



REUSING, RECYCLING AND UP-CYCLING OF BIOMASS

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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 been reported for the evaluation of different processes for the recycling, reuse and upcycling of biomass. Keywords:-General classifications of biomass, Processing of biomass resources, Practical applications, Reusing and recycling, Herbaceous biomass, Pyrolysis and bio-oil production, Other types of biomass sources upcycling

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 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].

1.1 General classifications of biomass

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

Primary biomass:- It 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 [1].

Secondary biomass:- It results from the processing of the primary bio- mass such as sawdust (physical processing), black liquor (chemical processing) or manure production by animals (biological processing) [1].

Tertiary biomass:- It is post-consumer byproducts such as animal fat, used vegetable oils, construction and demolition debris and packing by products [1].

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:

(i) 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

(ii) 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.

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

(iv) 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 [1].

1.3 Processing of biomass resources

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

(i) Combustion, which is the burning of biomass in the air to produce hot gases, ash and consequently converting the stored chemical energy into heat which can be then converted to kinetic energy through heating water to produce vapour which is used for gas engines.

(ii) Gasification, which is the partial oxidation of biomass (for example rice husk) at high temperatures to convert the biomass to a combustible gas mixture which can be burnt directly or used as a fuel for gas engines, gas turbines or can be used for the production of chemicals in the case of the medium energy gases.

(iii) Pyrolysis, which is the thermal degradation of the biomass in an oxygen-free environment which results a char (solid

product), condensable vapour (bio-oil) along with the gaseous products

(iv) Liquefaction, which is the conversion of biomass into stable liquid hydrocarbons at low temperatures and high hydrogen pressures [1].

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. 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 on-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. Therefore, monitoring the temperature, volatile organic compounds (VOC), carbon monoxide (CO) and controlling the moisture is crucial to avoid the ignition [2].

2.2 Introductory piece on kinetic modelling
Understanding the thermal kinetic behavior 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 (isoconversional) 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 isoconversional method is a simple method that eliminates the error related to the model fitting. In the isoconversional 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 isoconversional method is the most suitable method and, consequently, the most commonly used in this case. As biomass is pre-dominantly composed of three different components (cellulose, hemicellulose and lignin), each behaves differently and separately during the biomass thermal decomposition. Thus, this complex behaviour of biomass decomposition should be considered in kinetic modeling [2].

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 which had been typical during the 19th Century, but became stigmatized in the 20th Century [3].

More recently there has been a marked increase in secondhand use, which may have been financially driven by the impact on consumers from the 2008 economic crisis. 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 including 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, thereby reducing

environmental impact

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. Given that ability of biomass to be converted to solid, liquid and gas fuels, biomass is a suitable energy resource for heat, power and transport.

While the utilisation of liquid and gaseous biofuels typically requires some chemical transformation/valorisation of the biomass, this is not necessarily the same for solid fuels [3].

In order to use unprocessed biomass as a solid fuel, it is normally blended with other fuels, such as coal, in order to compensate for the low calorific value and high moisture content inherent in the biomass source. Woody biomass, can, in theory, be combusted without much processing and as such, the application of woody biomass as a fuel can still be considered a low-grade use [3].

3.2 Herbaceous biomass

Herbaceous biomass usually contains components such as seeds, cones, leaves and stems that require further size reduction 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. As discussed previously, size reduction methods such as the grinding process require energy. Naimiet al, studied the required energy input for five herbaceous biomass (miscanthus, wheat straw, switch grass, 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 [3].

Herbaceous biomass such as miscanthus is typically characterized based on its silica and inorganic contents. These components cause various problems during the thermal decomposition via valorization and melting of the low potassium silicates compounds. In the

case of woody biomass this problem is less noticeable due to the low alkali and Si content in the biomass. 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. Forbes et al. studied the physicochemical characteristics of eight different biomass fuels such as aspine, 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 [3].

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 [4].

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. 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. 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.

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 [5].

The combination of high Na and Cl concentrations promote the risk of alkali chloride-related operational problems. There are several studies reporting on the complex ash composition that arises from seaweed-based feedstocks. 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 utilisation, and washing/leaching with water or weak acids are the most common practice to remove mineral matter and halogens

4. Up-cycling approach

4.1. Herbaceous biomass

(i) Pyrolysis and bio-oil production

Recently, the production of bio-oil from biomass has gained great attention as an alternative to fossil fuels. 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 [5].

The pyrolysis of cellulose is endothermic while pyrolysis of hemicellulose and lignin is exothermic. 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 [5].

In general, the highest yield of liquid (mostly anhydro sugars) is produced by the decomposition of cellulose [6] 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.

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. 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. The bio-oil composition and yield are unfavourably affected by the amount of the ash content in the biomass feedstock, therefore washing it with water, surfactant or either acid improves both the yield and the composition of the bio-oil. For instance, washing the biomass with water showed an effective way to reduce the inorganic materials such as (K, P and Cl) [5] and it is an ideal pre-treatment choice for woody biomass (low ash content). Again,

washing with a surfactant such as Triton X-100 can effectively reduce the ash content in comparison to the untreated biomass. Washing the raw biomass with HCl reduced the metal content and consequently increased the volatile materials during the pyrolysis which in turn increased the bio-oil yield and also reduced the hemicellulose present in the polymer structure of the biomass [5].

Banks et al. reported that using stronger acid could lead to hydrolyse both cellulose and hemicellulose completely that eventually decreased the bio-oil yield [5].

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. 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.

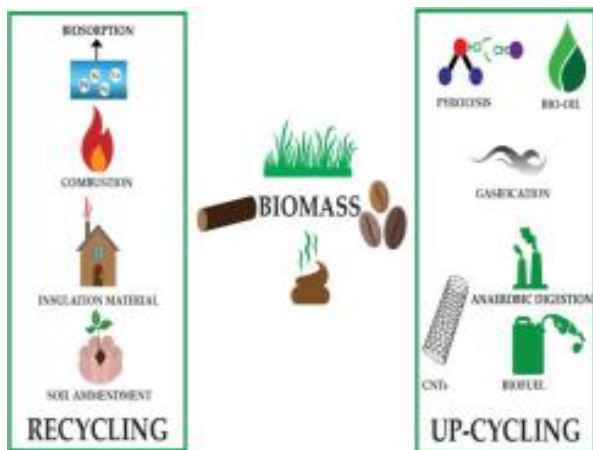
4.3 Other types of biomass sources upcycling

Ross et al. have noted that the char yield from the slow pyrolysis/carbonisation of macro-algae should not be neglected and should be utilised. 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 [6].

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.]. 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 [6].

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.



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 Fig. 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 utilisation 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.

6. References

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