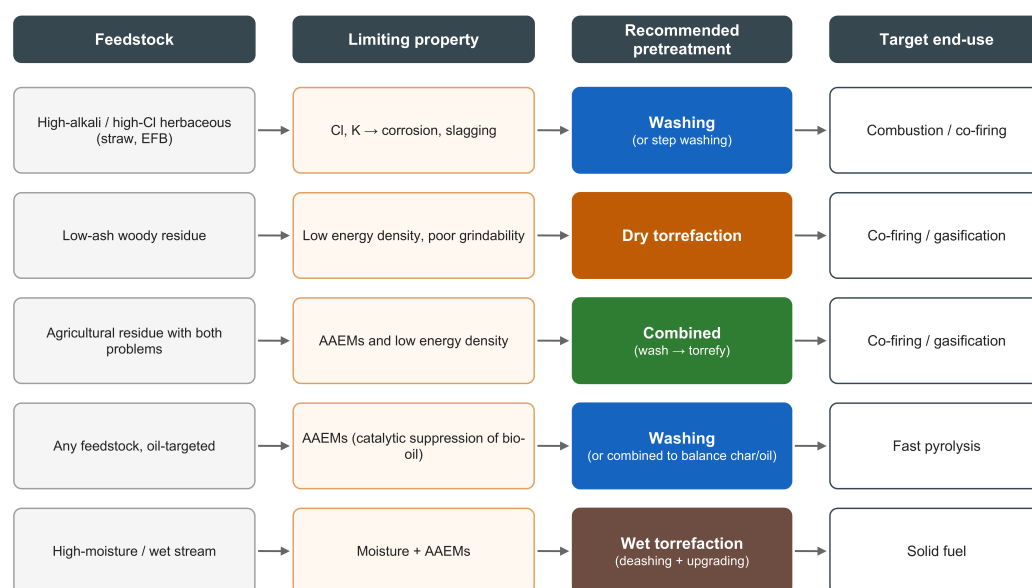


Figure 10. Feedstock and end-use-based framework for selecting a biomass pretreatment.

On the performance side, the upgrading translates into measurable end-use benefits. Torrefied and densified fuel can be co-fired with coal in existing power plants with only minimal modifications [155]. When washing precedes torrefaction, the removal of K and Cl further reduces corrosion and fine-particulate emissions during combustion, thereby extending boiler availability [160,168]. Turning to the economics of the combined washing–torrefaction chain, Abelha and Kiel [167] evaluated both prewash (washing before torrefaction) and postwash (torrefaction before washing) routes for roadside grass, wheat straw, and miscanthus, and showed that the economically preferred sequence is governed by feedstock moisture: prewashing is favoured for wet feedstock such as roadside grass, whereas postwashing suits dry residues such as straw and miscanthus, because the hydrophobic torrefied solid mechanically dewateres to a far lower moisture content ($\approx 42\%$ versus 65% for straw) and thereby removes the supplementary natural-gas demand of the dryer. They reported an optimum plant size of $100\text{--}150 \text{ kt yr}^{-1}$ (dry input) common to all three feedstocks, with biocoal production costs of $\approx 1.4 \text{ € GJ}^{-1}$ for large-scale roadside grass, $\approx 4.6 \text{ € GJ}^{-1}$ for Southeast-Asian rice straw (including ocean freight to Rotterdam), and $\approx 7.7 \text{ € GJ}^{-1}$ for miscanthus. Profitability was likewise feedstock-dependent: prewashed and torrefied roadside grass returned an internal rate of return of 15.6% at a biocoal selling price of 4.8 € GJ^{-1} (assuming a 25 € t^{-1} gate fee), Dutch wheat straw was unprofitable without a gate fee, and Asian rice straw reached an IRR of 11.6% at 6.2 € GJ^{-1} with feedstock cost, CAPEX, consumables, and sludge disposal identified as the most critical parameters. Even so, this evidence rests on a single study limited to grasses and straw; comparable techno-economic data for the combined chain applied to other feedstock classes (for example, woody residues) and across the broader range of washing conditions surveyed in

this review remain scarce, and commercial-scale deployment of the integrated chain is still limited. Building out this broader evidence base is, in our assessment, the decisive step for combined pretreatment to progress toward commercial application.

6.3. Barriers to Commercialisation of Combined Pretreatment

Although CP corrects both fuel deficiencies (Table 10), three interrelated barriers currently prevent its commercial deployment.

Process complexity. CP couples two unit operations that differ in phase and temperature: an aqueous washing step followed by a thermal step at 250–280 °C (Table 8). Because washed biomass is saturated with water, an intermediate drying step is unavoidable, and this drying duty, rather than the torrefaction itself, becomes a major energy demand [167]. No integrated continuous plant has yet been demonstrated; the only evidence at larger scales comes from pilot combustion trials [160]. Future designs will therefore need to integrate heat between the torrefaction and drying steps, for example, by using the energy from the torrefaction volatiles to supply the dryer.

Effluent burden. Washing transfers K, Cl, and water-soluble organics into a leachate that must be treated or disposed of, and sludge disposal has been identified as one of the most critical cost parameters of the combined chain [167]. Freshwater demand can be reduced by step washing with recirculating wastewater, which achieved 64–68% K and 97–99% Cl removal in three 10-min steps [126], but recirculation has not yet been assessed within an integrated CP process, and valorisation of the nutrient-rich leachate remains unexplored.

Unoptimised conditions. The five CP studies reviewed used different washing agents (deionised water, HCl, acetic acid, torrefaction liquid, and simulated bio-oil), washing temperatures of 50–60 °C, and torrefaction times of 10–30 min (Table 8), so no optimum set of conditions can yet be identified for any feedstock. The process sequence introduces an additional conflict. Washing before torrefaction maximises AAEMs removal, because torrefaction binds free ions to the organic matrix [161], whereas techno-economically the reverse sequence is favoured for dry residues such as straw and miscanthus, because the hydrophobic torrefied solid dewateres to about 42% moisture compared with 65% for washed raw straw, reducing the drying demand [167]. The technical and economic optima, therefore, do not yet coincide. Moreover, the only techno-economic assessment of CP is limited to grasses and straw, and found wheat straw to be unprofitable without a gate fee [167].

Resolving these barriers requires systematic, feedstock-specific optimisation that considers AAEMs removal, drying energy, and effluent treatment together, followed by demonstration in an integrated continuous unit.

7. Conclusions

This review shows that no single pretreatment corrects both deficiencies that prevent agricultural residues from being used as high-quality solid fuels, namely their high AAEM content and low energy density, but that washing and torrefaction are complementary and, when combined, address both. Washing is the most cost-effective route for removing the water-soluble and ion-exchangeable AAEMs (chiefly K), together with Cl, that cause slagging, fouling, and corrosion. Bio-oil and acid washing outperform water, and they increase bio-oil yield during pyrolysis; however, they do not raise energy density. Dry torrefaction raises the HHV and the carbon content, but concentrates AAEMs in the solid, whereas wet (hydrothermal) torrefaction removes 60–90% of AAEMs while upgrading the fuel. Combined pretreatment (CP), with washing performed before torrefaction, corrects both deficiencies, achieving up to 98.8% K removal and, a lower bio-oil water content. The choice

of pretreatment should therefore be guided by the feedstock and end-use: washing for high-Cl herbaceous residues, dry torrefaction for low-ash woody biomass, CP for residues with both problems, and wet torrefaction for high-moisture streams.

Despite these benefits, CP remains at laboratory and pilot scale. Its future development depends on five priorities:

1. Feedstock-specific optimisation of the washing agent, solid-to-liquid ratio, and torrefaction temperature and time.
2. Integrated continuous reactors that recycle wash water and reuse torrefaction liquids or aqueous bio-oil as washing agents, reducing water, drying, and sludge-disposal costs.
3. Pilot- and demonstration-scale combustion and co-firing trials that quantify the reduction in slagging, fouling, and corrosion.
4. Techno-economic and life-cycle assessments to establish the cost and emission benefits of CP relative to single pretreatments.
5. Production of CP-upgraded fuels that meet solid-biofuel standards such as ISO 17225, enabling their market uptake.

If these challenges are addressed, CP could convert abundant, low-value residues such as straw and husk, currently burnt in the open or left unused, into a standardised, low-carbon solid fuel for combustion, co-firing, and gasification.

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Abbreviations

The following abbreviations are used in this manuscript:

5-HMF	5-Hydroxymethylfurfural	LCB	Lignocellulosic Biomass
AAEMs	Alkali and Alkaline Earth Metals	LHV	Lower Heating Value
AcOH	Acetic Acid	Mg	Magnesium
AFEX	Ammonia Fiber Explosion	MgSO ₄	Magnesium Sulphate
Al	Aluminium	MSW	Municipal Solid Waste
APBO	Aqueous Phase Bio-oil	N	Nitrogen
B/A	Base-to-Acid Ratio	N ₂	Nitrogen (gas atmosphere)
Ca	Calcium	Na	Sodium
CAPEX	Capital Expenditure	NaOH	Sodium Hydroxide
CELf	Co-solvent Enhanced Lignocellulosic Fractionation	pp	Percentage Points
Cl	Chlorine	RCG	Reed Canary Grass
CO ₂	Carbon Dioxide	RH	Rice Husk
CP	Combined Pretreatment	RS	Rice Straw
CS	Corn Stalk	RT	Room Temperature
		RWS	Rubberwood Sawdust

CTS	Cotton Stalk	S	Sulfur
CV	Calorific Value	SBO	Simulated Light Bio-oil
CW	Candlenut Wood	SBP	Sugar Beet Pulp
DESs	Deep Eutectic Solvents	ScCO ₂	Supercritical Carbon Dioxide
DI	Deionised (water)	SCFs	Supercritical Fluids
DTC	Dry Torrefied Corncob	SCW	Supercritical Water
EFB	Empty Fruit Bunch	Si	Silicon
FC	Fixed Carbon	SSF	Simultaneous Saccharification and Fermentation
Fe	Iron	TEA	Techno-Economic Assessment
H ₂ SO ₄	Sulfuric Acid	THB	Thai Baht
HCl	Hydrochloric Acid	THF	Tetrahydrofuran
HHV	Higher Heating Value	T _i	Initial Decomposition Temperature
ILs	Ionic Liquids	TPOMW	Two Phases of Olive Mill Waste
IRR	Internal Rate of Return	VM	Volatile Matter
ISO	International Organization for Standardization	VOC	Volatile Organic Compounds
K	Potassium	WS	Wheat Straw
LAT	Liquid Ammonia Pretreatment	WTC	Wet Torrefied Corncob

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