A Comprehensive Review in Microwave Pyrolysis of Biomass, Syngas Production and Utilisation

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Abstract: Lignocellulosic and waste materials, such as sewage sludge, can be broken down into its useful constituents and converted into fuel for engines. This paper investigates microwave pyrolysis to decompose biomass into H₂ and CO (syngas), which may be catalysed in the Fischer–Tropsch (F-T) process to liquid biofuels. Using microwave radiation as the heat source for pyrolysis proves to yield large quantities of gas with higher concentrations of H₂ and CO compared to conventional heating methods. This is largely due to the energy transfer mechanism of microwaves. Pyrolysis parameters such as temperature (which increases with input power), feedstock type, microwave absorber, and biomass moisture content influence syngas yield. Several papers reviewed for this study showed differing optimal conditions for microwave pyrolysis, all being heavily dependent on the biomass used and its composition. However, all researchers agreed on the thermal efficiency of microwave heating and how its material-selective nature can increase syngas yield. Compared to diesel fuels (while processing a similar efficiency and a higher cetane number), FT fuels and specifically pyrolysis may yield the benefit of reduced nitric oxides (NOx), particulate matter (PM), unburnt hydrocarbons (HC) and carbon monoxide (CO) emissions.

Keywords: microwave pyrolysis; syngas; Fischer–Tropsch Synthesis; biofuels; lignocellulosic biomass

1. Introduction

The need to replace diesel and gasoline with fuels derived from renewable sources is fast approaching. The world is rapidly depleted of its fossil fuel reserves; S. Shafiee et al. [1] predict that around 30 years from now, oil and gas supplies will be completely exhausted. Additionally, increased CO₂ emissions due to fossil fuel combustion have shown noticeable effects on our climate. This leads to the need to research cleaner methods of producing energy. Biofuels can be made from biomass such as wood, agricultural residues, and other organic materials. Using this as a replacement for fossil fuels reduces the energy-intensive method of extracting oil and gas from the Earth [2] and the amount of greenhouse gases produced over the fuel’s life cycle [3–5]. In addition, atmospheric methane, which is 30 time [5] more effective as a greenhouse gas than CO₂, is reduced by converting waste, sewage sludge, and biomass into fuel [5,6].

First-generation biofuels such as ethanol and bio-esters are sourced from food crops, which are quickly fermented or trans-esterified [7] to produce fuel. It is currently possible to mass-produce this biofuel, but its use has become increasingly controversial. Finding the land space needed to accommodate these crops is proving difficult and has created competition between growing for food or fuel [8,9]. For this reason, second-generation biofuels (extractable from lignocellulosic biomass) are becoming interesting. They are more sustainable than the first generation and can be produced from inedible waste [10].

It has been estimated that energy harnessed from agricultural waste can provide up to 64% [11] of the world’s energy demand. There is now a push for new and innovative measures to scale up Biomass-to-Liquid (BTL) technology. As it stands, the process of
extracting useful compounds from biomass on a scale large enough to overrun the use of fossil fuels is not yet available.

The main aim of this study was to investigate the use of pyrolysis to decompose biomass into syngas, i.e., CO and H\textsubscript{2} thermochemically. Pyrolysis is a method of heating substances anaerobically, thus heating in the absence of oxygen. The syngas released because of this procedure can then be treated in the Fischer–Tropsch (F-T) process (Figure 1). Mostly aliphatic hydrocarbon chains are formed over a catalyst to produce liquid biofuel for engines.

![Figure 1](image_url). A simplified view of the processes involved in producing F-T fuel.

Using microwave radiation as the source of heat for pyrolysis has recently received a lot of attention, having proved to produce cleaner fuel products compared to conventional heating methods. This paper has evaluated microwave pyrolysis technology to validate this further. A review of F-T biofuel is also included, with a look into its emissions, efficiency and compatibility with modern engines.

2. Literature Review

2.1. Biofuels

First-generation biofuels are sourced from foods such as sweetcorn and wheat. These consist predominately of starch, which is easily broken down into simple sugars [11], and then converted into fuel [12]. Inedible second-generation feedstock contains cellulose, hemicellulose and lignin, collectively known as lignocellulose, which is much more challenging to break down [8]. One of two methods is then required to decompose this structural unit and convert the complex polymers (cellulose and hemicellulose) into simple sugars, a thermochemical or biological process. Biological processes in this context refer to the fermentation of biomass, which Y-F. Huang et al. [13] have considered a difficult and expensive way to convert lignocellulosic feedstock. Gasification and pyrolysis (examples of thermochemical techniques) are typically used to convert biomass to second-generation biofuels.

2.2. Gasification vs. Pyrolysis

The difference between these two processes is that the feedstock is heated with oxygen and/or steam in gasification. Suitable feedstock for both methods includes waste material such as sewage sludge and primarily all lignocellulosic biomasses [5].

The pre-treatment of the samples differs; however, pyrolysis requires the feedstock to be ground to fine pieces (around <2 mm in size) [14,15]. L. Burhenne et al. [16] found that with varying moisture content, specifically of 2.4%, 16.4% and 55.4%, their results for pyrolysis showed that the most gaseous products were produced for 2.4% at 500 °C, followed by 16.4% then 55.4% moisture. The most H\textsubscript{2} and CO were also made at 2.4%, with their volumes decreasing with increasing water content. This is following C. Li et al. [17] who state that pyrolysis (450–600 °C) should be performed on feedstock with a moisture content of less than 10% of its total weight. For gasification, on the other hand, the feedstock size can be as large as a couple of inches and should have moisture content in the range of 10–20% [18].

The yield and quality of the products from gasification and pyrolysis vary considerably. The research paper aims to extract high quantities of permanent gases from biomass, specifically H\textsubscript{2} and CO (syngas). Gasification is known to yield larger volumes of gas and char (solid) products than pyrolysis, with the latter also distributing its total fuel yield to bio-oil (liquid fraction).
The main problem when decomposing biomass via gasification is the tar [19], a toxic by-product produced in parallel with syngas. This tar refers to the liquid product of gasification, which differs from the liquid product of pyrolysis (bio-oil). The primary reactions in a reactor are the desired, intended reactions. The condensable gas released from biomass during pyrolysis is termed bio-oil (or primary tar) and is a result of these primary reactions [20]. Unwanted secondary and tertiary reactions are more likely to occur with increasing temperatures. Tar is a product of tertiary reactions, and its presence during gasification is explained by the high temperatures involved in this process. A. Sharma et al. [20] have shown that pyrolysis can occur at relatively low temperatures, usually between 400–700 °C whereas in gasification, temperatures beyond 700 °C are necessary for decomposition.

A.S. Al-Rahbi et al. [21] mentioned in their paper that tar reduction catalysts have been used with the gasifier. However, they were costly, and the regeneration of the active sites of the catalysts proved difficult. F. Collard and J. Blin [22] validate this and have rooted the problem to stable phenols deposited on the catalysts, affecting biomass conversion to syngas during gasification. They suggested that the temperature of the reactors plays a significant role in how the biomass decomposes, directly affecting the phenol produced.

In addition to reduced tertiary tar production, pyrolysis is more efficient than gasification at de-volatilising syngas since it can be achieved at lower reactor temperatures. This reduces the costs and the energy consumed during the decomposition of biomass.

2.3. Pyrolysis Oil

Only the syngas released from the biomass are considered useful products for this investigation. The bio-oil produced from pyrolysis has received some attention as a potential fuel, but its varied composition is causing many problems. L. Qiang et al. [23] state that over 300 organic compounds can be found in this bio-oil which depends on the diverse range of biomass feedstock available [24]. This means that each pyrolysis oil from different resources must be analysed and treated accordingly to meet the property requirements of engine fuel. Therefore, the focus here remains on extracting large quantities of syngas, allowing more tailored biofuel to be produced. The CO and H\textsubscript{2} gases released after pyrolysis are fed into the Fischer–Tropsch (F-T) process, where the reactants chemically bond to form long-chain hydrocarbons over a suitable catalyst.

2.4. Fischer–Tropsch Synthesis

Once the clean-up and conditioning of syngas have taken place after pyrolysis, the composition of the Fischer–Tropsch (F-T) fuel produced after that is independent of its biomass source [5]. It is this process that follows the syngas production that determines the biofuel type. Dimethyl-ether (DME) and F-T fuel are common alternatives to standard diesel produced from catalysing synthesis gas. F-T is a syngas-conversion process typically used in Biomass-to-Liquid processes to produce either paraffin (alkane) or olefin (alkene) hydrocarbons [6,25].

The conditions at which F-T provides optimum fuel composition vary slightly in different literature reviews. However, all mentioned below agree on its dependence on temperature, H\textsubscript{2}/CO feed ratio, pressure and catalyst used in the F-T process [4].

T.L. Alleman et al. [26] states that low-temperature F-T (200–240 °C) significantly reduces the number of aromatic compounds in the F-T fuel, with a high output of linear alkanes. However, the hydrocarbon chains may be too long for diesel engine use. S.S. Gill et al. [25] mentions that upgrading F-T fuel is often necessary via a hydrocracking process, making the liquid more compatible with diesel fuel. High paraffin content in the F-T fuel corresponds to a lower C/H ratio, which is determined by the H\textsubscript{2}: CO feed. Miyamoto et al. [27] has found that for diesel fuels with a low C/H ratio, a lower adiabatic temperature is reached, which can reduce the production of NO\textsubscript{x}. Since F-T products are synthesised to have almost no aromatics, NO\textsubscript{x} emissions are expected to be
even lower \[28,29\]. This is supported by Szybist et al. \[30\] who show NOx emissions to be reduced by 21–22\% compared to conventional diesel.

The scarcity of aromatic compounds found in F-T fuel reduces its harmful emissions but to the detriment of its lubricity as Y-D. Kim et al. \[31\] has concluded. This would lead to mechanical wear and damage to engine parts, but this factor may be improved by using additives in the fuel.

Suitable catalysts for low-temperature F-T synthesis include cobalt and iron due to its process efficiency and relatively low use cost. H. Jahangiri et al. \[32\] believes cobalt reigns superior as a catalyst for this process due to its resistance to the deactivation of its sites and it favouring the formation of longer hydrocarbons. J. Tayebi et al. \[33\] agreed and stated that cobalt is more durable than iron and conducted F-T synthesis using the catalyst at a pressure of 1 atm (higher pressure values decreased the production of long-chain hydrocarbons). For an industrial-sized low-temperature F-T experiment, M. Riyahin et al. \[34\] used an iron-based catalyst which was performed using a feed having the H\(_2\)/CO ratio of 2 and at approximately 1 atm pressure, again to minimise forming of short-chain hydrocarbons such as methane.

2.5. Comparison to DME

Dehydrating methanol (typically a gasoline alternative) produces a product more suited for diesel engines, namely dimethyl-ether or DME \[35\]. This fuel type could also be produced directly from syngas that is gasified from biomass feedstock, which is the preferred method of production as it is a single-step procedure \[36\].

\[
3H_2 + 3CO \rightarrow CH_3OCH_3 + CO_2 \tag{1}
\]

Many of DME’s fuel properties enable it to reap in better results than diesel in terms of cleaner emissions. S.H. Park et al. \[37\] state that due to the lack of carbon–carbon bonds in DME, no soot is produced upon its combustion. Their paper also includes the oxygen content of DME to be that of 34.8\%, whereas diesel and F-T fuel have none. The presence of oxygen allows for complete combustion of the fuel, which means that lower levels of PM are released. This typically comes at the cost of higher nitric oxides emissions, but M. Himabindu and R.V. Ravikrishna \[36\] declare that the higher cetane number of DME compared to diesel allows for a lower ignition delay which reduces NOx emissions. This also applies for F-T fuel which typically has high cetane numbers (>74) \[26\] and so exhibits similar results to DME in this respect.

Only slight modifications to compression ignition engines are necessary to account for the differences between diesel/DME fuels (Table 1) such as lower viscosity and lubricity for DME \[37\]. This includes preventing the volatile DME fuel from leaking and reducing the damage that can incur from inadequate lubrication. These can be improved by the use of additives to enable the long-term use of both alternatives to diesel. An essential advantage of F-T fuel and DME over diesel is their widely reported zero sulphur content, which eradicates toxic sulphate emissions. In addition, the efficiency of F-T fuel is very similar to that of conventional diesel (Table 2), with marginal differences in lower heating values. In contrast, the lower heating value of DME is almost half that of either \[31\].
Table 1. A comparison of the fuel properties of F-T fuel, DME and diesel [25,26,36,38–40].

<table>
<thead>
<tr>
<th>Fuel Properties</th>
<th>F-T Diesel</th>
<th>DME</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_nH_{2n+2}</td>
<td>CH_3OCH_3</td>
<td>C_{14}H_{30}</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>46.07</td>
<td>198.4</td>
<td></td>
</tr>
<tr>
<td>Density at 20 °C</td>
<td>0.76</td>
<td>0.67</td>
<td>0.83</td>
</tr>
<tr>
<td>Normal boiling point (°C)</td>
<td>200–350</td>
<td>–24.9</td>
<td>125–400</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>43.247</td>
<td>28.882</td>
<td>42.791</td>
</tr>
<tr>
<td>Viscosity [mm²/s] at 20 °C</td>
<td>4</td>
<td>0.15</td>
<td>5</td>
</tr>
<tr>
<td>Octane number</td>
<td>&gt;74</td>
<td>55–60</td>
<td>40–55</td>
</tr>
<tr>
<td>Oxygen content (%)</td>
<td>0</td>
<td>34.8</td>
<td>0</td>
</tr>
<tr>
<td>Sulphur content (ppm)</td>
<td>0</td>
<td>0</td>
<td>≈250</td>
</tr>
</tbody>
</table>

Table 2. The percentage difference between F-T and DME fuel compared to conventional diesel [26,41,42].

<table>
<thead>
<tr>
<th>Emissions</th>
<th>F-T Diesel</th>
<th>DME (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>–6</td>
<td>–75</td>
</tr>
<tr>
<td>PM</td>
<td>–37</td>
<td>–100</td>
</tr>
<tr>
<td>HC</td>
<td>–42</td>
<td>–76</td>
</tr>
<tr>
<td>CO</td>
<td>–27</td>
<td>–50</td>
</tr>
</tbody>
</table>

3. Motivation to Produce F-T Fuel

The results tabled above are extracted from T.L. Alleman et al.’s [26] and R. Verbeek et al.’s [42] papers on F-T and DME fuel emissions, respectively. Both data sets are based on emissions from light-duty vehicles and thus are somewhat comparable. It has been noted that the release of individual emissions, i.e., NOx and PM, are heavily engine-dependent [26]. This explains the variations of results between different studies depending on test conditions, but many support the conclusion that is drawn from Table 2.

Although the results of DME show superiority over F-T with regard to emissions, the higher calorific value of F-T fuel, as well as easier handling (liquid form at atmospheric pressure) (Table 1), make it a more viable option in replacing conventional diesel.

4. Microwave Pyrolysis

A typical pyrolysis set-up is illustrated in Figure 2, where in conventional pyrolysis, a furnace/hot wall would replace the microwave oven. The gaseous fuel produced from pyrolysis is collected into the gas-sampling bag to be fed into the Fischer–Tropsch process. For pyrolysis, nitrogen is used as an inert carrier gas for the process and specifically for microwave pyrolysis, a quartz reactor is commonly used.

![Figure 2. A microwave pyrolysis experimental set-up. (1) Nitrogen cylinder; (2) suspended body flowmeter; (3) quartz-fixed bed or quartz reactor; (4) thermocouples; (5) microwave oven; (6) computer; (7) condensing system; (8) gas-sampling bag [43].](image-url)
4.1. Heating Mechanism

Microwave pyrolysis (MWP) involves irradiating the biomass material that is contained within a pyrolysis reactor. This confinement of microwaves leads to the formation of standing waves which penetrate the feedstock. There are then cold spots at the nodes (where destructive microwave interference occurs) and hot spots \(^{[44]}\) at the anti-nodes. This continuous radiation causes microwave-absorbing molecules at these hot spots within the biomass to polarise. Applying an alternating current forces these molecules to constantly realign themselves parallel to the electromagnetic field; this realignment results in molecular friction which is then dissipated as heat to neighbouring molecules.

Conventional pyrolysis (CP), however, involves bulk heating of the sample; the surrounding environment must reach high temperatures before the biomass begins to warm via conduction and convection (Figure 3). The temperature profile of the material is much smoother than that from microwave pyrolysis, with higher temperatures at the surface of the biomass decreasing to its lowest at its centre \(^{[45]}\). This comparison of methods of heat transfer promotes microwave pyrolysis as the more efficient technique to decompose biomass material, as no bulk heating is required.

![Figure 3. Temperature gradients of sample material in a convective cavity (left) with cooler regions at the centre and a microwave cavity (right) beginning with cooler regions nearer the surface of the sample \(^{[42]}\).](image)

4.2. Advantages of Microwave Heating

4.2.1. Heating and Energy Transfer

Irradiating a substance with microwaves requires no contact between the sample and the radiation source. Electromagnetic waves can penetrate the material and transfer energy within it instead of relying on the transfer of heat from the material’s surface towards its centre \(^{[44]}\). The latter process is slow as is expected of conventional heating methods, where heat is transferred via convection and conduction. The temperature distribution is thus uneven, with the material’s interior being much more excellent than its surface. Microwave radiation has the advantage of distributing the heat evenly so that if a thermocouple was used to measure the temperature of the samples, the reading would represent the whole object.

Microwaves are within a frequency range of the electromagnetic spectrum which means the radiation is non-ionising (expected of very-high-frequency radiation such as far-end UV). Yet, it can penetrate far enough into materials to excite them thermally.

4.2.2. Higher Heating Rate and Efficiency

Microwave radiation volumetrically heats \(^{[46]}\) substances which means the temperature of the material increases due to its increase in internal energy. Bulk heating involves heating the whole system, including the sample and surroundings and the average temperature of this system is recorded. This method leads of a lot of wasted energy and is the problem with conventional heating. Since microwave radiation heats within the body of the substance, it is a thermally efficient process, enabling higher temperatures of the material to be reached for the same power input \(^{[47]}\). This then accelerates the heating
rate of the sample, encouraging chemical processes to occur much sooner in microwave pyrolysis.

4.2.3. Material Selective Heating

In order for microwaves to be effective in heating, molecules that absorb its radiation, dielectrics, need to be present within the sample material. A molecule’s dielectric properties depend on its dielectric loss factor [48] and the higher this value, the more effective it is in transferring heat. Carbon is commonly used to aid microwave absorption during MWP and is mixed into biomass material. Since energy is not transferred to non-dielectrics, it can be said that microwave heating is material-selective [49,50]. A high concentration of carbon, for example, within areas of biomass would enhance the temperatures within those regions via the means described under the ‘Heating mechanism’ section. Microwave heating is, therefore, more selective and flexible when compared to conventional methods.

The ease and control of using microwave radiation in industrial processes make it a very attractive tool [13]. Since an electric power supply sources the microwaves, this needs to be switched on, and the alternating field is present. When a material has fully decomposed in pyrolysis, for example, the magnetrons [50] can be switched off without environmental cooling. This is because only dielectric molecules absorb microwaves whilst non-dielectrics are transparent to the radiation and thus experience no energy absorption. Whereas if a furnace was used in conventional pyrolysis, the surroundings need to cool after a process. This comparison promotes microwave radiation as a safer, efficient and more easily controlled energy source. In addition, conductors such as metals reflect microwaves and are commonly used in household ovens to contain radiation; the use of microwaves can easily be confined.

Despite these advantages over conventional fast pyrolysis, microwave pyrolysis has some challenges regarding heating uniformity, energy efficiency and capital costs which require more research and investigation. This includes large-scale processing as well.

5. Optimum Microwave Pyrolysis (MWP) Parameters

5.1. Microwave Absorbers

In MWP, heat transfer is only possible with the help of molecules that absorb microwave radiation, termed dielectrics. Unfortunately, most biomass and waste are poor absorbents of microwaves and require supplementary material such as activated carbon (AC) or lignite carbon (LC) [51]. Mixing these with the pre-treated biomass enables pyrolysis to occur, but too low/high concentrations can hinder progress. Char produced during MWP can be reintroduced into remaining biomass as a microwave absorber (MWA) to continue the decomposition of a sample. Y. Pianroj et al. [52] were able to find the mixture ratio of 75:25 for oil palm shell to AC that yields the most gaseous products from MWP. The highest temperature of the biomass (700 °C) was also achieved at this blend, suggesting for at least this feedstock type that it was the most thermally efficient mixture. Mamaeva et al. [51] experimented with AC and LC absorbers for pine sawdust and found that a blend of 8:2.5 pine sawdust to LC produced the best gas distribution out of the mixtures tested for the biomass following MWP. These reviews agree on a roughly 3:1 split of biomass to MWA mix for high gas production; however, this will vary slightly depending on feedstock type and pyrolysis temperature. Also, there was no study into the composition of the gases released in these papers, which is of importance for this investigation.

5.2. Feedstock Types and Syngas Production

The main issue with biomass conversion is the diverse range of feedstock that is available for use. It has already been noted that a particular microwave absorber (e.g., AC or LC) may interact better with a certain type of biomass. Each type’s composition varies; so, the treatment of the different feedstock, before pyrolysis, will also vary, such as sample drying time (to achieve suitable moisture content) and MWA type. Y-F. Huang et al. [53] conducted MWP on seven biomass sources; the composition of each is described in Table 3,
where the feedstock from left to right are rice straw (RS), rice husks (RH), corn stover (CS), sugarcane bagasse (SB), sugarcane peel (SP) waste coffee grounds (CG) and bamboo leaves (BL) [53].

Table 3. The composition of 7 biomass sources [50].

<table>
<thead>
<tr>
<th>Biomass Source</th>
<th>Moisture</th>
<th>Calorific value (MJ/kg)</th>
<th>Proximate analysis (wt.%)</th>
<th>Ultimate analysis (wt.%)</th>
<th>Lignocellulosic analysis (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RS</td>
<td>RH</td>
<td>CS</td>
<td>SB</td>
<td>SP</td>
</tr>
<tr>
<td>Moisture</td>
<td>9.32</td>
<td>6.34</td>
<td>8.58</td>
<td>8.61</td>
<td>5.30</td>
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<tr>
<td>Calorific value</td>
<td>16.16</td>
<td>15.91</td>
<td>17.06</td>
<td>16.92</td>
<td>17.03</td>
</tr>
<tr>
<td>Proximate analysis</td>
<td></td>
<td></td>
<td>Volatile matter</td>
<td>Fixed Carbon</td>
<td>Ash</td>
</tr>
<tr>
<td></td>
<td>79.22</td>
<td>80.45</td>
<td>82.58</td>
<td>86.02</td>
<td>80.4</td>
</tr>
<tr>
<td></td>
<td>12.27</td>
<td>8.70</td>
<td>12.48</td>
<td>9.93</td>
<td>15.42</td>
</tr>
<tr>
<td></td>
<td>8.51</td>
<td>10.85</td>
<td>4.94</td>
<td>4.05</td>
<td>4.54</td>
</tr>
<tr>
<td>Ultimate analysis</td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>45.76</td>
<td>43.98</td>
<td>49.38</td>
<td>48.88</td>
<td>46.47</td>
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<td></td>
<td>6.22</td>
<td>5.94</td>
<td>6.52</td>
<td>6.71</td>
<td>6.23</td>
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<tr>
<td></td>
<td>0.52</td>
<td>0.40</td>
<td>0.63</td>
<td>0.27</td>
<td>0.92</td>
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<tr>
<td></td>
<td>47.50</td>
<td>49.68</td>
<td>43.47</td>
<td>44.15</td>
<td>46.38</td>
</tr>
<tr>
<td>Lignocellulosic analysis</td>
<td></td>
<td></td>
<td>Extractives</td>
<td>Hemicellulose</td>
<td>Cellulose</td>
</tr>
<tr>
<td></td>
<td>4.39</td>
<td>5.52</td>
<td>5.27</td>
<td>5.44</td>
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<td></td>
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<td>43.97</td>
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<td>26.35</td>
<td>36.02</td>
<td>21.82</td>
<td>20.61</td>
<td>24.31</td>
</tr>
</tbody>
</table>

MWP was performed on each biomass type at varying power levels to determine which setting gives the best gaseous output and syngas distribution; this is displayed in Table 4. Overall, the corn stover and sugarcane bagasse produced the most desirable results with a high yield of gaseous fuel. In this respect, rice husk performed the worst. To explain this, the correlation between the cellulose content and CO production, and between hemicellulose and H₂ production was included in their paper, both of which displayed a positive linear relationship. CS and SB continued to outperform the other feedstock types in this respect as the microwave power was increased from 300 W to 500 W, which relates to the temperature achieved within the biomass. What can be concluded from these findings is that the feedstock composition and MWP temperature play key roles in the release of syngas.

Table 4. The composition of the gas yield per feedstock type at varying power levels [50].

<table>
<thead>
<tr>
<th>Agricultural Residual</th>
<th>Microwave Power Level (W)</th>
<th>Molecular of Gaseous Component (mmol)</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw</td>
<td></td>
<td>H₂</td>
<td>7.75</td>
<td>2.53</td>
<td>26.26</td>
<td>7.43</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
<td>13.88</td>
<td>4.16</td>
<td>35.98</td>
<td>9.46</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
<td>20.13</td>
<td>5.46</td>
<td>41.46</td>
<td>11.42</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>5.56</td>
<td>1.03</td>
<td>23.32</td>
<td>4.93</td>
</tr>
<tr>
<td>Rice husk</td>
<td></td>
<td>H₂</td>
<td>10.79</td>
<td>3.79</td>
<td>19.90</td>
<td>6.59</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
<td>17.38</td>
<td>4.89</td>
<td>35.40</td>
<td>8.83</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
<td>7.52</td>
<td>2.91</td>
<td>32.72</td>
<td>6.06</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>12.79</td>
<td>4.56</td>
<td>39.40</td>
<td>8.53</td>
</tr>
<tr>
<td>Corn stover</td>
<td></td>
<td>H₂</td>
<td>19.54</td>
<td>6.88</td>
<td>50.32</td>
<td>10.30</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td></td>
<td>H₂</td>
<td>6.34</td>
<td>2.35</td>
<td>38.64</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
<td>11.47</td>
<td>6.56</td>
<td>43.37</td>
<td>7.61</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>18.56</td>
<td>7.38</td>
<td>50.72</td>
<td>9.27</td>
</tr>
</tbody>
</table>
Table 4. Cont.

<table>
<thead>
<tr>
<th>Agricultural Residual</th>
<th>Microwave Power Level (W)</th>
<th>Molecular of Gaseous Component (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>Sugarcane peel</td>
<td>300</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>8.81</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>15.31</td>
</tr>
<tr>
<td>Coffee grounds</td>
<td>300</td>
<td>7.50</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>11.59</td>
</tr>
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<td></td>
<td>500</td>
<td>19.52</td>
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<tr>
<td>Bamboo leaves</td>
<td>300</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>9.20</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>13.53</td>
</tr>
</tbody>
</table>

5.3. Moisture Content

The moisture content of each source in Table 3 is below 10%, which is in agreement with many other microwave pyrolysis investigations. Biomass is naturally high in moisture, which generally aids the absorption of microwaves (due to the dielectric properties of water) and can encourage H₂ production [54,55]. However, large amounts of moisture would eventually result in very high biomass temperatures, leading to unwanted secondary/tertiary reactions and their products. H. Li et al. [56] delved into this further by performing MWP on rice straw to find the following (Figure 4):

![Figure 4](image-url)

Figure 4. The components of the gas yield per moisture content of rice straw [53].

For high H₂ and CO production, a moisture content of 7.5% weight provided the most satisfactory results with H₂ and CO volumes also peaking for a pyrolysis temperature of 600 °C. The relatively low water content and mid-range microwave pyrolysis temperatures go hand in hand as more water leads to very high biomass temperatures. This leads to the formation of secondary/tertiary products (Figure 5).
Figure 5. The components of the gas yield per temperature increase in the rice straw [33].

6. Comparison of Microwave and Conventional Pyrolysis

6.1. Gas and Syngas Yields

Y-F. Huang et al. [13], in their paper titled ‘A review on Microwave Pyrolysis of Lignocellulosic Biomass’, collected an average gas yield and composition across a range of lignocellulosic feedstock. Figure 6 (a-left) shows that microwave pyrolysis mainly extracts gas products from biomass. This is separated from the results of conventional pyrolysis by a huge margin (around 30%), with the reverse applying for the liquid fraction. It is ideal for keeping bio-oil yield relatively low, as these liquids need stabilisation and upgrading treatment after pyrolysis [23]. Microwave pyrolysis has performed well on distributing product yield to mainly gas and char. The latter can be incorporated into the biomass feedstock as a microwave absorber. Figure 6 (b-right) depicts the quality of the gas yield, showing appreciably higher portions of H₂ and CO compared to CP. For F-T synthesis, the desired feed ratio of H₂: CO is around 2 [6,34,57,58], which unfortunately, does not show in the results in Figure 6 for both MWP and CP. This must be adjusted before syngas is catalysed in the F-T process.

Figure 6. (a) Average values of product yield from a selection of biomass from MWP and CP. (b) The average gas composition from the same biomasses after MWP and CP [12].

In a separate study, F. Mushtaq et al. [45] gathered average values for yield on a selection of biomass feedstock. Table 5 supports the findings collected in Y-F. Huang et al.’s paper [13], especially the results for coffee hull where MWP achieved almost double the maximum syngas yield compared to CP.
Table 5. The product yield and composition from MWP and CP of a variety of biomass [42].

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Product Yield and Comparison</th>
<th>Microwave</th>
<th>Conventional Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee hull pellets</td>
<td>Oil yield (wt.%)</td>
<td>9.80–13.57</td>
<td>7.90–9.19</td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>H2 vol%</td>
<td>16–32</td>
<td>55–65</td>
</tr>
<tr>
<td></td>
<td>CO col%</td>
<td>41–48</td>
<td>0.17–0.36</td>
</tr>
<tr>
<td></td>
<td>CO2 Vol%</td>
<td>6–28</td>
<td>0.45–0.65</td>
</tr>
<tr>
<td>Coffee hull</td>
<td>Gas yield (wt.%)</td>
<td>60–75</td>
<td>55–65</td>
</tr>
<tr>
<td></td>
<td>Syngas (H2 + CO) L/g of biomass feed</td>
<td>0.41–0.62</td>
<td>0.17–0.36</td>
</tr>
<tr>
<td></td>
<td>CO2 production</td>
<td>0.20–0.34</td>
<td>0.45–0.65</td>
</tr>
<tr>
<td>Wheat straw bales</td>
<td>Syngas (H2 + CO) vol.%</td>
<td>54% of total gas vol. (37% H2)</td>
<td>&lt;40% of the total gas vol.</td>
</tr>
<tr>
<td>Corn straw bales</td>
<td>Syngas (H2 + CO) vol.%</td>
<td>54% of total gas vol. (35% H2)</td>
<td>&lt;40% of the total gas vol.</td>
</tr>
</tbody>
</table>

6.2. Hot Spots and Microplasmas

MWP can harness large volumes of gas and syngas from biomass compared to CP due to the formation of hot spots (introduced under ‘Heat mechanisms’), microplasmas and water content.

Addressing the enhanced gas yield during MWP, the dielectric water molecules within the biomass absorb microwaves and evaporate to produce steam as this steam exerts pressure and escapes the biomass, the pore concentration of the material increases [48]. This enables more de-volatilised gas to emerge from the sample.

Why MWP favours the specific release of syngas is due to the formation of hot spots [47]. When microwaves within the reactor cavity form standing waves, parts of the biomass sample are exposed to these hot spots. The bulk material reaches higher temperatures in MWP than in CP due to the internal energy transfer through radiative means. However, dielectrics absorb the intense energy at these hot spots, and the region achieves even higher heating rates. Due to these regions, delocalised π electrons [59] from surrounding carbon molecules become so excited that they encourage the ionisation of neighbouring water molecules and biomass material—a microplasma is formed. These ionised species tend to recombine to form simple molecules such as H2 and CO [47].

6.3. Rates of Decomposition

Y-F. Huang et al. [60] investigated the decomposition rate of rice straw: Figure 7a illustrates the quickening heating rate with increasing power input. At 500 W, MWP shows a clear superiority in heating rate, which means more chemical reactions occur in the feedstock compared to CP at the same power. Figure 7b demonstrates how a biomass’ weight reduces considerably during MWP compared to CP at low temperatures. This indicates a quicker decomposition and thus a more efficient method to break down biomass feedstock into fuel products. Collectively, the graphs validate the theory above, suggesting hot spots and, generally, microwave interactions with matter inside the biomass create higher temperatures and faster decomposition within the biomass.
7. Improvements for Microwave Pyrolysis Technology

7.1. Improvements on Syngas Yield

A general disadvantage of biomass to syngas conversion technology is the small production scale. S. Zhang et al. [43] has proposed a method to convert liquid (bio-oil/tars) and solid (char) fractions that result from MWP into syngas by using char-supported metallic catalysts. Their results showed an improved gas outlet (53.9% of total yield) when using rice husk on char-supported Ni catalyst, with 69.96% of that gas produced being syngas.

In another study by D. Beneroso et al. [61], they suggested a two-step process to achieve a total yield from biomass decomposition of over 80% into H₂ and CO. The first step consists of the usual microwave pyrolysis (at 400 °C) from which the syngas produced is then collected. The second step involves the condensable products (bio-oil/tar) being treated to a similar method to that used by S. Zhang et al. A catalytic bed comprising of the char product from the first step is heated to 800 °C with the tar to encourage further syngas production.

In general, similar to all biorefinery processes, the by-product of the pyrolysis which includes all liquid, bio-oil, bio-char, and syngas needs to be characterised and post-treated for the required application.

7.2. Scalability

The above two approaches, however, only optimise pyrolysis results from the same sized samples and reactors. Y. Pianroj et al. [52] looked into intensifying the electromagnetic field using two magnetrons, which source the microwave radiation, instead of one, which is typically used now in MWP. This complicates the system but is more cost-effective than increasing the input power. The aim here was to investigate scaling up pyrolysis reactors for industrial use. Thermocouple readings showed that much higher temperatures were
achieved within the biomass than using one magnetron at the same power input. This suggests the potential of using larger feedstock in this process.

D. Beneroso et al. [62] investigated scalability concepts for MWP and mentioned that, along with using intensified radiation, it would also have to be continuous. A continuous operational mode for MWP means that batch processing can no longer be considered on an industrial scale. This is due to two main reasons: the stopping and starting of pyrolysis decrease energy efficiency, and there are also limitations on the feedstock size that can be used caused by the inhomogeneity in batch heating (due to the depth of microwave penetration). The latter means that increasing magnetrons for larger samples can only go so far. D. Beneroso et al. evaluated the use of a circular conveyor disc for the feedstock to be placed on and exposed to microwaves—the biomass can be spread so that to reduce inhomogeneity of heating and can be continually fed into the process.

Another avenue of research that can be taken to improve and justify the use of microwave pyrolysis is to increase the range of material that can be used as feedstock. Aishwarya K.N et al. [63] focused their attention on pyrolysis of mixed plastic waste, the condensate of which has potential use as a transport fuel. Z. Song et al. [64] conducted a similar investigation on waste tires which can be decomposed to form simpler structures such as H2 and CH4. Both studies show the range of waste products than can be used beyond biomass and sewage sludge, and shows MWP as a way to aid recycling. However, the main issue addressed within these papers was again the scalability of the process.

8. Conclusions

The need for alternatives to petroleum-based fuels is ever-growing; its resources are limited, and its harmful emissions cause concern. Second-generation biofuels offer lower greenhouse gas emissions and can be produced from organic waste materials, which are of plentiful supply. Compared with thermochemical processes, such as gasification and conventional pyrolysis, used to decompose lignocellulosic biomass and waste into fuel components (i.e., syngas), microwave pyrolysis is quick and the most effective way in doing so. This can be attributed to the electromagnetic field properties of microwaves. This radiation penetrates biomass feedstock and transfers energy within it. This reduces the power needed during pyrolysis for the material to reach high temperatures and thus, for reactions to occur. High heating rates within the body of biomass can be achieved through radiative heating, which is further encouraged by the presence of hot spots. The interaction of microwaves with carbon and water molecules within naturally moisturised biomass makes it very suitable for the task of de-volatilising gas products. Microwaves’ selective heating property and microplasma formation within biomass, especially those with a large cellulose and hemicellulose content, favour the high production of syngas.

This large volume of useful products can then be synthesised into F-T fuel or DME, both of which reign over standard diesel concerning reduced NOx, PM, HC and CO emissions. In terms of fuel properties and calorific value, F-T fuel is very similar to conventional diesel and due to this, as well as higher cetane numbers and ease of handling, it is currently more suited than DME for use in compression ignition engines.

Microwave heating efficiently produces syngas for F-T synthesis and can be easily controlled and confined, ensuring its safe use. The problem now lies with the size of the pyrolysis reactor and the feedstock used within it. In order for microwave pyrolysis-F-T biofuel to meet worldwide demands, these processes will need to be scaled up while maintaining process efficiency and the quality of the produce. Increasing electric field density and introducing a circular conveyor system in pyrolysis are examples of promising steps towards improving microwave pyrolysis technology, all in the hope that more renewable waste can be synthesised into fuel and provided on a global scale.

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