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**Reusing, recycling and up-cycling of biomass: a review of practical and
kinetic modelling approaches**

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Abstract

There is a growing interest in the utilisation of biomass for a range of applications. Coupled with this is the appeal of improving the circular economy and as such, there is a focus on reusing, recycling and upcycling of many materials, including biomass. This has been driven by society in terms of demand for more sustainable energy and products, but also by a paradigm shift in attitudes of the population to reduce their personal carbon footprint. Herein we have selected a number of types of biomass (woody, herbaceous, etc.) and surveyed the ways in which they are utilised. We have done this in combination with assessing some kinetic modelling approaches which have been reported for the evaluation of different processes for the recycling, reuse and upcycling of biomass.

Keywords: Biomass, Recycling, Valorisation, Circular Economy, Kinetic Modelling, woody biomass, herbaceous biomass, aquatic biomass.

1. Introduction

Worldwide, there are issues around “waste” that are prevalent. Perhaps the most pressing issue is the attitudes and behavioural issues in terms of designating something as “waste”. From a chemical, and in turn energy, perspective there is normally an intrinsic (carbon) value in such materials; so that it would be better to deem this as “resources” rather than waste. This way of thinking can be considered part of the circular economy, a model by which as much value (and quality) as possible is retained via reuse, recycling, repurposing and up-cycling with aspirations towards zero waste. As such, there is interest in evaluating the potential value in the circular economy that was highlighted recently by Zacho [1].

The attitude of developing economies is much better suited to a circular economy perspective, since there is already an emphasis of extraction of maximum value from finite resources, despite the fact that challenges still need to be overcome to further support a transition to circular economies [2]. In more developed economies there has been more of a throwaway culture and this has had an impact in terms of landfill and environmental issues associated with non-biodegradable materials (e.g. plastics). Consequently, there have been increased movements to address issues around non-biodegradable materials [3].

It should be recalled that it is not ideal to send organic materials (e.g. biomass) to landfill since the degradation process will result in the production of methane gas which can escape to the atmosphere, thereby contributing to the Greenhouse Gas (GHG) effect [4-6]. As part of the circular economy, biomass resources should be utilised either by reuse (same purpose/application), recycled (repurposed for further use, typically in an application of similar value or below) or up-cycled/valorised (repurposed for an application of higher value e.g. extraction of biofuels and biochemical feedstocks as part of the bio-refinery concept).

1.1 General classifications of biomass

In general, biomass can be classified as primary, secondary and tertiary, where:

Primary biomass is produced directly via photosynthesis and is taken directly from the land. For instance, herbaceous and woody biomass along with the seeds of oil crops and the residues after the harvesting of forest trees and agricultural crops (corn stover, limbs, bark and wheat straw) are all considered primary biomass source [7].

Secondary biomass results from the processing of the primary biomass such as sawdust (physical processing), black liquor (chemical processing) or manure production by animals (biological processing).

Tertiary biomass is post-consumer byproducts such as animal fat, used vegetable oils, construction and demolition debris and packing byproducts.

1.2 Classification of biofuel generations

Biomass, when used as a biofuel, can also be classified to the first, second, third and fourth generation where:

- 1st generation biofuels come from edible biomass such as the ethanol production from fermenting sugars. There are major drawbacks of this generation in terms of the food versus fuel debate, low land use efficiency along with the geographical limitations.
- 2nd generation biofuels are derived from lignocellulosic biomass, either non-edible of food crop (rice husks) or non-edible whole plant biomass resources (grasses). The major challenge related to this generation is that processing can be expensive and a technological breakthrough is still required to make them more feasible.

• 3rd generation biofuels are produced using non-arable land such as algae and typically need a high capital cost to operate.

• 4th generation biofuels can be made using non-arable land and do not require the destruction of biomass to be converted into fuel such as the photobiological solar fuels [7].

In 2015, it was reported that the UK has reached an annual food “waste” of 7.3 million tonnes compared to only 1 million tonnes in the Republic of Ireland [8, 9]. This is not considering the abundance of other potential biomass resources, for example:

- Herbaceous materials (such as grass cuttings)
- Wood materials (such as hedges and trees)
- Consumer/manufacturing by-products (such as cork wine stoppers and sawdust);
- Aquatic/marine debris
- Agricultural manures.

The sheer volumes of biomass which would traditionally be designated as waste have prompted much action in terms of resource management worldwide. The European Union (amongst others) have been at the forefront of promoting the circular economy to avoid the production of waste [10-14] and the increased use of renewable resources [15, 16]. Significantly, there has been substantial research funds delegated to this area, e.g. the Resource Innovation Network for European Waste (ReNEW) was a €4.88 million project funded by The European Union’s Interreg programme [17].

1.3 Processing of biomass resources

Typically biomass resources can be processed in a number of ways such as:

- 109 (i) Combustion, which is the burning of biomass in the air to produce hot gases, ash and
110 consequently converting the stored chemical energy into heat which can be then
111 converted to kinetic energy through heating water to produce vapour which is used for
112 gas engines [18, 19].
- 113 (ii) Gasification, which is the partial oxidation of rice husk biomass at high temperatures to
114 convert the biomass to a combustible gas mixture which can be burnt directly or used as
115 a fuel for gas engines, gas turbines or can be used for the production of chemicals in the
116 case of the medium energy gases.
- 117 (iii) Pyrolysis, which is the thermal degradation of the biomass in an oxygen-free
118 environment which results a char (solid product), condensable vapour (bio-oil) along
119 with the gaseous products [20].
- 120 (iv) Liquefaction, which is the conversion of biomass into stable liquid hydrocarbons at low
121 temperatures and high hydrogen pressures.
- 122 (v) Torrefaction: which is a thermal treatment (200-300 °C) of raw biomass in an inert
123 (typically nitrogen) environment. The dry torrefaction (DT) is a mild pyrolysis process
124 that occurs in the temperature range of 200-350 °C [21].
- 125 (vi) Steam explosion: which is a process where the biomass is treated under pressure with
126 hot steam (200-260 °C), typically for relatively short periods of time (<10 min) [22].
- 127 (vii) Hydrothermal carbonisation (HTC): which is a moderate temperature (180-350 °C) and
128 high pressure (2-10 MPa) method with water that converts biomass to biochar, a carbon-
129 rich material. It is a combination of a number of chemical processes including
130 polymerization, hydrolysis, dehydration and decarboxylation [22]. It is a wet treatment

process to upgrade solid fuel for the production of more energy dense hydrophobic hydrochar while reducing the sulfur and ash contents [23].

- (viii) Anaerobic Digestion (AD): which is a biological process where microorganisms break down biodegradable material in an oxygen-free environment to produce biogas (a mixture of methane and carbon dioxide) which is combusted to generate electricity and heat or upgraded into biomethane [22].

2. Introductory piece to reusing and recycling approaches

2.1 Practical applications:

Firstly, using biomass for combustion in the energy sector depends upon the quality, chemical and physical parameters of the feedstock or feedstocks in question. Mancini *et al.*[24] developed a combined technique of near-infrared spectroscopy with multivariate analysis to predict the gross calorific value (GCV) and the ash content in the biomass feedstock, with a standard error of 0.23 kJ.g⁻¹ and 0.4%, respectively. This approach could be used at-line or off-line for providing an indication of the quality of the feedstock and its suitability for the industrial application. Unlike coal, biomass is characterised by its larger volatile content while also being a porous material i.e. biomass allows the ingress of bacteria and O₂, thus, increasing the risk of self-heating and ignition in storage and transportation [25]. Therefore, monitoring the temperature, volatile organic compounds (VOC), carbon monoxide (CO) and controlling the moisture is crucial to avoid the ignition [25].

2.2 Introductory piece on kinetic modelling:

Understanding the thermal kinetic behaviour of the thermal decomposition of biomass is crucial in order to identify the physicochemical combustion characteristics that hinder some of the energy generation applications. Thus, determining the activation energy (E_a) and the pre-

exponential factor using either model-fitting or model-free (iso-conversional) approaches, which are the two common methods for studying the Differential scanning calorimetry/Thermogravimetric analysis (DSC/TGA) solid-state kinetic data, is important. The model-fitting method is based on the best fit of the different models with the experimental thermogravimetric data using a single TGA/DSC curve, which might actually fit with more than one model. Conversely, the model-free iso-conversional method is a simple method that eliminates the error related to the model fitting [26]. In the iso-conversional method, different heating rate curves are required to calculate the kinetic parameters as a function of the extent of conversion (α) i.e. the E_a is calculated for a series of different conversion points. It is well known that the thermal analysis mechanism is complicated as it tends to take place in multiple steps with different reaction rates and, as such, an iso-conversional method is the most suitable method and, consequently, the most commonly used in this case. As the biomass composed of three different components (cellulose, hemicellulose and lignin), where each behave differently and separately during the biomass thermal decomposition. Thus, this complex behaviour of biomass decomposition should be considered in kinetic modelling. It was reported that there is a possibility of nine mechanisms of smoldering combustion during the thermochemical conversion of biomass [27, 28]. The Kissinger method is the only method in the model-free approach that does not determine the E_a as a function of progressive conversion (α), so it is not considered as an iso-conversional method as it instead assumes a constant E_a along the reaction progress [28, 29]. The basic principles of iso-conversional methods are outlined below.

The rate of thermal decomposition of the biomass can be described in terms of conversion (α) and temperature (T), as shown in Equation 1:

$$\frac{d\alpha}{dt} = k(T) f(\alpha). \quad \text{Equation 1}$$

where: α can be expressed as the decomposed mass fraction of the biomass as shown in Equation 2:

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \quad \text{Equation 2}$$

where: m_i , m_a and m_f are initial, actual and final masses, respectively.

The Arrhenius equation describes the temperature dependent function in terms of the activation energy (E_a) and the pre-exponential factor (k_0) as shown in Equation 3 [30, 31].

$$k(T) = k_0 e^{\left(\frac{-E_a}{RT}\right)} \quad \text{Equation 3}$$

where: E_a is the activation energy in kJ.mol^{-1} , T is the absolute temperature in Kelvin (K), R is the ideal gas constant ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$) and k_0 is the pre-exponential factor (min^{-1}).

By combining Equations 1 and 3, the thermal decomposition equation of biomass can be expressed as shown in Equation 4.

$$\frac{d\alpha}{dt} = k_0 e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad \text{Equation 4}$$

In the non-isothermal iso-conversional method, using different linear heating rates ($\beta = dT.dt^{-1}$), the thermal decomposition equation can be expressed as shown in Equation 5.

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad \text{Equation 5}$$

Non-isothermal iso-conversional methods such as the ASTM- E698 method is suitable for a single step reaction and can be expressed as shown in Equation 6.

$$\beta \frac{d\alpha}{dt} = k_0 e^{\left(\frac{-E_a}{RT}\right)} (1 - \alpha) \quad \text{Equation 6}$$

The Flynn-Wall and Ozawa (FWO) method propose the calculations of the variations in the apparent activation energy in terms of different linear thermogravimetric curves using the integral iso-conversional analysis method [32, 33]. The E_a can be calculated by plotting the natural logarithm of the heating rates ($\ln\beta$) versus inversely T , which represents a linear relationship with a corresponding α at different heating rates as shown in Equation 7.

$$\ln\beta = \ln \left(\frac{k_0 \cdot E_a}{R \cdot g(\alpha)} \right) - 5.331 - 1.052 \frac{E_a}{R \cdot T} \quad \text{Equation 7}$$

where: $g(\alpha)$ is constant at a given value of α .

In Kissinger-Akahira-Sunose method (KAS), the E_a can be calculated by plotting the natural logarithm of $\beta \cdot T^{-2}$ versus the inverse temperature [34] as shown in Equation 8.

$$\frac{\ln\beta}{T^2} = \ln \left[\frac{k_0 \cdot R}{E_a \cdot g(\alpha)} \left(1 - \frac{2RT}{E_a} \right) \right] - \left(\frac{E_a}{R \cdot T} \right) \quad \text{Equation 8}$$

On the other hand, isothermal iso-conversional methods, such as the isothermal Friedman method, assume that the thermal decomposition is independent of the temperature but, dependent on the reaction progress (rate of the mass loss), hence $f(\alpha)$ is constant at any given α . By taking the natural logarithm of both sides of Equation 5, yields Equation 9. Thus, by plotting $\ln\beta \frac{d\alpha}{dT}$ versus T^{-1} , E_a can be calculated from the gradient $\frac{E_a}{R}$.

$$\ln\beta \frac{d\alpha}{dT} = \ln[k_0 f(\alpha)] - \frac{E_a}{RT} \quad \text{Equation 9}$$

Vyazovkin discussed the common misconceptions related to the modern iso-conversional kinetics which are the estimation of the preexponential factor and reaction model, meaning of iso-conversional activation energy, single-step approximation and the application of iso-conversional methods to the process taking place on cooling [35]. Vyazovkin mentioned that the most significant advance in modern iso-conversional kinetics is associated with the quantitative interpretation of variations in the iso-conversional E_a as a sign of a multistep reaction mechanism.

3. Reusing and recycling

3.1 Woody biomass

There are significant opportunities to recycle and reuse wood. Many items, such as furniture, can be sold second-hand and used again; and there has been human behavioural/attitude changes with regards to secondhand consumption/use [36] which had been typical during the 19th Century [37], but became stigmatized in the 20th Century [38]. More recently there has been a marked increase in secondhand use [39, 40], which may have been financially driven by the impact on consumers from the 2008 economic crisis [41]. This was likely not the only driver in such a paradigm shift. Consumers are typically much more informed now than previous generations and are aware of environmental issues such as land use concerns such as deforestation for agriculture, the eat versus heat debate and landfill capacity. As such, consumers are very conscious of their carbon footprint and consequently, this is also being factored into their decisions. For example, it has been reported that the reuse/recycle pathways can help reduce GHG emissions [42], thereby reducing environmental impact.

This awareness has created an acceptance and, perhaps, even a demand for materials and products which originate from recycled/sustainable or deconstructed resources. Such materials include:

- Composites from by-products (e.g. sawdust) of the forestry/timber industry [43-45].
- Building materials from recovered/deconstructed solid wood [37, 46-48].
- Packaging/joinery/furniture/pallets from recovered solid wood [49].

Generally, with the reuse and recycling of woody biomass there is little, if any, chemical conversion and so there are not many examples of kinetic studies or modelling for such processes.

247 With fossil fuel reserves being depleted there has been a significant movement to
248 sustainable/renewable energy, and bio-energy is now a major contributor to this [22]. Given
249 that ability of biomass to be converted to solid, liquid and gas fuels, biomass is a suitable energy
250 resource for heat, power and transport [22, 50]. While the utilisation of liquid and gaseous
251 biofuels typically requires some chemical transformation/valorisation of the biomass, this is not
252 necessarily the same for solid fuels [50]. In order to use unprocessed biomass as a solid fuel, it
253 is normally blended with other fuels, such as coal, in order to compensate for the low calorific
254 value and high moisture content inherent in the biomass source [50, 51]. Woody biomass, can,
255 in theory, be combusted without much processing and as such, the application of woody biomass
256 as a fuel can still be considered a low-grade use [16] (i.e. no valorisation/up-cycling).

257 There are a number of methods by which fuel pellets can be prepared from heterogeneous
258 compositions of biomass including wood; size reduction, torrefaction, steam explosion,
259 hydrothermal carbonisation and biological treatment [22]. Some of these methods can be used in
260 isolation or in combination with each other.

261 *Size reduction:* Typically, this is a mechanical transformation via force/compression/pressure or
262 by cutting/shearing/grinding. The intention of this process is to increase surface area [22, 52-54].
263 These processes can be quite an energy intensive and while high energy costs can be covered
264 when the biomass is been used for value-added processing, the energy costs for producing pellets
265 for combustion needs to be kept to a minimum [52].

266 Torrefaction was used for the dehydration and decarboxylation in order to increase energy
267 density and improve the heating value whilst removing moisture and improving the
268 hydrophobicity of the pellets [22, 50]. This process does induce chemical changes and there are
269 some reports of kinetic studies of the torrefaction of woody biomass [55-59].

Sarvaramini *et al.* [55] studied mild (240 °C) and severe (280 °C) isothermal torrefaction of trembling aspen and birch woody biomass compared with samples of cellulose, xylan and lignin. Samples were heated inductively and samples were held at the target temperatures for 15 and 60 minutes in order to study the time dependency. C, H, N and S elemental analysis of the residual solids after the torrefaction was conducted while heating values were derived based on a method reported in the literature [60]. A kinetic model was derived which was determined from the weight loss of the samples as a function of time as observed using a thermogravimetric analyser (TGA), a method which was also previously reported in the literature [61]. The model was developed taking the distributed activation energy model (DAEM) approach. Using a log-normal distribution function the maximum activation energies of cellulose, xylan and lignin torrefaction were found to be 207 kJ.mol⁻¹, 132 kJ.mol⁻¹ and 196 kJ.mol⁻¹, respectively. The DAEM was found to accurately predict the volatile release observed by TGA for xylan and lignin, and less so for cellulose. Significantly, combining the individual activation energy models in three-parallel reaction meta-models could accurately model the experimental torrefaction data for the aspen and the birch.

Ren *et al.* also utilised thermogravimetric analysis for the torrefaction of douglas fir sawdust, but applied a two-step reaction model developed previously for xylan [62], which has also been applied to willow [63], to their study. The first and second reaction stage activation energies were determined to be 112 kJ.mol⁻¹ and 150 kJ.mol⁻¹, respectively and the two-step model was deemed to fit the torrefaction process well. Ren *et al.* [56] also reported a comparison of the pyrolytic decompositions of raw and torrefied biomass using a one-step, first order model and it was found that biomass which had undergone severe torrefaction were more likely to undergo multi-step pyrolysis.

Bates *et al.* [57] have reported a detailed one-dimensional model for the heat transfer, mass transfer, chemical kinetics and drying for the torrefaction of a single particle of woody biomass; a model which has been based on measured and/or previously determined characteristics from literature (for beech and willow) as opposed to utilising fitting parameters. Solved using MATLAB, it was reported that the model could accurately describe the torrefaction process in terms of the thermal behaviour, the residual mass and the initial energy yield of raw single woody biomass particles. Gul *et al.* [59] have reported a similar methodology to incorporate kinetic, volatile species release model and average solid composition models, but applied to beech, pine, wheat straw and willow.

Klinger *et al.* [58] conducted their aspen torrefaction experiments between 260 and 300 °C (at 10 °C intervals) for a period of 90 minutes in a micro-pyrolysis unit with the released volatiles analysed with a gas chromatograph (GC) and quadrupole mass spectrometer (QMS) to determine a mass normalized intensity, i.e. the MS signal divided by the initial mass of aspen. The reported model was comprised of a consecutive 3-step degradation which was deemed to be representative of the early stages of torrefaction (i.e up to 30% weight loss). This 3-step degradation model was found to accurately predict gas phase product kinetics, with water evolving initially and organic compounds evolving later on. An Arrhenius correlation was observed for this reaction model and so pre-exponential factors and activation energies were determined for the three steps.

It should be noted that there is no consensus in terms of the kinetics reported in any of the torrefaction studies, but given that different wood species were studied, from different geographic locations and with no accounting for seasonal variations for harvesting, this is not unexpected.

Steam explosion has been used to produce pellets with increased bulk density and higher mechanical strength by activating the lignin and changing the cellulose structure to enhance the

317 binding within the biomass [22, 64]. Lam *et al.* utilised drying and size reduction prior to the
318 steam explosion of Douglas-fir which was conducted at 200 and 220 °C for 5 minutes in a 1 L
319 high-pressure steam vessel [64]. Tooyserkani *et al.* [65] used conditions of similar severity
320 (220 °C; 5 mins) for Spruce, Douglas-fir and Pine. Wojtasz-Mucha *et al.* conducted a mild steam
321 explosion on Norway spruce at 150 °C for 15 and 30 min [66]. Significantly, the steam explosion
322 method was found to improve the calorific value [65]. Higher performance of steam explosion
323 was observed when high temperature was used for short durations and conversely at low
324 temperatures for longer periods [67].

325 There are limited kinetic studies associated with a steam explosion, though Lam *et al.* [68] have
326 reported a kinetic model using ordinary differential equations (and solved in MATLAB) for the
327 pseudo-lignin formation during the steam explosion of aspen wood.

328 Steam explosion is also used as a biomass pre-treatment to aid the optimisation of other processes
329 including anaerobic digestion [69, 70] and bio-refinery applications [71-73]. Steam explosion
330 can be enhanced with the addition of catalysts (e.g. acids) in order to improve hemicellulose
331 recovery and/or the enzymatic hydrolysis [67]. The addition of any catalyst, however, tends to
332 increase costs and so would only really be feasible in instances of higher grade use of the pellets
333 than combustion.

334 Jung and Kruse [74] have taken an Arrhenius-type approach of the previously reported
335 coalification model proposed by Ruyter [75] to evaluate the kinetics of HTC based on an
336 extensive range of HTC experimental data from the literature, which has included various
337 feedstocks including woods such as fir, poplar, pine, massaranduba and garapa [76-78]. The
338 approach calculates carbon content, oxygen content and hydrochar mass yield and it was reported
339 that the modelling is accurate enough to make predictions on the hydrochar yield.

Reza *et al.* [79] have reported an Arrhenius-type kinetic model based on their own experiments of HTC of loblolly pine. For the reported method, it is important to have accurate structural compositions of the biomass (cellulose, hemicellulose, lignin, and water extractives). A two-chamber reactor was used for the HTC which was studied at 200, 230, and 260 °C and weight loss measurements taken at 11-time points in the 0-30 mins interval. While all treatments resulted in biochar with improved higher heating values, the higher temperature HTC processes achieved greater improvements. It has been determined that the HTC process proceeds via two parallel first order reactions; cellulose degradation (activation energy of 73 kJ.mol⁻¹) and hemicellulose degradation (activation energy of 30 kJ.mol⁻¹).

There are various studies which have reported the kinetics of the combustion of woody biomass. While the studies discussed below are mostly focused on directly harvested wood and primary by-products, it should be noted that there are many other examples in the literature, including for different grades of waste wood [80] and reclaimed wood from used furniture [81, 82].

Fang *et al.* [83] reported a kinetic model for the two-stage combustion of red pine (as well as corn straw, Bermuda grass and bamboo). TGA was utilised to study the combustion characteristics in the temperature range from 80-815 °C at a heating rate of 30 °C.min⁻¹. Ignition of each of the samples occurred in the region of 250-280 °C and burnout in all cases was ~520 °C. As with the studies discussed previously herein, the first order Coats-Redfern method was used to calculate the activation energies, although a poor linear correlation was observed. Three steps in the process were observed; drying, pyrolysis and char combustion. A two-stage reaction kinetic model (for the pyrolysis and char combustion) was based on the experimental data and then was used to model the global process using weighted averages. The kinetics of the overall process were deemed to be very similar to the pyrolysis stage observed during the TGA. As this is the stage where the greatest mass loss was observed and so it is perhaps not surprising that this

would be a rate-limiting step as is indicated in the ~1% variation between the activation energies of the global process and the pyrolysis.

Other kinetic analysis studies of biomass combustion also used TGA but have applied the Coats-Redfern approach. Álvaro *et al.* determined that this was the most appropriate approach for the kinetic analysis of biomass combustion from their studies on woody biomass such as apple tree, eucalyptus tree and chestnut tree (along with other biomass) [84]. Importantly it was reported that Flynn–Wall–Ozawa and KAS model-free methods were not suitable approaches to employ to study the kinetics of biomass combustion since the assumptions of these two methods are not applicable for the entire range of combustion conditions which are observed for biomass combustion.

Yorulmaz *et al.* [85] have reported the combustion kinetics for pine, medium density fibre (MDF), particle board and plywood. Applying TGA in the temperature range of 30–900 °C, the thermal kinetics of the samples were studied at three different heating rates; 10 °C.min⁻¹, 20 °C.min⁻¹ and 30 °C.min⁻¹. The Coats Redfern approach for the determination of kinetic parameters was used to calculate activation energies and pre-exponential constants. Results were compared with similar studies in the literature [86-92].

In summarising, Yorulmaz *et al.* [85] identified three regions of thermal degradation that were observed during the course of the experiments: moisture and highly volatiles removal, 2) volatiles oxidised and removed 3) residual char oxidised. Given that three of the samples were treated (MDF, plywood and particle board) that are typically used in construction, it is important to note that the treatments resulted in the materials being less combustible than the untreated wood (pine). Furthermore, it was observed that the oxidation mechanisms of the treated woods were modified by the additives and glues.

Wang *et al.* [93] studied combustion of sawdust (as well as cornstalk, rice straw, rice hull) using thermogravimetric analysis from ambient conditions up to 850 °C using various ramp rates (10, 20, 50 °C.min⁻¹), with weight loss plotted as a function of temperature and the kinetic parameters for the volatile combustion stage and fixed carbon burning stage were obtained. Coats-Redfern plots were also used to determine activation energies and frequency factors. Of all the samples studied, the sawdust was found to have the lowest combustion reactivity. While combustion of this material could be considered a low-grade use, for this reason, it has been reported that when there is a significant amount of such material readily available, such as the sawmills in the Amazon, that there is a great potential for combustion for electrical production [94]. There is some advantage, therefore, in combustion of woody biomass to produce “bioenergy” as it has also been shown that compared to non-woody materials (e.g. fossil fuels), the greenhouse gas emissions can be lower when woods are used [18], while some industries, such as wine production, can become more profitable by using their own residual biomass as a fuel [95]. It should be noted that, in the spirit of the circular economy, that the residual char/ash left after combustion can also have further use as catalysts/filters/scrubbers [96-98].

Dhahak *et al.*[99] recently studied the thermochemical behaviour of three types of woody biomass (oak, fir and beech). They developed a kinetic model (Biomass Pyrolysis and Oxidation (BioPOx)) which involved 710 species and included 5035 reactions. They also claimed that BioPOx can predict results obtained from different experimental setup systems such as fluidized bed, tubular, jet-stirred reactor and closed ampoule along with various operating conditions such as temperature and pressure. Kim *et al.*[100] applied the multi-Gaussian distributed activation energy model (DAEM) and Kissinger equation to obtain the kinetic parameters of wood pellets thermal decomposition. The calculated E_a for each wood pellet component was 182, 191 and 203 kJ.mol⁻¹ for hemicellulose, cellulose and lignin, respectively.

3.2 Herbaceous biomass

Herbaceous biomass usually contains components such as seeds, cones, leaves and stems that require further size reduction (as described above in section 3.1) as a post-harvest handling procedure to increase the bulk density of the biomass, thus facilitating its storage and transportation alongside increasing the surface area, hence, increasing the chemical process reaction rate [101]. As discussed previously, size reduction methods such as the grinding process require energy. Naimi *et al.* [101], studied the required energy input for five herbaceous biomass (miscanthus, wheat straw, switchgrass, corn stover and canola straw) and found out that it was in the range of 22-35 kWh.t⁻¹ at a lab scale while using an industrial grinder showed a required energy input of 59.4 kWh.t⁻¹ [102].

The torrefied biomass or biochar derived from the thermal conversion of biomass is not classified as biomass according to the current European regulations, thus it cannot replace biomass in the energy production from renewable feedstocks [103].

Herbaceous biomass such as miscanthus is typically characterised based on its silica and inorganic contents. These components cause various problems during the thermal decomposition via valorisation and melting of the low potassium silicates compounds. While in the case of woody biomass this problem is less noticeable due to the low alkali and Si content in the biomass [104]. Thus, herbaceous biomass is usually mixed with other woody fuel or coal to harness the energy inherent in these types of biomass. Furthermore, the high ash content in the herbaceous biomass is problematic as it catalyses the thermochemical reactions and affects the yield of the pyrolysis products and their subsequent composition as well [105]. Forbes *et al.* studied the physicochemical characteristics of eight different biomass fuels such as pine, spruce, brash, Wr (riddled willow), Ws (open air dried chipped willow), miscanthus and commercially available wood pellets. They reported that the standard wood pellet fuel showed the best combustion performance while miscanthus showed the largest clinker formation due to the

highest ash content [106]. Biomass-coal co-firing has been shown to diminish the dangerous greenhouse gas emissions and particulates derived from the coal-fired power plants. However, due to the low bulk, low energy density and wet nature of biomass along with the seasonal availability, it makes it a more challenging process. Co-HTC (miscanthus-coal) showed increased higher heating values (HHV) compared with miscanthus (27.3 and 16.81 MJ.Kg⁻¹, respectively). While it decreased regarding the pure coal, due to the low mass density with HHV of 28.10 MJ.Kg⁻¹ [23].

It is well known that the main drawbacks of utilising biomass in energy applications are the moisture content along with low HHVs. Thus, different pretreatments could be applied to decrease the moisture content and increase the HHV such as DT as well as the aforementioned HTC. Recently, Wu *et al.* prepared charcoal briquettes from different types of biomass wastes using HTC and DT in a temperature range of 200-260 °C, followed by a carbonisation process at 400 °C. The results showed that the mass density and the compressive strength of the charcoal briquette prepared by the HTC are better than that of the DT method [21].

It is worth noting that biomass waste materials can be considered as challenges and opportunities at the same time. For instance, byproduct of AD in the form of digestate is rich in nutrients and can be recycled into fertilizers and pelletized for energy applications (combustion). There is a need to regulate digestate since it generates chemical oxygen demand, pathogens and other hazardous materials that can pollute the water [107]. In general, raw digestate contains up to 80 wt.% water content with a low bulk density which is problematic in storage, transportation and utilisation [108]. Thus size enlargement process (granulation) increases its bulk density, reduce the water content and enhance its flowability [108].

Emission control should be taken seriously in the case of using biomass in combustion engines as the gaseous and particulate emissions could be of potential risk to the environment and health. Those emissions could travel deeply into the respiratory tract [109].

The thermal degradation and the kinetic parameters during the combustion of *Arundo donax* and *miscanthus giganteus* was performed to quantify the gaseous and particulate emissions during the combustion. The results revealed that the thermal degradation of *miscanthus giganteus* was higher than that of *Arundo donax*, while the gaseous emissions along with the particulate matter of both were comparable. The *miscanthus giganteus* particulate emissions showed a value of 1.8×10^{13} particles.g⁻¹, while the dominant gaseous emissions were observed for CO₂, CO and VOC (volatile organic compound) with a value of 26.8 mmol.g⁻¹ [109].

3.3 Other types of biomass

Species of seaweed are conventionally characterised by their physical colour. The contents of organic based constituents such as carbohydrates, fats and proteins vary considerably in different types and species of seaweeds [110]. For instance, brown seaweed is very rich in carbohydrates with its protein content is relatively low, whereas approximately 33 wt.% of red seaweed is protein [111]. This feature of brown seaweeds may be useful in carbonisation based processes since carbohydrates can produce volatile gaseous compounds, as well as some char in the pyrolysis/carbonisation processes.

Phaeophyta or “brown seaweed” as it is more commonly known, is the most common type of seaweed. Mannitol, fucoidan, laminarin and alginic acid are the main building blocks of this particular type of seaweed [112, 113]. Conventionally, seaweed is classed as unsuitable for thermochemical conversions such as combustion and gasification unless pre-treatments are carried out or the application is carried out in conjunction with a co-existing feedstock. It is the inorganic matter that is contained within the seaweed that gives rise to some problems. Typically, this will lead to a higher variation in ash-forming elements, ash content and high levels of salts (e.g. sodium chloride) compared to other fuel sources available such as coal or diesel. The

combination of high Na and Cl concentrations promote the risk of alkali chloride-related operational problems [114]. There are several studies reporting on the complex ash composition that arises from seaweed-based feedstocks [115-117]. For example, compared to land-based biomass, the composition of seaweeds are heterogeneous with high concentrations of ash-forming elements, higher ratios of Na/K and Mg/Ca and higher Cl contents. These higher concentrations can be explained by the region and environment in which the biomass grows (i.e. sea water). Characterisation for this type of biomass and its ash content is extremely important because numerous problems (fouling, deposit formation or slagging) can arise when using as a fuel application. These problems will likely cause a financial and time burden in the form of potential shutdowns of apparatus or there being substantial periodical maintenance required. In most cases, seaweeds require a pre-treatment step prior to utilization, and washing/leaching with water or weak acids are the most common practice to remove mineral matter and halogens [116].

Looking at the fuel fingerprints from Skoglund *et al.* [115] of both the raw and washed seaweed, elemental composition of K, Na, Mg, P, S, Cl all lowered when washed. Cl showed the most significant loss out of all of these problematic elemental species, while the Ca composition nearly doubled.

Skoglund *et al.*, therefore, proposed a washing procedure of seaweed that was used to remove alkali chlorides which enabled seaweed use in combustion [115]. This washing procedure directly affected the fuel by reducing the ash content from 45.7 to 35.9 wt.% and increasing the LHV by approximately 50%, going from 9.3 to 13.9 MJ.kg⁻¹. Furthermore, the high ash content of washed seaweed (35.9 wt.%) suggests that adding seaweed to a fuel blend (even at low blend ratios) will have a large impact on the total ash composition.

Using a fuel design approach, a composition of seaweed with Ca-containing bryozoans was combined with *miscanthus* to avoid issues related to alkali-silicate melt formation during

509 combustion. In the combustion experiments, the Ca from the seaweed was found to be more
510 efficient than a mineral-based CaCO_3 additive to prevent the ash melting problems. Besides the
511 synergetic co-combustion with *miscanthus* performed here, this approach opens the possibility
512 for system integration advantages such as a thermochemical step in future algal-based
513 biorefineries.

514 One prevalent advantage of utilising aquatic biomass such as seaweeds is that it has higher
515 photosynthetic efficiency and faster growth rate in comparison to terrestrial land-based biomass.
516 On average, the photosynthetic efficiency of aquatic biomass changes in the range of 6–8% while
517 that for terrestrial biomass varies between 1.8 and 2.2% [118].

518 Ross *et al.* have noted that the char yield from the slow pyrolysis/carbonisation of macro-algae
519 should not be neglected and should be utilised [116, 119]. The abundance of alkali metals in the
520 biomass directly affects the char yield as it alters the pyrolysis mechanism as reported by Ross
521 *et al.* themselves elsewhere [111].

522 Such marine biomass accumulates considerable amounts of heavy metals since they act as a sink
523 for such pollutants; the naturally occurring biosorption properties of seaweed contributes to this
524 accumulation [120].

525 Haykiri-Acma *et al.* published a study on the production of bio-briquettes from carbonised brown
526 seaweed. The carbonisation process was conducted at temperatures up to 900 °C, with a heating
527 rate of 10 °C.min⁻¹ in a nitrogen-based atmosphere. The residue that was left over was then
528 pressed in a steel mould using a hydraulic press at a pressure of 187 MPa with a mixture of
529 different binding agents. Thermal analysis of brown seaweed indicated that both carbonisation
530 and combustion are multi-step reactions in which different mechanisms occur and govern the
531 mass losses and heat flow properties because of the complex structure of this particular type of
532 biomass species. Carbonisation of seaweed eliminated the majority of the volatile matter, leading

to subsequent increases in calorific value, fixed carbon and ash content. Furthermore, thermal reactivity and exothermic characteristics during the combustion of seaweed were also affected positively by the carbonisation process. Thus, the carbonisation technique improved the fuel quality of the parent material. Briquetting of the carbonised sample with some binding agents such as sulfide liquor, molasses, and Linobind yielded briquettes that are highly durable against the impacts of compressibility. However, the falling stability of the briquettes was found to be intimately dependent on the type of the binder. The addition of molasses provided very high values of falling stability, while sulfide liquor was deemed to be an unsuitable binder for this particular application. Additionally, the water resistance of the produced briquettes was not good and so they should be prevented from any close interaction with water.

Bae *et al.* looked at bio-oil resulting from the pyrolysis of three species of seaweed: two brown (*Laminaria japonica* and *Undaria pinnatifida*) and one red (*Porphyra tenera*) in a temperature range of 300-600 °C with an unspecified heating rate and left for one hour [110]. An acid washing pre-treatment phase was selected to reduce the ash content. The optimum temperature for maximum production of bio-oil was at 500 °C with the yield varying from 37.5-47.4 wt.%. The *Porphyra* type produced the maximum amount of bio-oil. C1-C4 hydrocarbons were found to increase after 400 °C. The resultant bio-oil constituents were different for each type of seaweed tested. Bae *et al.* have suggested that this bio-oil be used for fine chemical upgrading or as a precursor, as the high nitrogen content does not look attractive for the prospects as a fuel.

Looking at the AD potential of brown seaweed, Tabassum *et al.* tested five different types and concluded that the highest biomethane potential (BMP) was 286 L.CH₄.Kg.VS⁻¹ from *L. digitate* and the lowest BMP of the five types was *L. hyperborean* with 118 L.CH₄.Kg.VS⁻¹. The specific yield per net weight of the brown seaweed was found to be 10-32 m³ [121]. Of the different selective regions of the seaweed strain, the frond was deemed to be the most significant and suitable region for biogas production from brown seaweed. It should be noted that biogas

production from seaweeds has been previously reported by Ross *et al.* to be more expensive than terrestrial biomass [111].

Cassava (*Manihot esculenta*) is extensively grown in countries such as Columbia and Indonesia as one of the major staple food resources and a multipurpose agro-industrial crop. Since cassava peel contains cyanogenic glucosides mainly linamarin and lotaustralin, the disposal and improper handling of this waste often create an environmental burden due to the release of hydrogen cyanide (HCN) from cyanogenesis activity of endogenous linamarase enzyme [122, 123].

In order to further predict the yield of pyrolysis products from slow pyrolysis and compare with that of fixed-bed reactor experiments, a mechanistic-based model was designed. This was an adaption of a model originally developed by Van de Velden *et al.* [124]. The model was found to give good accuracy at predicting the pyrolysis products over the temperature range of 400-600 °C producing a mean squared error of 0.49, 16.34 and 13.37 for gas, bio-oil and char, respectively. The overall bio-oil yield from the slow pyrolysis process of cassava peel was found to be 38.7-51.2 wt.%, with the optimum yield of 51.2 wt.%, corresponding to a temperature of 525 °C. Above this temperature, the yield was found to decrease and this was attributed to secondary thermal cracking. The resultant bio-oil properties satisfied all the ASTM D7544 standard requirements which suggest that bio-oil coming from the pyrolysis of cassava peel could be used as a resultant bio-fuel.

Alternatively, there is potential to produce activated carbon from cassava peel. The main application of activated carbon adsorbents is to purify and separate gas/liquid mixtures [125, 126]. Sudaryanto *et al.* [127] conducted a study where high surface area activated carbon was prepared from cassava peel by chemical activation using KOH as an activating agent. Different impregnation ratios, carbonisation time and temperature were all studied to determine how this would affect the pore characteristics and surface chemistry of the cassava peel feedstock. It was

found that carbonisation time had little effect in the yield or pore characteristics of activated carbon, but, the carbonisation temperature had an important effect on the yield. Carbonisation temperature of 450 °C produced the highest yield out of the four temperatures used (450, 550, 650 and 750 °C). Increasing the carbonisation temperature from 450-650 °C, increased both the micropore and total pore volume. Above 650 °C, promotion of a higher total pore volume and a lower micropore volume occurred [127]. This is due to the surface metal complex promoting further carbon gasification leading to a widening of the micropores to increase in size to become mesopores as described by Ganan *et al.* [128]. Furthermore, it was deduced that increasing the impregnation ratio decreased the overall yield of activated carbon. At lower impregnation ratios, the structure of the activated carbon consisted mainly of micropores and increasing this led to the creation of mesopores due to widening [127].

Moreno-Piraján further extended this research by preparing activated carbon from cassava peel and studying the adsorption of copper from aqueous solution. Instead, the activation was carried out using zinc chloride. It was determined that it was possible to gain surface areas as high as 1567 m².g⁻¹ and pore volumes as large as 1.18 cm³.g⁻¹ [129]. The trend on impregnation ratio was the same as Sudaryanto *et al.* in that as it increased, this promoted more mesopores [127]. The sorption capacity of activated carbon of cassava peel to uptake copper ions was determined to be 55 mg.g⁻¹ by using four different best-fit three parameter isotherms Vieth-Sladek, Toth, Sips and Radke-Prausnitz [129]. This was found to be more than five times the sorption capacity for uptake of copper ions of activated charcoal [130]. It was also close to the sorption capacity of Humic acids and bark pine pulp at 51.47 and 45.2 mg.g⁻¹, respectively [129, 131].

Interestingly, Kosasih *et al.* took a different approach and looked at the sequestering of Cu²⁺ using cassava peel as a standard biosorbent. The biosorption process was carried out isothermally at three separate temperatures (30, 45 and 60 °C). The metal binding occurred between the functional groups located on the cassava's surface and the Cu²⁺ ions. The biosorption process

was found to be pH dependent, which is in agreement with what was reported by Ekmekyapar *et al.* [132]. The optimum pH was determined to be 4.5 and the thermodynamic parameters suggest that the biosorption process is completely irreversible, endothermic and spontaneous. The maximum adsorption capacity was found to be 41.77 mg.g⁻¹ which was obtained at 60 °C [133]. Kurniawan *et al.* in a similar work studied the sequestering of Ni²⁺ using cassava peel as a standard biosorbent. The biosorption process was carried out isothermally at three separate temperatures (30, 45 and 60 °C), respectively. Again, the optimum pH was determined to be 4.5 and the thermodynamic parameters suggest that the biosorption process is completely irreversible, endothermic and spontaneous which is in agreement with work published by Kosasih *et al.* [133]. The Sips model was found to demonstrate the best fitting with the maximum uptake of Ni²⁺ ions with a maximum sorption capacity of 57 mg.g⁻¹ for Ni²⁺ ions [134]. This was found to be approximately six times higher than the sorption capacity of orange peel (9.82 mg.g⁻¹) as reported by Feng *et al.* [135]; subsequently, this was still lower than the sorption capacity of pomegranate peel (69.4 mg.g⁻¹) reported by Bhatnagar *et al.* [136].

Moshi *et al.* [137] looked at multiple scenarios as to what was the best way to harness the energy inherent within the cassava peels. The pre-treatments used in their study were alkali, enzyme and a combination of one another for the production of bioethanol or biogas, or both. The study showcased that wild cassava peel can be upgraded into both biogas and ethanol concurrently. This resulted in a higher fuel energy value compared to the option of separate processes. Alkali combined with enzyme pre-treatment was proven to be the best method, indicating a 56% improvement in methane yield for the AD process compared to the untreated counterpart. The combined methane and ethanol production resulted in 1.2-1.3 times the fuel energy yield compared to the generation of sole methane and 3-4 times the fuel energy yield compared to solely ethanol production [137]. Adekunle *et al.* reviewed ways in which to produce bio-ethanol from cassava peels and provided a design conceptualisation. It was their suggestion that although

some challenges occur to the industrialisation of any given process, the best case scenario would be to integrate directly with the petrochemical industry to ensure proper blending of the bio-ethanol into biofuel and ensure profitability [138]. They also suggested the potential co-production of ethanol/biogas with the biogas part contributing to power generation, in agreement with Moshi *et al.* [137] had published earlier.

In the local western world demographic, coffee plays a major role in the global economy. It has been said to be the second most traded commodity in the world after oil [139]. Spent coffee grounds (SCG) contain polysaccharides, oligosaccharides, lipids, aliphatic acids, amino acids, proteins, alkaloids (e.g., caffeine, trigonelline) and phenolics, minerals, lignin, melanoidins and volatile compounds [140-142].

One issue with utilising spent coffee grounds (SGC) as a fuel type is the energy or time required to dry the feedstock as the raw form is approximately 65% moisture. Kang *et al.* conducted a study using SCG as a fuel in a 6.5 kW combustion boiler after drying SGC for 2 days to lower the moisture content to less than 15%. The combustion process consumed 1.17 kg.hr^{-1} , was able to heat up 40 Kg of water from 9 to 78 °C in 146 minutes. The O₂, CO and NO_x concentrations were measured to be 17.8%, 643 and 163 ppm, respectively. Although the O₂ concentration of the flue gas was higher than a conventional domestic gas boiler, it was noted that these emissions could be lowered with further optimisation of the fuel boiler design to suit this type of feedstock [143].

Looking at the activated carbon made from SCG, Jutakridsada *et al.* [144] produced activated carbon with a fixed pyrolysis heating rate of 10 °C.min^{-1} for 4 hrs. SCG was chemically activated using ZnCl₂ and there were three concentrations (5, 10 and 15 wt.%), three impregnation times (8, 12 and 24 hrs) and three carbonisation temperatures (400, 450 and 500 °C) tested in the particular study. The optimum concentration, impregnation time and temperature were found to

656 be 15 wt.%, 24 hrs and 500 °C, respectively. This led to an average specific surface area and
657 average pore volume of 831 m².g⁻¹ and 0.44 cm³.g⁻¹, respectively. The adsorption capacity of
658 Cu²⁺ was 18% removal with 100 ppm of CuSO₄ [144].

659 Babu *et al.* studied the removal of lead and fluoride from contaminated water sources using
660 exhausted coffee grounds. The biomass was firstly acid activated by adding to HCl and boiled
661 for 2 hours. They then created synthetic wastewater by adding lead nitrate and sodium fluoride.
662 The maximum adsorption capacity for the lead was found to be 61.6 mg.g⁻¹ at pH 6, dosage
663 0.15g.100mL⁻¹, time of 75 min., the temperature of 303 K for an initial concentration of 100
664 mg.L⁻¹. The maximum adsorption capacity for fluoride was determined to be 9.05 mg.g⁻¹ at pH
665 4, dosage 0.2g.100mL⁻¹, time of 105 min., the temperature of 303 K for an initial concentration
666 of 20 mg.L⁻¹. The kinetics for removal of both these species follows the pseudo-second-order
667 model and the adsorption behaviour follows the Langmuir isotherm model [145].

668 Liu *et al.* conducted a study in which SCG biochar was prepared by CO₂ sequestration at 400 °C
669 under a nitrogen flow rate of 100 mL.min⁻¹. Three methods for the ammoxidation of the biochar
670 was tested and then chemically activated using potassium hydroxide. The CO₂ sorption
671 capacities of the three sample were found to be 2.04-2.67 mmol CO₂.g⁻¹_{sorbent} at 35 °C under
672 atmospheric pressure using completely dry CO₂. The most successful sample was one prepared
673 using sonication, melamine and hydrothermal treatment. This was attributed to the unique
674 properties of the adsorbent including a highly developed microporosity as the ratio of the
675 micropores volume to the total pore volume was approximately 82%.

676 Interestingly, Chen *et al.* [146] proposed a method of using SCG as a co-combustion material
677 alongside sewage sludge (SS). They tested mixing ratios of 60/40, 70/30, 80/20 and 90/10 % of
678 SS to SCG, respectively. It was suggested that there were chemical interactions between both
679 the feedstocks and that the impacts were mostly positive. Adding SCG promoted the mass loss

rate and the reactivity of SS to increase and the charring of both feedstocks subsequently decreased. The activation energies were determined using the KAS and Ozawa-Flynn-Wall methods and the average values were 166.8 and 168.8 KJ.mol⁻¹, respectively. The lowest activation was located at SCG content =40% [146].

Primaz *et al.* [147] recently looked at the influence of temperature on the yield of bio-oil from the fast pyrolysis of SCG. They produced the bio-oil at five different temperatures (400, 450, 500, 550 and 600 °C), using a heating rate of 100 °C.min⁻¹, a flow rate of 150 mL.min⁻¹ of nitrogen and a hold time of 15 min., once the temperature was reached. The gases and oil were passed through a condenser with circulation of ice water (-5 °C). The maximum bio-oil yield was found to be 30.51 wt.% at 500 °C with the major components in the bio-oil to be palmitic acid (19%), oleic acid (11%) and stearic acid (10%) [147]. This is lower than the 56.09% reported by Luz *et al.* and is likely due to their use of a screw-based reactor which can optimise vapour residence times [148]. After 500 °C, the bio-oil decreases and climatizes around 27%. The decrease in yield with increasing temperature occurs usually due to secondary side reactions of the pyrolysis vapours which contributes to the increase in gaseous product and possible decrease of other products [149, 150].

Recently Kim *et al.* [151] conducted an anaerobic co-digestion study using SCG alongside other feedstocks such as ulva, food waste, waste activated sludge and whey. For each additive, they tested a pure SCG sample and mixing ratios of 75/25, 50/50, 25/75 and 0% SCG/100% co-feedstock. The individual feedstock's composition was saw to have a significant effect on the biomethanation performance. Every co-feedstock had comparable or higher methane production rates or yields except for the waste activated sludge feedstock which showed negative impacts. The co-digestion with whey, ulva or food waste increased the reaction rate of the AD process without losses in biomethane potential. A 75/25 mixing ratio of food waste to spent coffee grounds showed the most promising results. It produced the largest biomethane potential of all

the 69 tests. The cumulative methane production at 28 days was $0.355 \text{ L.CH}_4.\text{g}^{-1}.\text{VS}_{\text{in}}^{-1}$ and the methane production potential was $0.344 \text{ L.CH}_4.\text{g}^{-1}.\text{VS}_{\text{in}}$. The 50/50 mix of food waste to spent coffee grounds was ever so slightly lower than this result so both mixing ratios could be deemed suitable [151].

Similarly, Luz *et al.* studied AD under mesophilic conditions at 37°C for 22 days of the liquid fraction from spent coffee grounds (SCL) mixed with cow manure and compared this with a reference of pure cow manure. An inoculum ratio of 1.5 was used (g volatile solids (VS) substrate per g.VS). They found that the SCL reactors showed a pH reduction in the first days compared with the pure cow manure samples. The addition of the SCL produced more stable values for the lower heating value (28.24 MJ.Kg^{-1} , as opposed to 26.30 MJ.Kg^{-1} for the pure cow manure sample), biogas composition (peaks of 60% methane when SCL is used; 9% higher than the pure cow manure sample) and carbon conversion efficiency (38% higher than the pure cow manure sample). SCG was indicated to have an individual contribution up to $254 \text{ ml CH}_4.\text{g}^{-1}.\text{VS}^{-1}$ [152].

Hazelnut is Turkey's most important agricultural drop as they are one of the main producers of hazelnuts in the world. Although mainly used for its fruit the shells have significant importance in being a potential source of energy. The main way the shell is utilised in the Black Sea region of Turkey is direct combustion for domestic purposes [153].

Hazelnut shells are a unique type of biomass in that they have above 40% cellulose content [154], abundant hydrocarbon, low moisture and high carbon content which are appropriate to the thermochemical conversion method of pyrolysis [155].

728 **Table 1:** The ultimate and proximate analysis of different types of biomass.

	Biomass type	Elemental composition (wt.% on					Proximate analysis (wt.% on				[ref.]
		dry basis)					dry basis)				
		% C	% O	% H	% N	% S	% moisture	% ash	% volatile	% fixed Carbon	
Woody biomass	Plywood	47.1	45.7	5.9	1.2	<0.1	--	0.8	85.8	13.4	[85]
	Pine	53.3	40.2	6.4	0.2	--	--	0.6	88.0	11.3	[85]
	Medium-density fibreboard	49.6	39.7	6.3	4.4	--	--	2.3	86.7	11.1	[85]
	Particleboard	46.3	45.5	5.8	2.4	<0.1	--	1.2	83.8	14.4	[85]
	Furniture wood waste	47.9	41.4	6.0	2.9	<0.1	--	1.8	--	--	[81]
	Solid Wood	52.7	40.8	6.2	--	<0.1	--	0.3	--	--	[81]
	Engineered Wood	49.4	39.3	6.1	3.9	<0.1	--	1.3	--	--	[81]
	Spruce	49.9	--	--	0.14	<0.1	--	0.4	73.7	12.8	[106]
	Brash	50.8	--	--	0.3	<0.1	--	0.7	72.7	14.6	[106]
	Wood pellets	51.3	42.1	6.1	0.3	<0.1	--	2.5	80.7	16.8	[25]
	Herbaceous biomass	Miscanthus	48.6	43	5.8	0.3	0.3	15.1	2.1	--	--
Miscanthus		42.8	50	5.8	1.2	0.1	2.9	3.4	72.5	21	[157]
Mountain brome		44.8	39.5	7.9	1.4	--	70.5	6.4	81.9	11.8	[158]
Tall-Oat grass		47.2	37.6	6.8	1.5	--	69.9	6.6	80.4	12.9	[158]
Tall fescue		44.4	41.6	6.5	1.4	--	68.1	6.3	81.9	11.8	[158]
<i>C. ciliaris</i>		39.8	52.7	5.7	1.7	0.1	8.5	8.9	81.2	12.2	[159]
<i>P. pedicellatum</i>		40.9	53.0	5.8	1.0	0.1	7.2	6.8	80.5	11.3	[159]
Switch grass		38.0	50.6	6.2	0.6	0.3	11.3	4.4	83.2	12.3	[159]
redtop		45.5	40.3	6.4	1.6	--	84.3	6.3	83.5	10.2	[158]

	Arundo donax	42.7	48.7	7.5	0.8	0.2	8.2	5.0	68.4	18.4	[109]
	Reed canary grass	41.4	42.2	7.4	1.9	--	66.9	7.1	82.3	10.6	[158]
	<i>Achnatherum splendens</i>	42.6	48.5	5.7	--	--	11.1	3.1	69.6	16.2	[160]
	Hybrid perun	49.4	41.4	7.7	1.3	--	75.8	6.3	80.7	13.0	[158]
	Hybrid Becva	44.0	41.3	7.0	1.5	--	73.3	6.4	80.1	13.5	[158]
	Miscanthus	43.7	44.8	5.7	1.1	0.2	10.0	2.7	78.8	9.5	[109]
	Hybrid lofa	46.4	38.7	6.8	1.7	--	70.8	6.6	81.2	12.2	[158]
	Smilo grass (leaves)	48.5	43.6	6.2	1.7	1.0	--	11.5	75.7	13.8	[161]
	Smilo grass (trillers)	49.0	44.2	5.5	1.3	1.2	--	4.6	70.0	11.0	[161]
	Red Clover	46.8	31.9	6.6	2.9	--	85.2	11.8	77.2	11.0	[158]
	Miscanthus	47.6	43.9	5.3	0.1	0.5	6.9	1.4	79.2	12.1	[162]
Other types of biomass	Hazelnut shell	50.4	41.9	6.8	0.8	0.1	8.9	1.5			[163]
	Hazelnut shell	51.3	43.2	5	0.5		7	0.7	75	15.5	[153]
	Hazelnut Shell	48.1	48.9	2.6	0.4	--	--		87.2		[155]
	Saccharina latissima	26.9	19.6	3.4	6	--	--	45.7		9.3	[115]
	Washed Saccharina latissima	38.1	16.4	4.9	3.8	--	--	35.9		13.9	[115]
	Phaeophyta	42.7	44.6	6.8	4.2	1.7	5	22.5	63.3		[117]
	Enteromorpha clathrata	29.4	21.8	3.96	7.1	2.5	6.8	28.6	54.0	12.1	[164]
	Sargassum fusiforme	28.5	34.5	3.3	3.0	1.1	13.1	16.5	49.3	10.4	[164]

	Cassava Peel	53.7	37.9	7.1	1.2	0.1	1.8	2.3	74.5	17.9	[123]
	Rice husk	38.8	35.5	4.75	0.52	<0.1	---	20.3	63.5	16.2	[165]
	Rice husk	37.6	32.6	4.9	1.9	<0.1	---	16.9	51.9	25.1	[166]
	Rice husk	39.5	39.3	5.7	0.7	0.1	---	14.8	68.3	16.9	[166]
	Rice husk	38	32.4	4.6	0.7	<0.1	10.3	14	55.6	20.1	[167]
	Rice husk	53.9	38.8	6.3	0.98	<0.1	9.8	9.9	64.9	15.4	[168]
	Rice husk	38.5	36.6	5.5	0.4	0.2	3.6	16.3	60	20.1	[169]
	Olive solid waste	57.8	34.4	7.1	0.7	0.1	--	5.3	76.6	12.3	[170]
	Goat manure	42.1	39.9	5.6	1.5	0.1	8.9	16.8	70.1	4.18	[171]
	Horse manure	43.3	49.2	5.9	0.9	0.8	8.2	10.5	70.4	11	[172]
	Swine manure	33.5	56.7	6.2	2.8	0.8	---	7.13	77.7	15.2	[173]

729

730 Rice represents one of the most essential and important agricultural products in our life
731 nowadays and it is commercially grown in 112 countries [165]. With the increased global
732 population, the global production of rice is also expected to increase. During the harvesting of
733 rice in the fields leaves, stems and roots are obtained, leaving rice with husk (paddy). The global
734 annual production of rice reaches about 670 million tones of paddy, of which Asia produced
735 about 90% [174, 175]. When processing paddy in the mills, grains of rice husk, which is the
736 natural sheath surrounding the rice, are generated. The estimated annual amount of rice husk
737 worldwide is ~150 million metric tons which is approximately 20 to 33% by weight of the paddy
738 rice [176]. More than 80 % of this amount of rice husk is discarded as waste, causing pollution
739 to water and soil [175]. The rice husk consists of 70–80% organic substances which includes
740 three polymer components: cellulose, hemicellulose and lignin. The remaining 20–30 % of the
741 rice husk mass consists of mineralogical components such as silica, alkalis and trace elements

[166]. The variations in the ratios of the rice husk's three constituents depend on different factors including weather conditions, agronomic handling and type of soil [166]. Due to its low nutritional value, rice husk is not suitable for feeding animals. In addition, the irregular abrasive surface and the high siliceous composition of rice restricts its natural degradation; this increases its potential candidate for environmental pollution through combustion and other polluting processes.

Considering the reusing and recycling approaches of rice husk, rice husk and its char are used mainly as an energy source. In addition, ashes and char produced as a byproduct of rice husk combustion and pyrolysis can be used for the removal of heavy metals from wastewaters. Furthermore, rice husk ash has additional uses such as the use in the production of high-performance concrete. The thermochemical conversion of rice husk represents the main route for the production of energy from rice husk and can be achieved by four different technologies [28]: combustion, gasification, pyrolysis and liquefaction processes.

Pyrolysis of rice husk using solar energy was studied by Weldekidan *et al.* [177] to produce fuels and chemicals. A parabolic dish was used with maximum heat flux concentrating capacity of 70 kW.m⁻² to generate pyrolysis temperatures from 500 to 800 °C on a reactor loaded with biomass. The highest gas, bio-oil and biochar yields obtained were found to be 25.48 wt.% at 800 °C, 43.13 wt.% at 700 °C and 43 wt.% at 500 °C, respectively. Lim *et al.* [178] studied the pyrolysis of rice husk using thermogravimetry and by applying the KAS method for the kinetic analysis of the pyrolysis process. The results indicated that the maximum degradation rate of rice husk increases from 4.42 to 21.87 wt.%.min⁻¹ by increasing the heating rate of 10 to 50 K.min⁻¹. Furthermore, in the range of heating rates studied, the predicted values of the activation energy ranged from 48.64 to 54.21 kJ.mol⁻¹ and the average value of activation energy is 51.19 kJ.mol⁻¹.

766 Yoon *et al.* [169] studied the gasification and power generation characteristics of rice husk and
767 rice husk pellet by using a downdraft fixed-bed gasifier in a temperature range of 600-850 °C,
768 fuel feeding rate of 40-60 kg.hr⁻¹ and gasification agent feeding rate of 50-75 Nm³.hr⁻¹.
769 According to the results, the gasification of rice husk pellet produces a higher heating value of
770 synthetic gas and higher cold gas efficiency than that in the case of rice husk gasification.
771 Kinetics of rice husk tar cracking was studied in a two-stage gasifier by Khonde *et al.* [179] at
772 different temperatures and residence times. They found that nitrogen and air were the best as
773 gasification media for secondary gaseous yield than other gases. In addition, hydrogen-rich
774 syngas was produced by increasing residence time and the temperature of gasification.

775 The thermochemical treatment processes of rice husk have attracted considerable interest in the
776 literature as a way for recycling, reuse and up-cycling of rice husk biomass. Madhiyanon *et al.*
777 [167] studied the combustion characteristics of rice husk in a short combustion chamber fluidized
778 bed combustor (SFBC) and successfully obtained high combustion efficiency and high heat rate
779 intensity without the use of a secondary solid to promote fluidization. Ninduangdee *et al.* [168]
780 studied the effects of co-combustion methods on gaseous emissions during the combustion of
781 rice husk. They investigated the effects of co-firing methods and operating parameters on the
782 emissions and combustion efficiency. They found that the proposed co-combustion methods and
783 the operating parameters have noticeable effects on the major gaseous emissions and combustion
784 efficiency of the combustor. In addition, the oxidation kinetics of rice husks combustion were
785 investigated by Alias *et al.* [180] by using an evolved gas analysis technique. They heated rice
786 husk samples inside a small pressurised reactor from 100-500 °C at a constant rate. A controlled
787 flow of oxygen-containing gas was passed through the reactor where the moisture had been
788 removed and the content of oxygen, carbon monoxide and carbon dioxide in the evolved gas was
789 continually analysed. According to the results obtained, they proposed a model for the oxidation
790 of the rice husks samples represented the simultaneous and competing for oxidation reactions by

791 three overlapping and competing reaction regimes in which the only reaction products are CO₂,
792 CO and H₂O.

793 García *et al.* [170] studied the pyrolysis of the two-phase olive mill solid waste. They
794 characterised the olive mill solid waste in terms of its physical-chemical properties. In addition,
795 they studied the solid waste behaviour on pyrolysis processes by dynamic thermogravimetry and
796 derivate thermogravimetry. The particle size analysis indicated that the two-phase olive mill
797 solid waste can be used directly as solid fuel in some of the available technologies. In addition,
798 the results indicated that calcium and potassium carbonates are the main inorganic material in
799 the solid waste and the sulfur content is low which is important environmentally. Furthermore,
800 the results of the proximate analysis and the gross calorific value indicated that the energy content
801 of the two-phase olive mill solid waste is sufficient to introduce it as a possible promising solid
802 fuel.

803 In a technical and economic evaluation study by Christoforou *et al.* [181], the competitiveness
804 of olive mill solid waste pellets against wood pellets as an energy source was examined in Cyprus
805 as an olive oil producing country. The technical analysis results indicated that olive mills solid
806 waste has a significant potential to contribute to the country's energy mix. The feasibility analysis
807 presents the competitiveness of olive mills solid waste over other commercially available pellets.
808 In addition, according to this study, the olive mills solid waste pellets could enter the energy
809 market with relatively low price and could contribute effectively in the households, industrial
810 and agricultural sectors.

811 Abdelhadi *et al.* [182] studied the production of biochar from olive mill solid waste for heavy
812 metal removal from water. They studied the production of biochar from olive solid waste from
813 two olive cultivars and two oil production process (two- or three-phase) at two temperatures (350
814 and 450 °C). The yield of biochar was 24–35 wt.% of the biomass, with a low surface area (1.65–

815 8.12 m².g⁻¹) compared to that of commercial activated carbon (1100 m².g⁻¹). However, the
816 biochar from olive mill solid waste shows a better performance for the removal of heavy metal
817 (Cu⁺², Pb⁺², Cd⁺², Ni⁺² and Zn⁺²) with more than 85 % compared to commercial activated carbon.
818 According to the results obtained, Abdelhadi *et al.* suggested that the surface area cannot be used
819 as a sole predictor of heavy metal removal capacity.

820 Elkhoully *et al.* [183] studied the feasibility of using waste date palm seeds as filler material
821 in glass-epoxy composites. The effects date seeds had as filler on the wear rate and impact energy
822 at different conditions were studied. A comparison between date seeds, silicon carbide and
823 alumina as filler was carried out from both the technical and economic perspective. The results
824 of the study indicated that the date seeds, as a filler, are less effective than silicon carbide and
825 more effective than alumina and the unfilled composite. According to the results obtained in this
826 study, the addition of 10 % date seeds reinforcement to the glass fibre had improved the wear
827 resistance rate and the toughness by about 71 and 80 %, respectively. In a recent study by Sirry
828 *et al.*[184], the chemically treated date seeds were used as an adsorbent for the extraction of
829 uranium ions from wastewater, providing a good substitution for current, expensive removal
830 procedures of such pollutants. In order to improve the adsorption capacity of the date seeds, it
831 was treated with petroleum ether, hydrochloric acid, sodium carbonate, a combination of
832 petroleum ether and hydrochloric acid and a combination of petroleum ether and sodium
833 carbonate. The characteristics of the treated date seeds as adsorbents was examined at different
834 contact times and different initial concentrations of uranium ions. According to the results of this
835 study, Sirry *et al.* concluded that the date seeds treated with hydrochloric acid and the
836 combination of petroleum ether and hydrochloric acid exhibit higher adsorption capacity
837 compared to the other treated date seeds and compared to other bio-adsorbents reported in the
838 literature. El Messaoudi *et al.* [185] studied the removal of cationic dyes (methylene blue and
839 crystal violet) from aqueous solutions using date stones treated with sulfuric acid and sodium

bicarbonate. The study investigated the effect of different parameters including contact time, initial dye pH, temperature and initial dye concentration on the efficiency of the adsorption process of dyes by the chemically treated date seeds. The results indicated a high efficiency of the chemically treated date seeds in the adsorption of the two dyes with adsorption capacities of 515.46 and 543.47 mg/g for methylene blue and crystal violet at 50 °C, respectively, and with the pseudo-second-order as the suitable adsorption kinetic model. In addition, the used chemically treated date stones were regenerated using nitric acid solution and performed well in four repeated cycles with high efficiency in the removal of both dyes.

Al-Omari [186] has investigated the potential of date seeds as an energy source for furnaces compared with coal. The comparison between date seeds and coal as fuels was carried out according to the combustion and heat transfer characteristics obtained in a furnace fueled with both fuels. According to the results obtained, the combustion and heat transfer rates per unit mass of the fuel were higher in the case of date stones compared with the coal used. According to Al-Omari, the higher combustion and heat transfer rates in the case of date seeds is due to its higher volatile matter content and the very low ash content compared with the coal.

Sekirifa *et al.* [187] succeeded in producing activated carbon with high surface area ($604 \text{ m}^2.\text{g}^{-1}$) from date seeds. The produced activated carbon was used as an adsorbent of a potent phenolic derivative compound 4-chlorophenol and showed high efficiency in the adsorption process with adsorption capacity of 23.25 and 28.57 $\text{mg}.\text{g}^{-1}$. Rezma *et al.* [188] have prepared microporous activated carbon electrode from date seeds for capacitive deionisation application without the use of a binder. The process involved the pyrolysis of the date seeds at a temperature of 1000 °C under nitrogen flow followed by physical activation of the obtained carbon monoliths at 900 °C under CO_2 flow. The prepared activated carbon exhibited a high surface area and well-developed microporosity and a good efficiency as a capacitive deionisation electrode in water treatment was observed. In a study by Abbas *et al.* [189], mesoporous activated carbon with surface area,

865 total pore volume and average pore diameter of 1144.25 m².g⁻¹, 0.656 m³.g⁻¹ and 3.004 nm,
866 respectively, were prepared from date stones by one-step microwave assisted K₂CO₃ pyrolysis.
867 The efficiency of the prepared activated carbon compared to raw date stones as adsorbents for
868 the extraction of methylene blue dye was investigated. The effects of different parameters
869 including radiation time, radiation power and impregnation ratio on the yield and dye uptake of
870 the prepared activated carbon were investigated. The activated carbon prepared from date stones
871 showed high efficiency in the removal of methylene blue dye with maximum adsorption capacity
872 of 504.79 mg.g⁻¹ compared to that of raw date stones (256.15 mg.g⁻¹). The kinetic data obtained
873 in this study were fitted well with a pseudo-second-order model at different initial concentrations.

874 Animal manure is one of the most important biomass wastes produced every day all over the
875 world in staggering amounts. Animal manure consists mainly of urine and faeces in addition to
876 other constituents that may be found in manure such as bedding materials, dropped feed, scurf,
877 and other farming wastes [190]. The amount of animal manure produced annually in the
878 European Union is about 1400 million tons [191]. Disposing of manure as a biodegradable
879 product containing high levels of nutrients and pathogens will contaminate soil, air and water
880 [192]. Consequently, it is necessary to find an effective and appropriate way to benefit from these
881 huge amounts of waste without damaging the environment. The traditional use of manure is as a
882 valuable fertilizer to provide the crops with the required nutrients for growth [192]. In addition
883 to the use of animal manure as fertilizer in farming, it can be used as combustive material to
884 produce heat and electricity (recycling) or can be used as a source of biogas and bio-oil (up-
885 cycling) through digestion processes [193].

886 In a study by Hadin *et al.* [194] the feasibility and potential to produce biogas and bio-fertilizer
887 from horse manure by anaerobic digestion were analysed via a thorough literature review in
888 combination with mathematical modelling and simulations. AD represents one of the best
889 manure management methods by which both waste treatment and bio-energy production goals

could be achieved [195]. In addition, AD has a high degree of resource conservation, both in terms of energy and nutrients [194]. Due to the low carbon to nitrogen (C/N) ratio in animal manures, the co-digestion of another carbon-rich substrate with the animal manures is required to improve its characteristics for anaerobic digestion by increasing the (C/N) ratio [192]. According to Hadin *et al.* the characteristics of the feedstock and the type of digestion method used are strongly affected by the type and amount of bedding material used. Burg *et al.* [54] studied the energy and greenhouse gas emissions benefits of using animal manure in Switzerland to produce biogas by anaerobic digestion. The study concluded that considerable quantities of energy can be recovered from animal manure which will reduce the greenhouse gases emissions. In addition, according to Burg *et al.*, suitable and effective techniques are required to remove water from the manure which will improve the energy extraction efficiency. Furthermore, the study recommended the increase in local availability by pooling the manure from multiple farms into a single AD facility. This will reduce the pre-storage losses which will increase the available bioenergy while decreasing greenhouse gases emissions. A spatial analysis of biogas potential from manure in Europe was carried out by Scarlat *et al.* [196]. They carried out a study to estimate the biogas potential of farm manure for the whole of Europe based on regional statistical data and spatial distribution of livestock and poultry population. According to this study, the amount of manure produced (wet weight) every year is about 1347 million tonnes throughout Europe and about 1200 million tonnes in the European Union. Despite the huge amount of manure produced in Europe and the European Union, only about 942 million tonnes could be collected in Europe and around 861 million tonnes in the European Union [196]. The study estimated the theoretical biogas potential could be 43 billion m³ in Europe and 30 billion m³ in the European Union in comparison to 30 billion m³ in Europe and 27 billion m³ in the European Union as realistic biogas potential. In addition, the study estimated the primary energy potential of biogas from farm manure to be about 924 PJ in Europe of which about 639.3 PJ would be

exploitable. The study developed a Geographic Information System (GIS)-based methodology that can be used as decision support tool on basis of the dataset of manure and biogas potential to analyse suitable locations and number of biogas plants and their capacities depending on resources. The study showed the capacity of biogas plants for both constant and variable collection radiuses [196].

In addition to anaerobic digestion, the thermochemical techniques (pyrolysis, combustion, gasification and liquefaction) are of great importance as waste-to-energy techniques used for the valorisation of animal manure [19, 171-173, 197-206]. The enhancement of energy production, as a form of syngas (CO and H₂), from chicken manure by pyrolysis in carbon dioxide was studied by Lee *et al.* [56]. The syngas (CO and H₂) is known to be used as a fuel for internal combustion engines. Lee *et al.* found that the CO production in the case of using CO₂ as pyrolysis atmosphere is higher than that in the case of using N₂. In addition, the CO production was also increased by the existence of CaCO₃ in both in N₂ and CO₂ atmospheres which means that the catalytic effects of CaCO₃ on the pyrolysis could act together with the influence of CO₂ in enhancing the CO production.

The results of this study showed the feasibility of pyrolysis as an effective waste-to-energy process that recovers energy from chicken manure. In addition, this study represents an approach for utilising CO₂ gas as a potent greenhouse gas. Pyrolysis of goat manure to produce bio-oil was studied by Erdogdu *et al.* [171] within the temperatures range 300-600 °C to investigate the feasibility of using goat manure as a source of energy or as a raw material for chemical production. The effect of changing the pyrolysis temperature within the 300–600 °C on the solid, liquid and gas product distributions was studied. According to the obtained results, the maximum non-condensable gas yield (33%) was obtained at 600 °C and the maximum bio-char yield (48.6%) was obtained at 300 °C. In addition, the maximum bio-oil yield (26.1%) was obtained at 500 °C. Fernandez-Lopez *et al.* [202] carried out a kinetic analysis study of manure pyrolysis

and combustion processes. They conducted a thermogravimetric analysis of the pyrolysis and combustion of three different biomass waste samples; two dairy manure samples (before and after anaerobic digestion) and one swine manure sample. Three iso-conversional methods (Friedman, Flynn-Wall-Ozawa and KAS) were used by Fernandez-Lopez *et al.* and were compared with the Coats-Redfern method. According to the kinetic analysis results, the activation energy values of pyrolysis devolatilisation stages were in the range of 152–170 kJ.mol⁻¹ for dairy manure before anaerobic digestion, 148–178 kJ.mol⁻¹ for dairy manure after anaerobic digestion and 156–209 kJ.mol⁻¹ for swine manure. Regarding the combustion process, the activation energy values of combustion devolatilisation stages were in the range of 140–175 kJ.mol⁻¹ for dairy manure before anaerobic digestion, 178–199 kJ.mol⁻¹ for dairy manure after anaerobic digestion and 122–144 kJ.mol⁻¹ for swine manure. It was also found that the anaerobic digestion process has no effect on the kinetics of the thermochemical processes as the activation energy values were practically the same for samples before and after the anaerobic digestion. The distributed activation energy model was the best fitting model with the experimental data in both pyrolysis and combustion processes.

962 **Table 2:** The combustion conditions along with the associated calorific values of different types
963 of biomass.

	Biomass type	Combustion gas	Temperature range (°C)	Heating rate (°C/min)	Calorific value (MJ/kg)	[ref.]
Woody biomass	Plywood	Air	30-900	10,20 and 30	18.6	[85]
	Pine	Air	30-900	10,20 and 30	19.7	[85]
	Medium-density fibreboard	Air	30-900	10,20 and 30	19.3	[85]
	Particleboard	Air	30-900	10,20 and 30	17.5	[85]
	Furniture wood waste	Air	Up to 550	--	15.8	[81]
	Solid Wood	Air	Up to 550	--	19.5	[81]
	Engineered Wood	Air	Up to 550	--	18.3	[81]
	Spruce	Air	Up to 600	20	20.0	[106]
	Brash	Air	Up to 600	20	20.5	[106]
	Wood Pellets	Air	900	--	20.8	[25]
Herbaceous biomass	Miscanthus	Air	<600	10	16.6	[157]
	Arundo donax	Air	bomb calorimeter	5	17.2	[109]
	Miscanthus	Air	bomb calorimeter	5	17.8	[109]
	Miscanthus	Air	bomb calorimeter	--	17.7	[162]
	Reed Canary grass	Air	**	--	18.4**	[20]
	Napier grass	Air	bomb calorimeter	--	16.74	[207]
	Smilo grass (leaves)	Air	bomb calorimeter	--	16.3	[161]
	Smilo grass (trillers)	Air	bomb calorimeter	--	18.2	[161]
	C. ciliaris	Air	Adiabatic bomb calorimeter	--	16.1	[159]
	P. pedicellatum	Air	Adiabatic bomb calorimeter	--	15.6	[159]

	Switch grass	Air	Adiabatic bomb calorimeter	--	19.7	[159]
Other types of biomass	Carbonized Seaweed (Phaeophyta)	Air	20-900	10	14.3 (HHV)	[117]
	Posidonea Oceanic seaweed	He/O ₂ = 4:1	25-650	5,10,20	undefined	[208]
	Agal HRD (Hydroprocessed renewable diesel fuel	Air	280	25	44 **	[209]
	Washed Saccharina latissima	Air	700	(undefined)	13.9	[115]
	Sodium free, pyrolytic char of Hazelnut Shell	Air	900	5, 10, 20, 30, 40, 50	18.3	[155]
	Hazelnut shells	Air	900	40	17.9	[210]
	Cassava peel bio-oil	air	Ambient - 800	10	27.43	[123]
	Spent coffee grounds based biodiesel	air	Ambient-800	20	--	[211]
	Rice husk	Air	450	5	14.98	[167]
	Dairy manure	oxygen	bomb calorimeter	-	18.4	[203]
	Dairy manure *	oxygen	bomb calorimeter	-	16.9	[204]
	Swine manure	oxygen	bomb calorimeter	-	16.1	[204]
	Horse manure	Air	985	----	19.4	[204]

* Dairy manure pretreated by anaerobic digestion

** LHV using method SS-EN 14918:2010/15400:2011

4. Up-cycling approach

4.1 Herbaceous biomass

(a) Pyrolysis and bio-oil production

Recently, the production of bio-oil from biomass has gained great attention as an alternative to the fossil fuel. Usually, bio-oil, which is typically dark-brown, is composed of different chemicals such as esters, acids, alcohols, ketones, aldehydes, phenols and lignin-derived oligomers. Bio-oil is thus characterised by its high acidity (pH 2-3), high moisture and viscosity [212]. Bio-oil typically has low heating value compared with fossil fuel with HHV of approximately 20 and 40 MJ kg⁻¹, respectively. In general, the pyrolysis of hemicellulose and cellulose occurred faster than that of lignin with weight loss in the range of 220-315 °C, 315-400 °C and 160-900 °C, respectively [213]. The pyrolysis of cellulose is endothermic while pyrolysis of hemicellulose and lignin is exothermic [213]. Previous studies reported four stages during the pyrolysis; water desorption followed by three decomposition stages for cellulose, hemicellulose and lignin. The product distribution depends upon the feedstock chemical and biochemical composition, the biomass taxonomy and the secondary interaction between liquid and char [158]. In general, the highest yield of liquid (mostly anhydrosugars) is produced by the decomposition of cellulose along with the lowest char yield. While hemicellulose decomposes to the highest yield of gas and liquid (mainly water, ketones and phenols), lignin produces the phenols in the liquid form along with the highest yield in char [158]. Woody biomass decomposes slower than that of the herbaceous biomass with less evolution of volatile matters due to the larger contents of cellulose and hemicellulose within the herbaceous biomass [158].

The produced biochar is characterised with higher calorific value than the raw biomass with values in the range of 25-26 MJ.kg⁻¹ which is due to the increase in the fixed carbon content [214].

990 **Table 3:** The pyrolysis conditions along with the produced bio-oil yield of different types of
 991 biomass.

	Biomass type	Pyrolysis gas	Temperature range (°C)	Heating rate (°C/min)	% bio- oil yield	[ref.]
Woody biomass	Birch	Nitrogen	Up to 500	3000	37	[215]
	Spruce (without bark)	Nitrogen	Up to 500	3000	36	[215]
	Pine Bark	--	400-625	--	43	[216]
	Maple	--	400-625	--	63	[216]
	Poplar Aspen	--	400-625	--	65	[216]
Herbaceous biomass	Mountain brome	Nitrogen	700	10	58.6	[158]
	Tall-Oat grass	Nitrogen	700	10	55.5	[158]
	Napier grass	Nitrogen	500-600	--	55±2.6	[217]
	Tall fescue	Nitrogen	700	10	51.5	[158]
	redtop	Nitrogen	700	10	48.7	[158]
	Napier grass	Nitrogen	600	50	51.6	[218]
	Reed canary grass	Nitrogen	700	10	56.0	[158]
	<i>Hybrid perun</i>	Nitrogen	700	10	55.7	[158]
	<i>Hybrid Becva</i>	Nitrogen	700	10	56.5	[158]
	<i>Achnatherum splendens</i>	--	300- 450	10	39-44	[160]
	<i>Achnatherum splendens</i>	--	300- 450	30	42-45	[160]
	Hybrid lofa	Nitrogen	700	10	55.7	[158]
	Red Clover	Nitrogen	700	10	48.1	[158]
Other types of	Hazelnut shells	Nitrogen	400-700	7	23.1	[153]
	Spent Coffee Grounds	Nitrogen	450-550	6000-30000	56.1	[148]
	Hazelnut shells	Nitrogen	550	20	41.95	[219]
	Spent coffee grounds	Nitrogen	400-600	100	30.51	[147]
	Cassava Peel	Nitrogen	400-600	20	51.2	[123]

biomass	Ulva lactuca	Nitrogen	550	200-2000	65	[220]
	Chlamydomonas reinhardtii	Nitrogen	400-550	30000	60.2	[221]
	Rice husk	Argon	500-800	160	43.13	[177]
	Rice husk	Nitrogen	150-900	50	21.9	[178]
	Rice husk	Nitrogen	400-550	--	46.9	[222]
	Rice husk	Nitrogen	450	--	52	[223]
	Rice husk	Nitrogen	450-650	--	53.8	[224]
	goat manure	Nitrogen	300-600	15	26.1	[171]
	Swine manure	Nitrogen	80-800	10, 20, 30 & 40	40	[173]
	Swine manure	Nitrogen	260-340	----	24.2	[198]

992

993 The bio-oil composition and yield are unfavourably affected by the amount of the ash content in
994 the biomass feedstock, therefore washing it with water, surfactant or either acid improves both
995 the yield and the composition of the bio-oil. For instance, washing the biomass with water
996 showed an effective way to reduce the inorganic materials such as (K, P and Cl) [225] and it is
997 an ideal pretreatment choice for woody biomass (low ash content) [226]. Again, washing with a
998 surfactant such as Triton X-100 can effectively reduce the ash content in comparison to the
999 untreated biomass [226]. Washing the raw biomass with HCl reduced the metal content and
1000 consequently increased the volatile materials during the pyrolysis which in turn increased the
1001 bio-oil yield [227] and also reduced the hemicellulose present in the polymer structure of the
1002 biomass [228]. Banks *et al.* [226] reported that using stronger acid could lead to hydrolyse both
1003 cellulose and hemicellulose completely that eventually decreased the bio-oil yield.

1004 Controlling the temperature is crucial in optimising the bio-oil yield. For example, Ozbay *et al.*
1005 [229] reported that the optimum temperature was 550 °C to get the maximum yield of bio-oil
1006 with 7 °C.min⁻¹ in a N₂ atmosphere in a tubular reactor (% yield was 25%). On a further increase

in the temperature beyond 550 °C, the yield decreased to approximately 21%. However, Putun *et al.* [230] reported a slightly lower temperature than that of Ozbay *et al.*, for the maximum bio-oil yield of 500 °C. Encinar *et al.* [231] agreed with the results of Putun *et al.*, as the maximum bio-oil yield at 500 °C. Again, Lu *et al.* [232] and Park *et al.* [233] stated even lower temperatures of 475 and 450 °C, respectively, for maximum bio-oil yield. However, this may be attributed to using different biomass types.

There is a debate in the literature regarding the relationship between the biomass particle size and the bio-oil yield as Brosse *et al.* [234] reported that the bio-oil yield was not significantly affected by the change in the particle size. While Demiral and Sensoz [235] found out that there is a decrease in the bio-oil yield with increasing the particle size of the biomass feedstock. In contrast, Demirbas [236] observed an increase in the bio-oil yield with increasing the biomass particle size.

Interestingly, for bio-oil production, the selectivity and its composition significantly vary with the addition of a catalyst, with zeolite the most commonly used. For instance, it was observed that the wt.% of water in the bio-oil increased upon using a catalyst compared with the uncatalysed condition [237]. It was reported that the bio-oil yield decreased in the presence of the catalyst, but also the oxygen content of the bio-oil decreased i.e. the catalyst promoted the production of valuable products such as the aromatic compounds within the bio-oil [237, 238]. The effect of the wt.% of catalyst (ZSM-5) on the bio-oil production showed that the char yield along with the bio-oil decreased with increasing the ZSM-5: biomass ratio [239]. The quality of the bio-oil increased by producing more benzene, xylene, toluene, polycyclic aromatic hydrocarbons (PAHs) along with naphthalenes while phenol yield decreased. This is attributed to the fact that catalyst promoted the deoxygenation reaction. Du *et al.* [239] found out that at the ZSM-5: biomass ratio of 5, naphthalenes were the most abundant product within the produced bio-oil. Further research is needed to optimize the bio-oil yield in the presence of the catalyst

along with using different pore size catalyst type on the distribution of the aromatic compounds within the bio-oil.

The effect of the heating rate along with the residence time during the pyrolysis is crucial for the production of the bio-oil, char and the gaseous products. In general, such high heating rate with residence time less than ten seconds is considered as fast pyrolysis with the possibility of a heating rate of $1000\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$. A residence time of less than a second is referred to as flash pyrolysis. Conventional pyrolysis takes place with slower heating rates with a residence time as high as 30 minutes. Thus, changing the heating rate could significantly change the bio-oil yield. Slow pyrolysis with a residence time of 24 hours was reported as the optimum condition for the char production, while fast pyrolysis was used for the production of a valuable bio-oil [240, 241]. Duman *et al.* [242] showed that the bio-oil yield increased two-fold with fast pyrolysis compared to that of the slow pyrolysis. Furthermore, the light and heavy bio-oil fraction vary with heating rate during the pyrolysis. It was reported that during the slow pyrolysis, the light bio-oil yield increased then remained constant in the temperature ranges of $400\text{--}500\text{ }^{\circ}\text{C}$ and $500\text{--}600\text{ }^{\circ}\text{C}$, respectively, while the heavy bio-oil yield remained constant throughout the whole temperature range of $400\text{--}600\text{ }^{\circ}\text{C}$. Both light and heavy bio-oil yield increased in the temperature range of $400\text{--}500\text{ }^{\circ}\text{C}$ then decreased in the temperature range of $500\text{--}600\text{ }^{\circ}\text{C}$, respectively [243]. A detailed comparison between different type of pyrolysis on the bio-oil production showed that the yield of bio-oil showed the following series; fast pyrolysis > intermediate pyrolysis > carbonisation > gasification > torrefaction processes. It is not surprising that torrefaction obtained the lowest bio-oil yield as it is designed generally for the production of char and takes place at considerably lower temperature range than that of the desired temperature range for the bio-oil production. Also, gasification is generally used for the production of gaseous species and is conducted at higher temperature ranges than that required for the bio-oil production. Interestingly, fast pyrolysis showed twice as bio-oil yield as that of the intermediate pyrolysis

with gas and char selectivity higher in the case of the carbonisation process [216]. In summary, fast pyrolysis showed the most suitable process for the maximum bio-oil yield.

As stated earlier, the bio-oil yield in catalytic systems should be lower than that of the corresponding uncatalyzed system due to an increase in the wt.% of water caused by the promotion of the deoxygenation route in the presence of the catalyst. One of the highest reported bio-oil yields (75%) for an uncatalyzed system was for fast pyrolysis of wood which included water in the liquid product. This fast pyrolysis used high heating rate ($25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) with short residence time and fast quenching to prevent the reverse reaction of liquid to gas phase [34]. Using intermediate pyrolysis for hazelnut bagasse with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ showed a lower bio-oil yield of 54.7% including water in the liquid product (17.1%). The lower bio-oil yield could be due to a combination of reasons; the change in the biomass type along with using lower heating rates [244]. Using different biomass feedstock such as miscanthus while keeping the heating rate the same as in the previous study i.e. ($10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) showed 55.2 and 57.3 % bio-oil yield in different studies [226, 233]. This implies that the heating rate could be of great influence on the bio-oil yield. A lower bio-oil yield was reported of 40% at $500\text{ }^{\circ}\text{C}$ with a heating rate of $200\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and decreased to 30% with increasing the final temperature to $600\text{ }^{\circ}\text{C}$. To sum up, the expected bio-oil yield in the uncatalysed system could be in the range of 40-75% (including water in the liquid products) while the common yield reported in the literature of approximately 55%. The catalysed system improves the selectivity and produces a higher quality bio-oil, albeit with a lower yield than that of the corresponding uncatalysed system which produces a lower quality bio-oil. One bio-oil yield in the presence of the catalyst which was closest to the yield of uncatalysed system reported were 51%, however, the wt.% of water increased by around 10 wt.% (35% - 45%) [233]. Using waste biomass such as olive oil waste feedstock showed a lower bio-oil yield of around 30%. This is perhaps in part due to the type of biomass or the long residence time along with the absence of a quenching process. The effect of

the catalyst: biomass ratio on the yield of the bio-oil yield showed 33% when the ratio was 1, while the yield decreased to 27% by increasing the ratio to 5 [239]. The bio-oil yield in case of catalysed cellulose pyrolysis was reported to be higher than that of pine using the same pyrolysis condition of 33.4 and 24.4%, respectively [245]. To sum up, the expected bio-oil yield in the catalysed system based on the literature is the range of $\sim 30 - 35\%$.

The produced bio-oil can be upgraded into high value-added chemicals or transportation fuels, while the char can be used in carbon sequestration, fertilizer, activated carbon or heavy metal removals and others [20]. Catalytic fast pyrolysis (CFP) is a distinguished thermochemical process for the production of high-quality bio-oil with zeolite catalyst again being the most common catalyst used [212].

Fermoso *et al.* [246] studied the effect of the indigenous and external catalysts (HZSM-5) on the fast pyrolysis of lignocellulose. They found out that in case of non-catalytic, mineral components and zeolite type catalyst showing different prominent route such as dehydration, dehydroxylation and decarbonylations, respectively as the main route of deoxygenation in the pyrolysis process. ZSM-5 decreased the bio-oil production, however, increased the production of aromatic compounds in the bio-oil, thus the produced bio-oil composition can vary according to the catalyst type, pyrolysis condition and the biomass type [246]. Other than aromatization, a series of complex reactions occur inside the pores of the catalyst such as cracking, oligomerization, ketonization, isomerization and aldol condensation of the produced pyrolysis vapour. Thus, catalysts with meso- and macroporous structure are preferred, otherwise coke deposition occurs and eventually, the catalyst deactivates.

Liang and McDonald studied the possibility of using potato peel waste (PPW) as a potential resource for biofuel and bioproducts production [247]. During the PPW fermentation, starch

was mainly consumed for the production of alcohol (ethanol) and organic acids (acetic and lactic acid), while under the pyrolysis conditions, a total of 51 products were detected; the main five products were CO₂, acetic acid, acetic anhydride, hexadecenoic acid and phenol [247]. In another study, orange peel waste showed calorific values in the range of 10.9-19.3 MJ.kg⁻¹ with a high absorption capacity for heavy metals such as lead [248].

4.2 Woody biomass

Woody biomass can be upcycled/valorised via torrefaction, gasification, hydrothermal carbonisation, biological treatments, pyrolysis, anaerobic digestion, fermentation and transesterification. Many of these processes have been described herein previously for recycling/reusing and/or applied to other types of biomass.

Primarily in this section, the focus will be on the bio-refinery and the extraction of platform and value-added chemicals from woody biomass. Woody biomass can be fed into anaerobic digesters for the conversion of solid/liquid heterogeneous biomass mixtures to biogas, though would typically require a higher residence time compared to some other types of biomass. Pyrolysis and hydrothermal liquefaction result in bio-oil which can then be upgraded to the value added chemicals or fuels [215, 249-253]. Pyrolysis is conducted between 450 and 500 °C for short residence times at atmospheric conditions and requires drying whereas the hydrothermal liquefaction is at lower temperatures (300-400 °C) at higher pressure (up to 25 MPa) and for longer times (up to 1 h) with the advantage of no drying step being required.

Ranzi *et al.* have conducted a kinetic study of the pyrolysis of reference components of woody biomass such as cellulose, hemicellulose and lignin [254]. Applying a particle scale mechanistic kinetic model, the relative contributions of transport processes and reaction kinetics was assessed. Using TGA of the devolatilisation stages of the biomass reference components, predictions were reported regarding the rate of weight loss as well as the evolution of gaseous

and vapour species. It was found that these predictions could be validated with the experimental results. In summary, this simple kinetic approach could accurately model degradation stages, durations and product evolution and the model has the potential to be applied to a wide range of gasifiers. The reality of course, as acknowledged by the authors, that the model is only in its early stages of application since it has been used so far for only for the main constituent parts of wood which were treated as references by Ranzi *et al.* [254]. There are reports of applying mathematical modelling to analyse both the reference components and wood samples, such as pine [255], though in this case, the model was only accurate for larger particles. For the first time in literature, an autocatalytic model was developed therein so as to better describe secondary degradation processes which were observed during the pyrolysis studies of the pine and the constituent components (except for lignin). Good agreement between experimental data and the kinetic modelling was reported as so it was reported that, in theory, this method could be applied for other biomasses.

A fluidized bed was used by di Celso *et al.* to conduct a kinetic analysis of the pyrolysis of spherical particles of wood from the *Ostrya carpinifolia* tree at 700, 800 and 900 °C [256]. Infra-Red (IR) and thermal conductivity detector (TCD) were employed to analyse the effluent of the pyrolysis CO, CO₂, CH₄ and H₂ specifically monitored. Separate semi-empirical models have been proposed for the two mechanistic stages of wood gasification, i.e. pyrolysis followed by char/tar combustion. For the most part, these models were found to be capable of reproducing the evolution of the experimentally monitored gas concentrations. The pyrolysis model was able to closely match the interaction of wood particle size on the gas yield (smaller particles meant faster pyrolysis), though the model could not adequately predict the impact of changing the temperature on these yields.

1154 Bioethanol, which can be used as both a fuel and as a chemical feedstock, can be extracted from
1155 woody biomass, such as eucalyptus wood via uncatalyzed steam explosion [72]. The time and
1156 temperature dependencies were monitored during this study, and the data could be fitted with an
1157 empirical equation, with the linear regressions being derived by the least squares method. There
1158 have also been reports in the literature of boosting the bioethanol yields by adding other biomass,
1159 such as cheese whey powder [257].

1160 Sheldon has provided a comprehensive review on the opportunities to apply catalysis to utilise
1161 biomass to support green chemistry and the circular economy by producing fuels, commodity
1162 chemicals and other products such as bio-plastics [258]. Cork, for example, is a potentially
1163 significant chemical feedstock, given the volumes produced (201 ktonnes per year [16, 259]) and
1164 the fact that due to a high suberin content it does not biodegrade. 40% of this cork is used as
1165 wine stoppers and there is only limited recycling of used wine corks, with 66% of these estimated
1166 to go to landfill. Aroso *et al.* [259] have provided an extensive discussion on possible uses of
1167 cork as a sustainable material, though the methods discussed could be applied to other types of
1168 woody biomass. Depolymerisation methods to extract value-added chemicals such as waxes and
1169 phenolic compounds from cork include chemical (acid/base [260] and catalytic [261],
1170 oxypropylation [262], liquefaction [263] and pyrolysis [264].

1171 As an example, Cordeiro *et al.* [260] have reported a kinetic study on the extraction of urethanes
1172 and polyurethanes from suberin derived from reproduction cork. The hydroxy index was
1173 determined and validated using FTIR (by monitoring decreasing OH peak and the increasing
1174 NCO peak). It was reported that a second-order kinetic model was the most accurate in fitting
1175 the experimental data.

1176 Evtigouguina *et al.* [265] conducted a kinetic study of the oxypropylation of cork powder, also
1177 for the extraction of urethanes and polyurethanes by exposing the cork to propylene oxide at high

pressure. In this case, a second-order kinetic process was observed and rate constants were determined. In summary, the authors state that their findings have demonstrated that oxypropylation is a reasonable and feasible process to extract valuable products from biomass

4.4 Other types of Biomass sources upcycling

Ross *et al.* have noted that the char yield from the slow pyrolysis/carbonisation of macro-algae should not be neglected and should be utilized [116, 119]. The abundance of alkali metals in the biomass directly affects the char yield as it alters the pyrolysis mechanism as reported by Ross *et al.* themselves elsewhere [111].

Looking at the AD potential of brown seaweed, Tabassum *et al.* tested five different types and concluded that the highest biomethane potential (BMP) was 286 L.CH₄.Kg.VS⁻¹ from *L. digitate* and the lowest BMP of the five types was *L. hyperborean* with 118 L.CH₄.Kg.VS⁻¹. The specific yield per net weight of the brown seaweed was found to be 10-32 m³ [121]. Of the different selective regions of the seaweed strain, the frond was deemed to be the most significant and suitable region for biogas production from brown seaweed. It should be noted that biogas production from seaweeds has been previously reported by Ross *et al.* to be more expensive than terrestrial biomass [111].

In order to further predict the yield of pyrolysis products from slow pyrolysis and compare with that of fixed-bed reactor experiments, a mechanistic-based model was designed. This was an adaption of a model originally developed by Van de Velden *et al.* [124]. The model was found to give good accuracy at predicting the pyrolysis products over the temperature range of 400-600 °C producing a mean squared error of 0.49, 16.34 and 13.37 for gas, bio-oil and char, respectively. The overall bio-oil yield from the slow pyrolysis process of cassava peel was found to be 38.7-51.2 wt.%, with the optimum yield of 51.2 wt.%, corresponding to a temperature of 525 °C. Above this temperature, the yield was found to decrease and this was attributed to

secondary thermal cracking. The resultant bio-oil properties satisfied all the ASTM D7544 standard requirements which suggest that bio-oil coming from the pyrolysis of cassava peel could be used as a resultant bio-fuel.

Alternatively, there is potential to produce activated carbon from cassava peel. The main application of activated carbon adsorbents is to purify and separate gas/liquid mixtures [125, 126]. Sudaryanto *et al.* [127] conducted a study where high surface area activated carbon was prepared from cassava peel by chemical activation using KOH as an activating agent. Different impregnation ratios, carbonisation time and temperature were all studied to determine how this would affect the pore characteristics and surface chemistry of the cassava peel feedstock. It was found that carbonisation time had little effect in the yield or pore characteristics of activated carbon, but, the carbonisation temperature had an important effect on the yield. Carbonisation temperature of 450 °C produced the highest yield out of the four temperatures used (450, 550, 650 and 750 °C). Increasing the carbonisation temperature from 450-650 °C, increased both the micropore and total pore volume. Above 650 °C, promotion of a higher total pore volume and a lower micropore volume occurred [127]. This is due to the surface metal complex promoting further carbon gasification leading to a widening of the micropores to increase in size to become mesopores as described by Ganan *et al.* [128]. Furthermore, it was deduced that increasing the impregnation ratio decreased the overall yield of activated carbon. At lower impregnation ratios, the structure of the activated carbon consisted mainly of micropores and increasing this led to the creation of mesopores due to widening [127].

Moreno-Piraján further extended this research by preparing activated carbon from cassava peel and studying the adsorption of copper from aqueous solution. Instead, the activation was carried out using chloride zinc. It was determined that it was possible to gain surface areas as high as 1567 m².g⁻¹ and pore volumes as large as 1.18 cm³.g⁻¹ [129]. The trend on impregnation ratio was the same as Sudaryanto *et al.* in that as it increased, this promoted more mesopores [127].

1227 The sorption capacity of activated carbon of cassava peel to uptake copper ions was determined
1228 to be 55mg.g⁻¹ by using four different best-fit three parameter isotherms Vieth-Sladek, Toth, Sips
1229 and Radke-Prausnitz [129]. This was found to be more than five times the sorption capacity for
1230 uptake of copper ions of activated charcoal [130]. It was also close to the sorption capacity of
1231 Humic acids and bark pine pulp at 51.47 and 45.2 mg.g⁻¹, respectively [129, 131].

1232 Moshi *et al.* [137] looked at multiple scenarios as to what was the best way to harness the energy
1233 inherent within the cassava peels. The pre-treatments used in their study were alkali, enzyme and
1234 a combination of one another for the production of bioethanol or biogas, or both. The study
1235 showcased that wild cassava peel can be upgraded into both biogas and ethanol concurrently.
1236 This resulted in a higher fuel energy value compared to the option of separate processes. Alkali
1237 combined with enzyme pre-treatment was proven to be the best method, indicating a 56%
1238 improvement in methane yield for the AD process compared to the untreated counterpart. The
1239 combined methane and ethanol production resulted in 1.2-1.3 times the fuel energy yield
1240 compared to the generation of solely methane and 3-4 times the fuel energy yield compared to
1241 solely ethanol production [137]. Adekunle *et al.* reviewed ways in which to produce bio-ethanol
1242 from cassava peels and provided a design conceptualization. It was their suggestion that although
1243 some challenges occur to the industrialization of any given process, the best case scenario would
1244 be to integrate directly with the petrochemical industry to ensure proper blending of the bio-
1245 ethanol into biofuel and ensure profitability [138]. They also suggested the potential co-
1246 production of ethanol/biogas with the biogas part contributing to power generation, in agreement
1247 with Moshi *et al.* [137] had published earlier.

1248 Looking at the activated carbon made from SCG, Jutakradsada *et al.* [144] produced activated
1249 carbon with a fixed pyrolysis heating rate of 10 °C.min⁻¹ for four hours. SCG was chemically
1250 activated using ZnCl₂ and there were three concentrations (5, 10 and 15 wt.%), three
1251 impregnation times (8, 12 and 24 hrs) and three carbonisation temperatures (400, 450 and

500 °C) tested in the particular study. The optimum concentration, impregnation time and temperature were found to be 15 wt.%, 24hrs and 500 °C, respectively. This led to an average specific surface area and average pore volume of 831 m².g⁻¹ and 0.44cm³.g⁻¹, respectively. The adsorption capacity of Cu²⁺ was 18% removal with 100 ppm of CuSO₄ [144].

Babu *et al.* studied the removal of lead and fluoride from contaminated water sources using exhausted coffee grounds. The biomass was firstly acid activated by adding to HCl and boiled for 2 hours. They then created synthetic wastewater by adding lead nitrate and sodium fluoride. The maximum adsorption capacity for the lead was found to be 61.6 mg.g⁻¹ at pH 6, dosage 0.15g.100mL⁻¹, time of 75 minutes, the temperature of 303K for an initial concentration of 100mg.L⁻¹. The maximum adsorption capacity for fluoride was determined to be 9.05mg.g⁻¹ at pH 4, dosage 0.2g.100mL⁻¹, time of 105 minutes, the temperature of 303K for an initial concentration of 20mg.L⁻¹. The kinetics for removal of both these species follows the pseudo-second-order model and the adsorption behaviour follows the Langmuir isotherm mode [145].

Liu *et al.* conducted a study in which SCG biochar was prepared by CO₂ sequestration at 400 °C under a nitrogen flow rate of 100 mL.min⁻¹. Three methods for the ammoxidation of the biochar was tested and then chemically activated using potassium hydroxide. The CO₂ sorption capacities of the three sample were found to be 2.04-2.67 mmol CO₂.g⁻¹_{sorbent} at 35 °C under atmospheric pressure using completely dry CO₂. The most successful sample was one prepared using sonication, melamine and hydrothermal treatment. This was attributed to the unique properties of the adsorbent including a highly developed microporosity as the ratio of the micropores volume to the total pore volume was approximately 82%.

Primaz *et al.* [147] recently looked at the influence of temperature on the yield of bio-oil from the fast pyrolysis of SCG. They produced the bio-oil at five different temperatures (400, 450, 500, 550 and 600 °C), using a heating rate of 100C.min⁻¹, a flow rate of 150mL.min⁻¹ of nitrogen

and a hold time of 15 minutes once the temperature was reached. The gases and oil were passed through a condenser with circulation of ice water (-5 °C). The maximum bio-oil yield was found to be 30.51 wt.% at 500 °C with the major components in the bio-oil to be palmitic acid (19%), oleic acid (11%) and stearic acid (10%) [147]. This is lower than the 56.09% reported by Luz *et al.* and is likely due to their use of a screw-based reactor which can optimize vapour residence times [148]. After 500 °C, the bio-oil decreases and climatizes around 27%. The decrease in yield with increasing temperature occurs usually due to secondary side reactions of the pyrolysis vapours which contributes to the increase in gaseous product and possible decrease of other products [149, 150].

Recently Kim *et al.* [151] conducted an anaerobic co-digestion study using SCG alongside other feedstocks such as ulva, food waste, waste activated sludge and whey. For each additive, they tested a pure SCG sample and mixing ratios of 75/25, 50/50, 25/75 and 0% SCG/100% co-feedstock. The individual feedstock's composition was saw to have a significant effect on the biomethanation performance. Every co-feedstock had comparable or higher methane production rates or yields except for the waste activated sludge feedstock which showed negative impacts. The co-digestion with whey, ulva or food waste increased the reaction rate of the AD process without losses in biomethane potential. A 75/25 mixing ratio of food waste to spent coffee grounds showed the most promising results. It produced the largest biomethane potential of all the 69 tests. The cumulative methane production at 28 days was $0.355\text{L.CH}_4.\text{g}^{-1}.\text{VS}_{\text{in}}^{-1}$ and the methane production potential was $0.344\text{L.CH}_4.\text{g}^{-1}.\text{VS}_{\text{in}}$. The 50/50 mix of food waste to spent coffee grounds was ever so slightly lower than this result so both mixing ratios could be deemed suitable [151].

Similarly, Luz *et al.* studied AD under mesophilic conditions at 37 °C for 22 days of the liquid fraction from spent coffee grounds (SCL) mixed with cow manure and compared this with a reference of pure cow manure. An inoculum ratio of 1.5 was used (g volatile solids (VS) substrate

per g.VS). They found that the SCL reactors showed a pH reduction in the first days compared with the pure cow manure samples. The addition of the SCL produced more stable values for the lower heating value (28.24 MJ.Kg^{-1} , as opposed to 26.30 MJ.Kg^{-1} for the pure cow manure sample), biogas composition (peaks of 60% methane when SCL is used; 9% higher than the pure cow manure sample) and carbon conversion efficiency (38% higher than the pure cow manure sample). SCG was indicated to have an individual contribution up to $254 \text{ ml CH}_4.\text{g}^{-1}\text{VS}^{-1}$ [152].

Pütün *et al.* conducted a study on the formation of bio-oil from hazelnut shells and its subsequent structure and yield using a standard fixed bed reactor. It was deduced that the optimum bio-oil yield was 23.1 wt.% at 500°C with a heating rate of 7 K.min^{-1} and a nitrogen flow rate of $100 \text{ cm}^3.\text{min}^{-1}$. They tested the yields at different purging rates of nitrogen and deduced above and below $100 \text{ cm}^3.\text{min}^{-1}$ the yield would be approximately 20% and the $100 \text{ cm}^3.\text{min}^{-1}$ flow rate of nitrogen accounts for the additional 3% yield. The analysis of the pentane soluble fraction of the bio-oil showed that it was a mixture of alkanes, alkenes and branched hydrocarbons and the C/H ratio in comparison to other fuels indicates that this oil lies between the light and heavy petroleum products [153].

Looking at the co-pyrolysis behaviour of hazelnut shells alongside another biomass-based feed, Zhao *et al.* [266] published a study looking at mixing municipal sewage sludge with hazelnut shells at four different heating rates ($5, 10, 15, 30 \text{ K.min}^{-1}$) using TGA-DTG-MS under a nitrogen atmosphere.

It was determined that adding the additional feedstock changed the number of thermal decomposition steps. In the co-pyrolysis case, it was found to be four stages. At the second and third stages, it was found that the biomass cracked into H_2 , H_2O , CO_2 , aromatic hydrocarbons and alkanes. The kinetics were evaluated using three different iso-conversional methods: Starink method, KAS method and the Flynn-Wall-Ozawa method. The apparent activation energy

1325 increased from 123.99 to 608.15 KJ.mol⁻¹ as the extent of conversion increased along the given
1326 reaction pathway [266].

1327

1328 Another use case for waste hazelnut shells is the production of levulinic acid as a precursor to
1329 biofuel production such as ethyl levulinate. Licursi *et al.* studied the hydrochar coming from the
1330 hydrothermal conversion of hazelnut shells to levulinic acid (LA). The hydrothermal conversion
1331 process was tested both using microwave-based technique and an autoclave technique. They
1332 found a maximum yield of LA to be 9-12 wt.% and the recovery yield of the hydrochar was
1333 found to be quite high at 43-47 wt.%. The hydrochar that was formed showed a behaviour similar
1334 to lignite and was found to be suitable for energy production [267].

1335 Another study on the valorization of hazelnut shells using the hydrothermal treatment was
1336 published by Gozaydin *et al.* [163]. They tested the product composition of value-added
1337 chemicals without the use of a heterogeneous catalyst and clarified the effects of reaction time,
1338 temperature, acid kind and concentration in a high temperature and pressure autoclave. The
1339 reactions were carried out between 150-280 °C for 15-120 minutes with varying concentrations
1340 of H₂SO₄ and H₃PO₄ of 0-125mM. It was determined that the main products were levulinic acid
1341 (LA), furfural and acetic acid whilst CO and CO₂ were the main gaseous products. An increase
1342 in temperature and reaction time resulted in a significant increase in yield of LA (13.05%) and
1343 the overall conversion (65.4%). LA production was enriched with the addition of H₂SO₄, whereas
1344 the other acid type H₃PO₄ promoted an increase in amounts of furfural [163].

1345 Looking at the bio-oils and biochar that are made from the pyrolysis of hazelnut shells, Özçimen
1346 *et al.* published a collection of results for multiple feedstocks. The optimum conditions for
1347 producing biochar from the hazelnut shells was a heating rate of 5K.min⁻¹, a temperature of 750K
1348 and a particle diameter between 1 and 1.4 mm in size. The optimum conditions for producing

1349 bio-oil from the hazelnut shells was a heating rate of $20\text{K}\cdot\text{min}^{-1}$, a temperature of 823 K, a particle
1350 diameter between 0.25 and 0.355mm and a purging flowrate of $1000\text{ cm}^3\cdot\text{min}^{-1}$. The gross
1351 calorific value (GCV) of the biomass, biochar and bio-oil were 18.33, 29.08 and $26.79\text{ MJ}\cdot\text{Kg}^{-1}$,
1352 respectively. The volatile matter, fixed carbon and ash percentage of the biomass and biochar
1353 were found to be:

1354 Hazelnut Shell: (71.67, 26.51 and 1.83%, respectively.)

1355 Hazelnut shell biochar: (30.26, 63.16 and 6.58%, respectively.)

1356 The porosity, total pore volume and BET surface area of the biomass and biochar were found to
1357 be:

1358 Hazelnut shell: 0.0463%, $0.0434\text{ ml}\cdot\text{g}^{-1}$ and $5.8421\text{ m}^2\cdot\text{g}^{-1}$

1359 Hazelnut shell biochar: 0.1130%, $0.1250\text{ ml}\cdot\text{g}^{-1}$ and $14.6836\text{ m}^2\cdot\text{g}^{-1}$

1360 This signifies that the solid products could replace conventional fossil fuels due to the high fixed
1361 carbon percentage and the high GCV. These values are compared with those of other types of
1362 biomass in Table 1 and 2. The biochars have significant potential for other carbon materials such
1363 as carbon nanotubes or activated carbon to help sequester heavy metals [219].

1364

1365
1366 In general, the energy in rice husk as biomass can be obtained by two processes which are
1367 thermo-chemical and biochemical processes. The biochemical processes represent a route for the
1368 conversion of biomass into value-added products such as ethanol, hydrogen and methane which
1369 represent energy storage material. In addition, these products (i.e. ethanol, hydrogen and
1370 methane) are raw materials for other important chemical compounds which represent the up-
1371 cycling route of rice husk biomass. According to Abbas *et al.* [268], the estimated world output

of bioethanol recovered from rice husk is in the range of 20.9 to 24.3 billion litres per year which is equivalent to around 37% of the global demand. In a recent study, Madu *et al.* [269] studied the production of bioethanol from rice husk using different pretreatments and fermentation conditions. They evaluated the effects of the pretreatment of rice husk feedstock with H₂O, HCl, NaOH and FeCl₃ on the production of bioethanol. They found that high quantities of ethanol were produced with FeCl₃ and NaOH which shows significant differences in the sugar-release patterns and ethanol produced.

The olive is an evergreen tree cultivated for the production of oil and table olives and is native to the flora of the Mediterranean basin land [270]. In the present time, over 10 million hectares are cultivated with more than 900 million olive trees, 98% of which are located in the Mediterranean Basin [271]. Each olive tree produces from 15 to 40 kg of olives per year depending on the climate conditions. In the Mediterranean basin area, Spain is the main producer of olive followed by Italy, Greece, Turkey, Morocco and Tunisia [270, 272]. The olive mills solid waste is the solid residue produced after the olive oil production process. The main components of olive mill solid residue are cellulose, hemicellulose and lignin with fat and protein. Potassium, calcium and sodium are the major content of minerals [270]. The chemical composition of olive mill wastes depends on different factors such as the olive fruit varieties and cultivation conditions in addition to the extraction method [270]. These solid wastes increase the environmental problems in the Mediterranean countries due to their high phytotoxicity and due to phenolic compounds, lipids and organic acids contained in these wastes. However, the olive mills solid waste represents a promising biomass feedstock that can be valorized through recycling reuse and up-cycling [270, 272].

The olive mills solid waste contains high percentages of organic matter and a vast range of plant nutrients which make a candidate for the reuse as plant fertilizers [273]. The conversion of solid olive mill wastes into a useful energy form can be achieved through different conversion

1397 processes depending on the type of the feedstock, the available quantities and the desired form
1398 of energy. The conversion of olive mill solid wastes to energy can be carried out using the two
1399 main pathways used with all biomass feedstock which are thermo-chemical (pyrolysis,
1400 gasification and combustion) and biochemical/biological. Many studies in the literature
1401 concentrated in the conversion of olive mill solid wastes to energy and/or value-added compound
1402 using the different conversion methods. Gunesser *et al.* [274] studied the production of flavour
1403 compounds of olive mill waste by fermentation processes using *Rhizopus oryzae* and *Candida*
1404 *tropicalis*. According to the results obtained, 2-pentanone, d-limonene and 2-phenylethanol were
1405 obtained from olive mill waste by fermentation of *R. oryzae*, while D-limonene and methyl
1406 butanoate were produced by fermentation of *C. tropicalis*. In a recent study, del Pozo *et al.* [275]
1407 succeeded in the extraction of value-added products from the intermediate pyrolysis of olive mill
1408 waste. These value-added products are divided into two groups: aqueous phase products and
1409 non-aqueous phase products. The aqueous phase products containing acetic acid,
1410 monosaccharides and phenolic derivatives while the non-aqueous phase products consist of
1411 phenolic derivatives and fatty acids and their methyl esters. In a study carried out by Serrano *et*
1412 *al.* [276], to valorize the olive mills solid waste by the recovery of phenols from the solid waste
1413 after the steam explosion. It was found that the steam explosion treatment increased the total
1414 phenol content; twice as much phenol content compared to the raw olive mills solid waste.
1415 Abdelhadi *et al.* [182] studied the production of biochar from olive mill solid waste for heavy
1416 metal removal from water. They studied the production of biochar from olive solid waste from
1417 two olive cultivars and two oil production process (two- or three-phase) at two temperatures (350
1418 and 450 °C). The yield of biochar was 24–35% of the biomass, with a low surface area (1.65–
1419 8.12 m² g⁻¹) compared to that of commercial activated carbon (1100 m² g⁻¹). However, the
1420 biochar from olive mill solid waste shows a better activity in the removal of heavy metal (Cu⁺²,
1421 Pb⁺², Cd⁺², Ni⁺² and Zn⁺²) with more than 85% compared to commercial activated carbon.

1422 According to the results obtained, Abdelhadi et al. suggested that the surface area cannot be used
1423 as a sole predictor of heavy metal removal capacity.

1424 AD and co-digestion technologies represent important and promising processes to valorize olive
1425 mill solid waste and other biomass. In the anaerobic co-digestion technology, several solid and
1426 liquid organic wastes are treated simultaneously to produce biogas which contributes to more
1427 efficient use of the AD process as multiple streams of wastes can be processed together in the
1428 same plant, at the same time. Carlini *et al.* [277] studied the production of bio-methane from
1429 anaerobic co-digestion of olive-mill solid waste, with cattle manure and cattle slurry. According
1430 to the results, the optimal mixture was obtained using 23.25% of olive mill solid waste, 4.65%
1431 of cattle manure and 72.10% of cattle slurry. The co-anaerobic digestion of olive mill solid waste
1432 and microalgae, *Dunaliella salina*, was studied by Fernández-Rodríguez *et al.* [278] to improve
1433 methane production. According to the results of this study, the highest methane production rate
1434 and the maximum methane yield were obtained for the co-digestion mixture containing 75%
1435 olive mill solid waste and 25% *Dunaliella salina*. The effect of pretreatment of olive mill solid
1436 waste with NaOH on its anaerobic digestion for methane production was studied by Pellerá *et al.* [271].
1437 The effect of different NaOH dosages, process durations and temperatures on waste
1438 biodegradability and methane yields was investigated. The results indicated that the parameters
1439 with the most effective were in the order of NaOH dosages > temperature > process duration.
1440 The highest yield of methane (242 NmL CH₄.gVS⁻¹) was obtained at a dosage of 1 mmol.gVS⁻¹
1441 (4% of VS) and a pretreatment temperature of 90 °C.

1442 The date palm tree represents one of humankind's oldest cultivated plants especially in the hot
1443 arid Arab regions where it has an important and essential role in the daily life of the people for
1444 more than 7000 years [279]. The date palm tree is characterised by its ability to adapt to with the
1445 very dry atmosphere and strong sunshine as long as its requirements of water are met. The date
1446 fruits are characterised with its rich content of essential nutrients including carbohydrates, salts,

1447 minerals, dietary fibre, vitamins, fatty acids, amino acids and protein which make it one of the
1448 most important human nutrients [187]. The wastes generated from date palm tree are leaflets,
1449 rachis, trunks, and date seeds. The date seeds represent about 10% of the date weight, so that, up
1450 to 900,000 tons of date seeds from the 7 million tons of dates that are produced worldwide every
1451 year. In general, the main constituents of date seeds are hemicellulose (23 %), lignin (15 %),
1452 cellulose (57 %) and ash (5 %) [187]. Date seeds represent a source of environmental problems
1453 in the countries that usually discard them as unwanted waste without strategies for valorisation.

1454 The possibility of extracting oils from date seeds was studied by Elnajjar *et al.* [280] using two
1455 cultivars of date seeds, namely, Khalas and Allig. Both of Soxhlet and Folch methods were used
1456 for the extraction of oil from date seeds with five different size ranges (300 nm, 0.1–0.3 mm,
1457 0.3–0.85 mm, 0.85–1.18 mm, and > 1.18 mm) in addition to the ungrounded date seeds. The
1458 results indicated that the size of the date seeds particles is an important factor that has clearly
1459 affected the oil extraction yield. It was found that the decrease in the date seed particle size
1460 increased the oil extraction yield percentage except in the case of the nano-particles where the
1461 extracted oil yield was reduced. The maximum oil extraction yields were achieved from Allig
1462 date seeds with the size range of 0.1–0.3 mm, which were 9.0 and 10.4%, using the Folch and
1463 Soxhlet extraction methods, respectively.

1464

1465 The wheat bran is the by-product of the roller milling of wheat grains for the production of white
1466 wheat flour. Millions of tons of wheat are produced every year worldwide, from which the bran
1467 consists about 25% [281-283]. The composition of wheat bran contains 6.1–6.5% ash, 5.9–6.8%
1468 lipid, 15–20% protein, 11–23% starch, 43–53% dietary fibre, in addition to other minor
1469 constituents. The dietary fibre consists of (5–20%) lignin, (16–30%) cellulose, (38–55%)
1470 arabinoxylan, in addition to other nonstarch polysaccharides [283]. The main use of wheat bran,

1471 as a renewable industrial resource, is in animal feeding. However, due to the low value of bran
1472 feed products, the wheat industry aims to convert the wheat bran into products of higher
1473 commercial value [282, 283]. According to the work reported in the literature, the valorization
1474 of wheat bran is carried out through two main ways. The first one is the biorefinery in which the
1475 wheat bran can be separated into fractions of high purity to produce new chemicals that can be
1476 used as precursors for higher polymerized compounds. The second way is the separation and
1477 purification of substances contained in wheat bran that are valuable, per se [284]. It is clear from
1478 the two main ways for the valorization of wheat bran that the up-cycling way is the main way
1479 used with this industrial bio-waste.

1480 Conversion of wheat bran into ethanol using mild treatments and highly fermentative yeasts was
1481 studied by Favaro *et al.* [281]. They studied the enzymatic hydrolysis pre-treatment of wheat
1482 bran for high hexose and pentose recovery using optimized dosages of commercial enzymes.
1483 Depending on the total sugar yield and inhibitory by-product release, a comparison between acid
1484 addition, milling and heat treatment was carried out. According to the results, the maximum total
1485 sugar amount was obtained when limited concentrations of acid were added to milled bran at the
1486 pretreatment step. High levels of ethanol production were reached by using highly fermentative
1487 wild-type yeasts for the fermentation of the whole unfiltered hydrolysates. Okamoto *et al.* [285]
1488 studied the direct production of ethanol from wheat bran and other biomasses by the white rot
1489 fungus *Trametes hirsute*. According to the results obtained, maximum ethanol concentrations of
1490 4.3 g.L⁻¹, corresponding to 78.8% of the theoretical yield, were obtained when the fungus was
1491 grown in a medium containing 20 g.L⁻¹ wheat bran. The pilot-scale isolation of the major dietary-
1492 fibre component of wheat bran, glucuronoarabinoxylans was studied by Hollmann *et al.*[286].
1493 At first, arabinoxylans was extracted with water followed by purification with boiling 70%
1494 ethanol. Then, Glucuronoarabinoxylans were extracted with 2% hydrogen peroxide of pH 11 at

1495 40 °C. The final product was precipitated with 70–80% ethanol and within one week, 350 g of
1496 glucuronoarabinoxylans were produced.

1497 The extraction of alkylresorcinols from wheat bran with supercritical CO₂ was studied by
1498 Rebolleda *et al.*[287]. They studied the changes in the extraction kinetics under the effect of
1499 different parameters including particle size, static extraction pretreatment with supercritical CO₂
1500 and extraction temperature, all at constant extraction pressure of 40.0 MPa. According to the
1501 results of the study, the extraction yield was found to increase by increasing the particle size and
1502 temperature. In a study by Ouyang *et al.*[288] a set of titania nanocomposites have been prepared
1503 by the incorporation of different TiO₂ content on wheat bran residues. The photocatalytic activity
1504 of the prepared titania nanocomposites was investigated in the oxidation of benzyl alcohol under
1505 UV light irradiation. According to the results obtained in this study, the optimum catalyst (10%
1506 Ti-Bran) produced a 20% yield of benzaldehyde at 33% conversion of benzyl alcohol, which is
1507 comparable to that of the commercial titania catalyst under the same conditions. Sayen *et al.*[289]
1508 reported the use of wheat bran for the production of a lignocellulosic substrate used in the
1509 sorptive removal of enrofloxacin antibiotic from aqueous solutions. The effects of different
1510 experimental factors including contact time, pH and concentration on the adsorption process
1511 were investigated. The results indicated that the pH value is the most important factor that affects
1512 the adsorption process where 100% of enrofloxacin was removed at pH 6 in less than one hour
1513 and more than 80% was removed above pH 4. In a study by Gopalan *et al.*[290] ferulic acid was
1514 extracted from destarched wheat bran using a feruloyl esterase enzyme. The effects of enzyme
1515 loading, reaction time, pH and temperature on the extracted amount of ferulic acid were studied.
1516 It was found that the statistical optimization of the process has improved the yield of extraction
1517 by 2.5 times with the extraction of 34.6% of total alkali releasable ferulic acid. When the process
1518 is scaled up in a packed column reactor, 32.5% of total alkali releasable ferulic acid has been
1519 extracted.

The variation in the utilisation of biomass is phenomenal; such as in the AD plants for the production of biogas, gasification for the synthesis of hydrogen-based gases and pyrolysis for the preparation of activated carbon (AC) carbon nanotubes (CNTs). The AC is a porous carbon that can be prepared using either physical or chemical activation methods and used in the adsorption of organic and inorganic compounds. The chemical activation method is more favourable method than that of the physical activation due to its less intensive energy requirement. Physical activation includes carbonisation along with high-temperature pyrolysis in the temperature range of 800-1000 °C, while in chemical activation method, chemical agents (ZnCl₂, H₃PO₄ and KOH) are used, followed by pyrolysis at a temperature of ~ 500 °C [291]. Jadwiga *et al.*, used the physical activation method for the production of AC from waste biomass in a fluidal reactor using steam or CO₂ at atmospheric pressure or in a closed high-pressure microwave reactor under hydrothermal conditions [292]. The results showed that steam and CO₂ activation gave better results than the microwave reactor with S_{BET} of 749, 539 and 430 m².g⁻¹, respectively.

The AC produced via chemical activation showed a high surface area of exceeding 2700 m².g⁻¹ with a pore volume of 1.39 cm³.g⁻¹ [291]. In the chemical activation method, various dehydrating agents were used such as Cao, H₃PO₄, NaOH, H₂SO₄, KOH and ZnCl₂, while H₃PO₄ showed the best results in activating the woody biomass due to its promotion of the dehydration, depolymerization and redistribution of constituents bipolymers along with its availability and environmentally safe [291]. Furthermore, H₃PO₄ increases the yield of AC as a result of favouring the conversion of aliphatic to aromatic compounds. It also promotes not only the pyrolytic decomposition of the initial material (cellulose, hemicellulose and lignin) but also the formation of the cross-linked structure during the chemical activation process [291]. Thus it acts as an acid catalyst to enhance the depolymerization of biomass macromolecules feedstock, while it also improves the formation of phosphates, phosphates bridges and cross-linked through the

dehydration, condensation and cyclization processes, thus leads to porous carbon materials [293]. While in the KOH activation process, the presence of a nucleophilic OH group leads to solubilization and fragmentation of the lignocellulosic biomass. The insertion of K atoms during the activation process is a result of the removal of carbonate, hydroxide and oxide species during the initial pyrolysis process which adds stress inside the structure of the produced carbon material. However, a further increase in the pyrolysis temperature leads to the removal of the K atoms from the intercalated system forming porous carbon materials [293].

ACs were prepared from woody materials using ZnCl_2 , H_3PO_4 and KOH with surface area in the range of 1275-2594 $\text{m}^2\cdot\text{g}^{-1}$ and found out that texture and the morphology of the produced AC depend upon the type and the concentration of the activating agent [294]. The surface area along with the porosity increased in this order $\text{KOH} > \text{H}_3\text{PO}_4 > \text{ZnCl}_2$. The largest surface area with 98% micropore AC structure was obtained by KOH activation. ACs produced using H_3PO_4 activation via different atmosphere; either self-generated or air flowing atmosphere showed that the former showed better BET surface area (S_{BET}) results than the latter of 2281 and 1638 $\text{m}^2\cdot\text{g}^{-1}$, respectively [295]. They used a moderate pyrolysis condition where the acid: precursor ratio =2 at 450 °C for 4hrs. Evergreen Oak was used to produce AC through the impregnation of H_3PO_4 (60%) at 85 °C for 2 hrs followed by pyrolysis at 450 °C, resulting in AC of S_{BET} as high as 1723 $\text{m}^2\cdot\text{g}^{-1}$ (mainly micro- and mesoporous volume) [296]. Zuo *et al.* studied the effect of the heating history along with the pore development during the H_3PO_4 activation process. They recommended of two-step heating program where intermediate isothermal treatment (5 °C.min⁻¹) and slow heating rate up to 300 °C, promote the pore development, however, above 300 °C, it has a detrimental effect [297].

ZnCl_2 was used for the production of ACs from Paulownia wood where the optimum conditions were reported as 400 °C carbonisation temperature along with the ratio of ZnCl_2 : biomass = 4,

resulting in AC of S_{BET} as high as $2736 \text{ m}^2 \cdot \text{g}^{-1}$ with micro- and mesopore surface areas of 1727 and $1009 \text{ m}^2 \cdot \text{g}^{-1}$, respectively [298].

Further processing of the AC is used for the production of CNTs, by doping the AC with nitrogen-based compounds such as melamine along with nickel or iron metals [299]. CNTs possess various characteristics to make them a value-added product in a variety of application such as electrical and thermal conductivity, high strength, toughness and stiffness [300]. Jiang *et al.* prepared an active Fe-N-C electrocatalyst in oxygen reduction reaction through the pyrolysis of a mixture of glucose coated CNTs, nitrogen and iron-based compounds [301]

Hydrogen production via catalytic reforming of pyrolysis vapour was investigated by Mahmood *et al.* [302] where the production of H_2 exceeded 50 vol.%.

Figure 1: The utilisation of different types of biomass through recycling and upcycling approaches.

5. Prospective overview and conclusion

A number of different types of biomass have been considered, while various processes have been discussed for their reuse, recycling and upcycling as seen in Figure 1. Additionally, the prospects of boosting the circular economy of biomass have been considered. There are significant literature contributions, of which the references of the current work are not an exhausted list, and it is clear that there is a strong desire for maximum utilization of biomass. By also considering the kinetic modelling of some processes it is hoped to demonstrate that such work can and does play a vital role in the understanding of biomass processing technology. It has also demonstrated that there is still potential to improve on both the actual technologies as well as the kinetic models. Finally, while it is clear that biomass is still required for some lower grade uses, it is preferable to extract the maximum value from the biomass sources if we are truly to achieve a circular economy. It is clear, however, that there is still some progress which is required in this field due to the energy-intensive nature of some of the processes.

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Dedication: KM dedicates this review to the memory of Dr Sergiy Shekhtman, one of his PhD supervisors, who passed away on 8th February 2018. Sergiy was an excellent mentor and teacher in kinetic modelling which has been the foundation of KM's research to date. His guidance, support and the many fruitful discussions with J.M. Yoda will be missed.

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