A Review of Intermediate Pyrolysis as a Technology of Biomass Conversion for Coproduction of Biooil and Adsorption Biochar

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1. Introduction

The ever increasing demand for energy and environmental protection concern has led to innovations on the appropriate conversion of nonrenewables and utilization of renewables [1, 2]. Currently, much emphasis has been on renewable energies such as biomass. The utilization of both fresh and waste biomass is advantageous in terms of energy recovery and environmental protection [3, 4]. The effective use of waste has been regarded as the backbone of the circular economy, effective energy conversion, and environmental protection [5]. In developing countries, organic biomass wastes have the potential to provide about 20–40% of the primary energy [6], and its effective conversion can bring sustainable energy and environment.

Different biomass conversion methods exist including direct combustion, biological, and thermochemical [7, 8], but thermochemical conversions have gained advantages over others [9, 10]. They are effective, environmentally friendly, fast, of low maintenance and labor costs, selective in targeting specific product, and able to convert biomasses which do not compete with food such as biomass wastes [11]. Among the promising innovations, pyrolysis has been appreciated in converting biomass [11] into useful products, which are solid, liquid, and gas in an effective way. Pyrolysis is a thermochemical decomposition of organic material in the absence of oxygen [12]. The distribution and quality of the products depend on effective control of process parameters, the type of reactor, and feedstocks [13, 14]. The products that have found great use that come from pyrolysis are biooil and biochar. Biochar derived from pyrolysis processes can be used as an adsorption agent and hence can reduce the use of fossil fuels in the production of the ever increasing demand for adsorbents [15]. Biooil produced from biomass pyrolysis can be used directly or with blending in engines and thus replace fossil oils.

Pyrolysis reaction may proceed as slow, intermediate, fast, or flash depending on the process operating parameters. Table 1 provides the range of operating parameters and product distribution of different categories of pyrolysis processes. It can be seen that slow and fast pyrolysis target biochar and biooil, respectively, while intermediate pyrolysis produces both simultaneously. Intermediate pyrolysis has been reported to be a type of pyrolysis that has a good...
distribution and quality of the three products [5, 16–18] and hence the possibility of coproduction of biooil and adsorption biochar.

Due to the high demand for biooil and adsorption biochar, the need for utilization of wastes, need for extra upgrading treatment procedures of fast pyrolysis biooil, and low quality and quantity of biochar from fast pyrolysis, intermediate pyrolysis seems to be a way to go. This new technology is regarded as a promising technology especially in coproduction and utilization of different biomass. Several researchers have published on intermediate pyrolysis from various feedstocks and reactors, process conditions, and catalyst and have identified the benefits of the process. Unlike other pyrolysis reactions, intermediate has been reported to have advantages such as low operating temperature, ability to treat a range of feedstock, and production of high quality products [19–22]. Tinwala et al. [23] researched agroindustrial biomasses and wastes on a fixed bench-scale pyrolyzer, identified distribution of biooil of 20.5–47.5% and biochar of 27.5–40%, and concluded that biooil can replace furnace oil. Mohammed et al. [24] studied the utilization of groundnuts shell in a vertically fixed bed reactor and found out that, among other things, the organic phase was of good quality and can be used as the precursor for chemicals. Other publications on intermediate pyrolysis have also reported its efficiency in treating wastes and producing quality biooil and biochar products [25–28].

The data that have been accessed shed light on the use of intermediate pyrolysis to generate usable biooil and biochar. Data on product characterization and quantity are available from a variety of feedstocks and reactors. Data on intermediate pyrolysis on some feedstocks and reactors show that coproducts are of high quality and can be used directly or with minimal processing as compared to other processes. Since this method is emerging and suitable for coproduction, data on product quality comparisons with other manufacturing processes should be available. Currently, such a comparison is not well documented. Thus, the comparison can give more emphasis on its utilization while enjoying the mentioned advantages above. Thus, this review article aimed at reviewing the possibilities of utilizing intermediate pyrolysis in the coproduction of biooil and adsorption biochar. These coproduced products should be of high quality, such that they can be used directly or with little upgrading. This was done by comparing the products from fast, slow, and intermediate pyrolysis, biodiesel, fossil diesel, and commercially activated carbon. The study also aimed at reviewing the possibilities of using intermediate pyrolysis in the utilization of the ever increasing and difficult wastes that are difficult to be handled by fast pyrolysis.

2. Intermediate Pyrolysis

Intermediate pyrolysis is the pyrolysis which is between fast pyrolysis and slow pyrolysis. From Table 1, intermediate pyrolysis has a good distribution of product and hence can be used in the coproduction of biochar, biooil, and gas [35]. Compared to other categories, intermediate pyrolysis has been reported to be flexible to various materials and has good product distribution, two phase’s separable biooil, high quality, and dry biochar [5, 16–18, 31, 36–38]. Its ability to treat waste biomass gives it advantages to be used in developing countries where waste biomass such as municipal solid wastes currently is a problem [12, 37]. Researchers also have documented that it has easily separable liquid phases with the organic phase having properties similar to biodiesel [37, 39–43]. The organic phase can be blended to 50% with fossil liquid [37]. Its aqueous phase is also useful in the production of biogas and ethanol, since it contains C2-C6 sugars, hydroxyacids, oligomers, and water soluble phenols [28, 35]. This gives advantages of not only little biooil upgrading compared to fast pyrolysis oil but also a total utilization of all products. Intermediate pyrolysis has the ability to treat high moisture content feedstock, and when this occurs, the biochar achieves the properties of activated carbon due to comprehensive interaction with steam [37].

The mentioned advantages above indicate that intermediate pyrolysis is suitable for the coproduction of biooil and adsorption biochar. The published data should be analyzed and concluded on whether it can replace other categories in biomass conversion, especially when coproduction is required. The following sections will evaluate the properties of these products and compare them with products from other categories and available commercial products, fossil diesel, biodiesel, and activated carbon.

2.1. Biochar. This is a solid carbon-rich product produced from pyrolysis with quality comparable to industrial coal, with a high amount of carbon and less amount of oxygen and hydrogen [44, 45]. It has a microporous structure that is used in soil quality control and acts as activated carbon in the removal of metals such as chromium, cadmium, nickel, mercury, lead, gold, and silver from solution [46–50].

<table>
<thead>
<tr>
<th>Property</th>
<th>Slow</th>
<th>Intermediate</th>
<th>Fast</th>
<th>Flash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (°C/s)</td>
<td>1.1–1</td>
<td>1–10</td>
<td>10–200</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Feed size (mm)</td>
<td>5–50</td>
<td>1–5</td>
<td>&lt;1</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>400–500</td>
<td>400–650</td>
<td>850–1250</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Vapor residence time (s)</td>
<td>300–550</td>
<td>0.5–20</td>
<td>0.5–10</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Feed water content (%)</td>
<td>Up to 40</td>
<td>Up to 40</td>
<td>&lt;&lt;10</td>
<td>&lt;&lt;10</td>
</tr>
<tr>
<td>Biooil yield (%)</td>
<td>20–50</td>
<td>35–50</td>
<td>60–75</td>
<td>60–75</td>
</tr>
<tr>
<td>Gas yield (%)</td>
<td>20–50</td>
<td>20–30</td>
<td>10–30</td>
<td>10–30</td>
</tr>
</tbody>
</table>

Table 1: Classification of pyrolysis processes [29–34].
Intermediate biochar has properties suitable for energy and adsorption [20]. It is a dry, high energetic, brittle structure, and less dust and tar, and hence less toxic [51, 52]. It has a heating value similar to semibituminous coal [39]. It is also suitable as an adsorbent, and its quality increases as feed moisture content increases [37]. Since intermediate pyrolysis can process high moisture content feedstock, it can be expected to have high quality biochar since steam acts as activating agents.

Always, a good adsorbent should have the high adsorptive capacity, adsorption rate, mechanical strength, and wear resistance, reactivation characteristics, and good particle size distribution [53]. Biochar to be used as an adsorbent with high absorption power and affinity to metals are those with lower carbon, high nitrogen and oxygen, as well as lower C/N and higher O/C and H/C ratios, higher pore volume, and higher pH [54]. It is always produced with low pyrolysis temperature at high pyrolysis time. Apart from slow pyrolysis, intermediate pyrolysis can be a good method of producing biochar with the ability to act as activated carbon.

Table 2 provides available published data on biochar from slow, intermediate, fast pyrolysis, and commercial activated carbon. The assessment on whether biochar from intermediate pyrolysis has a higher quality to be used as activated carbon is done by assessing the properties of different production techniques and commercially activated carbon. It can be seen that biochar from intermediate pyrolysis is drier (0.7–4%) than fast (3–6%) and slow (2–42%) pyrolysis. High moisture content in commercial activated carbon is more than those from intermediate due to water introduced during activation. Lower moisture content is advantageous in transport and storage. In terms of adsorption, the effect is not noticeable as moisture content does not affect adsorption capability [55].

While ash is not necessary, its composition is critical because the choice of metal to be adsorbed is influenced by the composition of ash, which can either impede or favor the process. There is not much of a difference in ash content between the items that are being compared. Adsorption is regulated by pH as well. In metal adsorption, an increase in pH simultaneously increases adsorption but is limited to a certain level [56]. From Table 2, it can be seen that biochar from intermediate pyrolysis has a pH range (8–9.6) close to activated carbon (5–8) and thus effective in metal adsorption compared to fast (7–11) and slow (6–12).

The rate of adsorption is controlled by high pores volume [53]. From published data, biochar from fast pyrolysis has a higher pore volume (0.1–1 cm$^3$/g) close to activated carbon (0.05–1.5 cm$^3$/g) compared to intermediate (0.05–0.16 cm$^3$/g) and slow of less than 0.14 cm$^3$/g (Table 2). The higher value of pore volume of biochar from fast pyrolysis is favored by high operating temperatures [93, 94]. This makes biochar from intermediate to be superior to those from slow pyrolysis. Furthermore, a good adsorbent should have high adsorption capacity which is determined by surface area. From published data in Table 2, biochar from intermediate pyrolysis has a high surface area (100–250 m$^2$/g) compared to fast (15–110 m$^2$/g), but less compared to activated carbon (500–2058 m$^2$/g). The large surface area in slow and intermediate pyrolysis biochar is due to high residence time compared to fast pyrolysis [95, 96]. This allows utilizing biochar from intermediate pyrolysis for the activation process compared to fast pyrolysis biochar.

In terms of H : C, C : N, and O : C ratios in which a good adsorbent should have lower C/N and higher O/C and H/C ratios, biochar from intermediate pyrolysis is favored as adsorbent compared to those from slow and fast pyrolysis biochar. These ratios for intermediate pyrolysis biochar are much close to those of activated carbon. An important note is biochar from intermediate pyrolysis is more of adsorption rather than stability due to high ratios of H : C and O : C. High H : C (low aromaticity) and high aliphatic content allow easy microbial attack [97]. Always, resistance to microbial reaction is achieved when the ratio of oxygen to carbon is less than 0.2 [98]. Thus, intermediate pyrolysis biochar is more of adsorption than stability and hence difficult to be used in soil adsorption. It is thus suitable in hydrometallurgical adsorption.

### 2.2. Biooil

Biooil can be defined as a condensate product of pyrolysis which is dark brown, viscous organic liquid comprised of several complex oxygenated compounds [99]. It has viscous water-insoluble tar, mainly the oligomeric lignin-containing fraction, which tends to spontaneously precipitate in the presence of a large amount of water [100]. It is thermally unstable due to the large amount of oxygen. For example, if stored for longer than two months, it becomes difficult to ignite and burn than fresh biooil [100]. The composition of biooil is dominated by the phenolic group (about 31%), carbonyl group, followed by the carboxyl group [27, 101].

Biooil which is mostly produced from fast pyrolysis is reported to have poor combustibility and less miscibility and hence difficult to be used directly in normal engines [39]. This is due to high viscosity, oxygen, and water contents. It also has low thermal stability and high corrosiveness. This is because fast pyrolysis simply liquefies a part of feedstock and does not upgrade the molecule structure significantly, and hence, reactive chemical compounds are still in the oil [102]. Thus, biooil from fast pyrolysis cannot be utilized without prior upgrading. This adds extra cost in terms of the extra process and catalysts used. Biooil is the one with good properties compared to biodiesel and fossil diesel and thus can be used directly or with little upgrading.

When compared to biooil from fast pyrolysis, biooil from intermediate pyrolysis has improved physical and chemical properties, such as low oxygen content in biooil, better oil miscibility with fossil fuels, and high calorific value [27]. It is reported to have a low amount of tar and less reactive tar [103, 104]. These improvements in properties make biooil easy to use in existing engines. Table 3 summarizes the properties of biooil from intermediate and fast pyrolysis and compares it with diesel and biodiesel. Always, a good fuel should have low moisture, ash, sulphur, oxygen, and nitrogen contents and high amounts of carbon, hydrogen, and high heating value.
Pyrolysis biooil has a high amount of carbon (49–74%) and nitrogen reduces pollution. From Table 3, intermediate quality of oil, and a low amount of oxygen, sulphur, and water content blend. It can be seen that it can be a good candidate when blending with fossil fuel to produce low fossil fuel and biodiesel, it can be shown that it can be a good candidate when blending with fossil fuel.

Table 3: Comparison of fast and intermediate biooil, fossil diesel, and biodiesel fuels.

<table>
<thead>
<tr>
<th>Property</th>
<th>Intermediate</th>
<th>Fast</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (%)</td>
<td>1.7–15.3</td>
<td>15–30</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>0.16–0.23</td>
<td>0.01–1.5</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>C (%)</td>
<td>49–74</td>
<td>54–61</td>
<td>85.6</td>
<td>78.8</td>
</tr>
<tr>
<td>S (%)</td>
<td>0.1–0.3</td>
<td>0.03–0.3</td>
<td>&lt;0.8</td>
<td>&lt;0.74</td>
</tr>
<tr>
<td>O (%)</td>
<td>8.72–33</td>
<td>35–40</td>
<td>1.01</td>
<td>8.36–11</td>
</tr>
<tr>
<td>H (%)</td>
<td>6.79–10.6</td>
<td>5.5–7</td>
<td>13.37</td>
<td>11–13</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.1–5.8</td>
<td>0.4–2</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Density (g/cc), at 25°C</td>
<td>0.95–1.082</td>
<td>1.14–1.2</td>
<td>0.82</td>
<td>0.88</td>
</tr>
<tr>
<td>Viscosity (cp), at 40°C</td>
<td>2.82–98</td>
<td>15–100</td>
<td>1.9–4.1</td>
<td>1.9–6</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>22–40</td>
<td>16–19</td>
<td>45–47</td>
<td>35–40</td>
</tr>
</tbody>
</table>

From published data (Table 3), intermediate biooil has low ash content (<0.23) that is comparable to biodiesel (<0.2%) and fossil diesel (<0.1%) which is of high quality when compared to fast pyrolysis biooil that can reach 0.15%. This leads to improved quality compared to fast pyrolysis biooil (up to 1.5%). Water content in fuel is not required since it reduces heating value, causes corrosion, and increases viscosity [105]. High water content also causes phase separation, thus causing corrosion, troubles in the burner, and emulsion formation [106]. Furthermore, high content reduces heating value, stability, density, and increases pH [105, 107]. Compared to fast pyrolysis biooil, intermediate pyrolysis biooil has less amount of water (2–15%) compared to fast pyrolysis oil (15–30%) (Table 3). When compared to fossil fuel and biodiesel, it can be seen that it can be a good candidate when blending with fossil fuel to produce low water content blend.

The high amount of hydrogen and carbon increases the quality of oil, and a low amount of oxygen, sulphur, and nitrogen reduces pollution. From Table 3, intermediate pyrolysis biooil has a high amount of carbon (49–74%) and hydrogen (6–11%) compared to fast pyrolysis biooil (hydrogen 4–7% and carbon 54–61%) and is approaching biodiesel and fossil fuel. Intermediate pyrolysis biooil has less amount of oxygen (8–33%) compared to fast pyrolysis oil (35–40%) and approaching biodiesel (8%). A high amount of oxygen in oil causes oil instability, low energy content, low miscibility, and increases pH [105]. This gives intermediate pyrolysis oil to be superior to fast pyrolysis oil and hence a candidate for blending with fossil fuel.

High viscosity causes difficulty inflow and hence problems in combustion. Intermediate pyrolysis has low viscosity (2–98 cp) compared to fast pyrolysis oil (15–100 cp) and close to biodiesel and fossil diesel (Table 3). This makes it easy for combustion and transportation. Low viscosity and miscibility due to the low oxygen content in intermediate pyrolysis oil makes it easy to be blended with biodiesel or fossil diesel and hence easy utilization in normal engine compared to fast pyrolysis oil. Easy blending is also associated with the presence of about 12% fatty acid methyl esters in intermediate pyrolysis biooil [42]. Above all, intermediate pyrolysis oil has a
higher heating value (24–40 MJ/kg) that is close to biodiesel (35–40 MJ/kg) and fossil diesel (45 MJ/kg) (Table 3). This makes it fit to be used as fuel, and with addition to above added advantages, it becomes superior to fast pyrolysis biooil.

3. Intermediate Pyrolysis as the Appropriate Process for Waste Utilization

The high demand for food and forest products for the ever increasing population has led to increased production of wastes. This increase in population and wastes put pressure on nonrenewable energy resources and the environment [122]. Poor treatment of wastes that lead to pollution and loss of energy is common in developing countries. If these wastes are well treated can generate 20–40% of primary energy is common in developing countries. If these wastes are well treated can generate 20–40% of primary energy in developing countries [123] and if well converted can help to reduce the pressure of feedstocks for biooil and adsorption biochar production.

An important challenge is to effectively treat these wastes at both environmental and economic effectiveness. The wastes contain a wide range of components that needs careful treatment before utilization. They may contain a high amount of water that may be difficult in direct combustion and fast and flash pyrolysis. They may also contain lignocellulosic materials that the biochemical process becomes difficult. Due to difficulties in collection and transportation, building large plants may not be economical. All the above challenges put the challenge on effective utilization of wastes at current common conversion methods. Therefore, a method that can take into account these challenges is required.

Intermediate pyrolysis is believed to be effective and environmentally friendly in treating wastes. It has the ability to treat difficult low-value, high-ash wastes such as sewage wastes and deinking sludge that cannot be treated by fast pyrolysis [37]. It can handle different types of feedstock, large sizes, high moistures, and operates economically at any plant size and thus be able to treat wastes [12]. The process is more reliable and robust and hence appropriate to small and medium scale [31]. The use of large size and production of directly usable biooil makes it reduce costs in small and medium plants. Therefore, intermediate pyrolysis is a good candidate in the processing waste with little or no pretreatment procedure while producing good quality of products. Since intermediate pyrolysis is a candidate for coproduction of adsorption biochar and biooil, the conversion of wastes can be a resource and environment serving technology.

Intermediate pyrolysis study on the production biooil from Eucalyptus sp. and Picea abies wood wastes found out that there was little or no need of upgrading biooil when compared to fast pyrolysis of such wastes [31]. The study of organic part of municipal solid wastes has revealed the production of biooil which is stable and non-Newtonian [5]. The study by Del Pozo et al. [124] on coffee silver skin resulted to increased energy biochar and biooil with 200–500 tons of gallic acid equivalents per year. The 2021 study of grape waste (grape pomace) done by Del Pozo et al. [125] has indicated intermediate pyrolysis is effective than torrefaction in processing this waste and production of antioxidants. The study also indicated the production of both good biochar and biooil with two separable parts. The study by Yang et al. [126] has suggested the use of intermediate pyrolysis of wastes in China can be profitable without subsidies. The intermediate pyrolysis of sewage sludge and deinking sludge found out that the biooil had high carbon and hydrogen content and thus high heating value that is comparable to biodiesel, with easy storage and transportation at the economic level [26]. It has also been proved that intermediate pyrolysis of rice straw wastes proved to offset carbon dioxide than the rest of types [32]. Other intermediate pyrolysis studies on wastes such as organic fraction of municipal solid wastes [12], sugarcane bagasse [127], sugarcane bagasse and oat hulls [128], chicken manure for fertilizer and heat production [5], wheat husk [27], waste tires [129], and Bambara groundnut shells [24] have appreciated the advantages of intermediate pyrolysis. These good results indicate the effectiveness of intermediate pyrolysis on the conversion of wastes when compared to current common technologies. Due to its ability to coproduce biooil and adsorption biochar, wastes are thus good candidate feedstock for the coproduction.

4. Opportunities and Challenges of Intermediate Pyrolysis

Intermediate pyrolysis is a relatively new technology but has shown more advantages such as ability to handle difficult feedstock [130]. It produces three products that have quality to be used directly or with little upgrade [52, 131]. It has a big chance of becoming a viable technology especially in treating wastes that currently are accumulating worldwide and hence reduce the cost of feedstock treatment and products upgrading. It also has a big opportunity of operating at small and medium plants, since it is still economically beneficial at a small scale. It also has a big opportunity in the coproduction of biooil and adsorption biochar that needs little or no upgrading. Such prospective opportunities have been raised in the economic benefit of treating coconut shell to produce high quality biooil [132], the combined heat and power production of intermediate pyrolysis related to economy and environment [37]. In other studies, such as noted in Section 4 in the utilization of wastes, intermediate pyrolysis gives the opportunity to recover energy and protect the environment from biomass waste materials.

The challenges that face this novel technology include the utilization of an aqueous phase which contains a certain amount of energy. A study done by Torri and Fabbri [28] showed that its utilization in biogas production required prior treatment or use of catalysts. Also, good distribution and quality depend on parameter control [132] and the use of appropriate reactors. Some promising reactors have been designed and others are in progress [130]. It is now an appropriate time to increase the research on optimization of parameters for coproduction of adsorption biochar and biooil. Also, more studies should be done to include the use of catalyst to increase the quality of products.
5. Conclusion

This review article has analyzed the possibility of utilizing intermediate pyrolysis as an emerging technology in the coproduction of biooil and adsorption biochar. The observed advantages of good product distribution and simultaneous production of biooil and biochar make it a candidate in the coproduction of biooil and adsorption biochar. The analysis has shown that the organic biooil has high quality that is comparable to biodiesel and fossil oil. It has a high heating value, low viscosity, high stability, and miscibility making it superior to biooil from fast pyrolysis. Also, the comparison has shown that biochar from intermediate pyrolysis is more suitable for hydrometallurgical adsorption and is thus used as activated carbon. It was also realized that it can effectively treat wastes that have varying composition, high moisture content, and large size and thus become a candidate for coproduction of biooil and activated carbon for the ever increasing wastes.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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