Physicochemical Characterisation and the Prospects of Biofuel Production from Rubberwood Sawdust and Sewage Sludge

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Abstract: This study aims to evaluate the physicochemical properties of rubberwood sawdust (RWS) and sewage sludge (SS) for producing biofuel or liquid products via pyrolysis and co-pyrolysis. The chemical and thermal properties of both samples were observed to have superior bioenergy production capabilities. RWS and SS had significantly different physicochemical properties, such as particle-size distribution, bulk density, ultimate and proximate analysis, lignocellulose composition, and a lower heating value of 11.65 to 17.66 MJ/kg, a lesser energy potential than that of fossil fuels. The chemical composition of extractives was found to only marginally affect the end product. Carbon and hydrogen content, the two main elements for biofuel enhancement, were found to correlate with the organic components of both RWS (48.49, 7.15 wt.%) and SS (32.29, 4.06 wt.%). SS had a higher elemental composition of iron, calcium, and potassium than RWS. Both samples had a higher heating value of 13.98 to 21.01 MJ/kg and a lower heating value of 11.65 to 17.66 MJ/kg, a lesser energy potential than that of fossil fuels. The findings from these blends are relatively moderate due to the related lignocellulosic potential composition. The novel contribution of this research was to optimize the use of local waste materials as a new raw material for biofuel production that could serve as a sustainable fuel source.

Keywords: biofuel; liquid; rubberwood sawdust; sewage sludge; physicochemical properties; characterisation

1. Introduction

Due to their limitations, fossil fuels will no longer be a reliable supplier of energy in the coming decades. Apart from dwindling resources, fossil fuels also have a negative and damaging impact on the environment [1]. Non-renewable energy sources, such as oil, natural gas, and coal, significantly contribute to greenhouse gases (GHG), as they are rich in carbon (C) and emit carbon dioxide (CO2) [2]. In much the same way, the mass consumption of fossil fuels emits extremely large quantities of GHG into the atmosphere, which contributes to global warming and destroys the ozone layer [3]. Therefore, many researchers are focusing on alternative and renewable energy sources, such as bioenergy or biofuel, to replace fossil fuels and reduce environmental pollution [4]. At present, biomass is gaining increasingly more attention worldwide, as it can be produced out of an...
abundance of by-products, contains a high cellulosic oil fraction (monomers converted to liquid yield), and has a rapid growth rate [5,6].

Energy is the key to several prosperity conveyances, including economic and industrial stability as well as improved standards of living [7]. Renewable energy is the most promising source of energy because it is not only environmentally friendly but more reliable [8]. Biomass is a more sustainable source of energy, as transportation costs are low, it is easier to handle and there is a better understanding of the product [9]. Furthermore, it is a great renewable energy resource regardless of geographic location. Rubber trees, agricultural residue, forestry residue, and municipal solid waste (MSW) are just some of the many sources of biomass. Rubber trees show great potential because they are not only low cost but also abundant in Southeast Asian countries [10]. As the primary agricultural plant of the country, Thailand is the largest rubber-tree cultivator in Southeast Asia [11].

The many steps involved in rubber-tree replantation and processing yields several types of biomass, including stumps, roots, leaves, branches, bark, and sawdust [12], the most plentiful of which are sawdust chips and fine powders. After the harvesting and processing steps, the sawdust is collected from factories and used to create particleboard and furniture. The leftover residual sawdust can then be utilised in the production of bioenergy and biofuels [13]. The production of biofuels and bioenergy from these kinds of biomass residues are highly profitable and can, potentially, fill gaps in energy resources that would help not only increase available energy sources but also reduce the utilisation of fossil fuels, thereby healing and mitigating devastating atmospheric and environmental issues in the coming centuries.

One-thousand-three-hundred-million tonnes of municipal solid waste is produced annually, and these numbers are expected to increase by 2025 [14]. As sewage sludge is the most abundant by-product of wastewater treatment, it is cheap and easily available and, therefore, an extremely suitable source of bioenergy and biofuel. After decomposition and breakdown at high temperatures, the biomass can be converted into the desired energy product. Biomass waste is more readily available in Asian countries, especially Thailand because this tropical region is home to large forests and crops, such as rubber trees, palm oil, rice husk, cassava, and coconut. Biomass is produced throughout the processes required in the replantation, processing, harvesting, and managing of agricultural products [15]. Sewage sludge is a well-known by-product of wastewater treatment plants and largely available as a low-cost source of sustainable energy [16]. A mixture of organic and inorganic compounds contains several pollutants and contaminants, including metals, pathogens, nitrogen (N), and phosphorus (P). Both cost-effective and abundantly available, it can be utilised as an energy source for residences as well as commercially [17,18]. The management of biomass, especially solid sewage-sludge residues, focuses on methods adopted during the last decade, namely, reuse and recovery, as well as conversion to valuable products [19].

Blending has been found to enhance the quality of many biomass products, such as blending woody and non-woody biomass coal with rubberwood sawdust and with sewage sludge [20]. Previous works have used different ratios of the woody or non-woody biomass, but no research has been found that has blended rubberwood sawdust with sewage-sludge biomass for liquid or biofuel production using the mixing method to improve its higher heating value (HHV) and heating rate.

Moreover, the criteria for the conversion of biomass into bioenergy or biofuel is based on several methods. These include mechanical conversion, thermochemical conversion, biochemical conversion, and combined processes [21]. The biomass-conversion method is more meticulous and a larger undertaking than the other options because it correlates the behaviours and types of biomass. Thermochemical biomass conversion methods, such as pyrolysis, combustion, and gasification, are important techniques for valorising waste. They are also more efficient than biochemical and biological techniques, as fewer reactions are required for decomposition, making them more environmentally sustainable [22].

Pyrolysis is one of the best and more efficient methods of biomass degradation, as it is more adept at decomposition under temperatures ranging between 300 °C to 600 °C.
and in the absence of an oxygen-rich environment [23]. It can be classified into three types: fast, slow, and flash. Pyrolysis is appropriate for producing three different products: bio-oil, biochar, and pyrolysis gas [24]. The co-pyrolysis of biomass has the potential to enhance the production of biofuel and is a low-cost and easy to manage process. The co-pyrolysis of biomass not only enhances the quantity of biofuel, but it can also improve the quality of the liquid in terms of potential heating values [25]. Furthermore, several types of waste material, such as plastic, cooking oil, solid municipal waste, old tyres, and biomass, can be pyrolyzed in an oxygen-free environment [15]. Thus, the thermochemical conversion processes, pyrolysis and co-pyrolysis, are the two key factors for managing all the woody and non-woody biomass wastage, providing the best and most suitable route for converting them into bio-energies. Therefore, the blending of rubberwood sawdust with sewage-sludge biowaste, resulting in biofuel production, has significant potential with opportunities in the energy industry, environmental management, and ecosystem services for sustainable development.

This study aims to evaluate the physicochemical properties of reused waste wood and bio-waste in order to make it valorised at an industrial level as well as reduce environmental pollution. Physicochemical properties—such as ultimate analysis, proximate analysis, particle size distribution, bulk density, thermogravimetric analysis (TGA), major and minor elemental composition, lignocellulose contents, higher heating value (HHV) potential, and lower heating value (LHV) potential—of two different types of biomass were compared through their energy values and basic characteristics with that of fossil fuels.

2. Materials and Methods

2.1. Biomass Preparation

Rubberwood sawdust (RWS) and sewage sludge (SS) were collected from a local wood-processing plant and a fish canning factory in Songkhla province, Thailand, respectively. The biomass was sun-dried for one month to keep the moisture content lower than 10 wt.%. Subsequently, the dried biomass was pulverised, sieved through a 1-mm sieve, and, finally, stored in air-tight plastic bags for chemical characterisation. For the co-pyrolysis study, the ground RWS was mixed with SS at the blending ratio of 50:50 and 75:25. These samples were labelled as RWS50:SS50 and RWS75:SS25, respectively.

2.2. Biomass Properties

The physical and chemical properties of the prepared biomass samples (RWS, SS, RWS50:SS50, and RWS75:SS25) were studied as described below. All the experiments were carried out in triplicate.

2.2.1. Particle-Size Distribution

Size distribution of the biomass samples was performed following ASTM E11 standards [26] using a Fritsch© Vibratory sieve shaker (ANALYSETTE 3 PRO™, Germany) with seven sieves with opening sizes of less than 0.08, 0.08, 0.11, 0.15, 0.21, 0.30, 0.60, and 1.18 mm.

2.2.2. Bulk Density

The bulk density of the ground biomass was determined in accordance with ASTM E873-82 standards. The dried biomass was poured into a container with a total volume of 0.5 L. The excess biomass was removed by striking a straight edge across the top of the container and then weighing the biomass sample using an analytical balance (4 digits). The bulk density was calculated using Equation (1) [27]:

\[
\text{Bulk density} = \frac{\text{Weight of dry biomass (kg)}}{\text{Biomass volume (m}^3\text{)}}
\] (1)
2.2.3. Proximate and Ultimate Analysis

The moisture content (MC), volatile matter (VM), fixed carbon (FC), and ash of each biomass sample studied were determined by a Thermogravimetric Analyser (TGA 701, LECO, St. Joseph, MI, USA), according to the ASTM D7582-15 standard [28,29]. The chemical composition, including carbon (C), hydrogen (H), N, sulphur (S), and oxygen, (O) of each biomass sample was analysed using an elemental analyser (FLASH™ 2000, Thermo Scientific, Milan, Italy) [15,28].

2.2.4. Thermogravimetric Analysis

The thermal degradation of the biomass was performed using TG-DTA (ASTM E1131) standards and a PerkinElmer® Thermogravimetric Analyser (USA). Biomass of 8–12 mg was placed in an aluminium crucible and heated from 50 °C to 1000 °C at a rate of 10 °C m⁻¹ under a nitrogen gas-flow rate of 50 mL min⁻¹. The volumetric weight of each sample and the furnace temperatures were recorded during the heating process. Later, a compositional analysis of hemicellulose, cellulose, and lignin in each biomass sample was conducted from the TGA and DTG curves.

2.2.5. Heating Values

Heating values in terms of the biomass HHV and LHV were estimated based on the chemical analysis composition of the biomass [30] using Equations (1) and (2). HHV and LHV were expressed in MJ/kg:

\[
HHV = 0.2791N + 0.3984C + 0.4030H - 1.8644S - 0.03153O \quad (MJ/kg) \quad (2)
\]

where C, H, N, S, and O are the compositions of the elements obtained from the ultimate analysis (in wt.% dry basis),

\[
O = 100 - C - H - N - S - Ash, \quad (3)
\]

where C, H, N, S, O and ash are expressed as a percentage,

\[
LHV = -5.5232 + 0.2373N + 0.4334C + 0.2360H + 0.3732S + 0.000838O. \quad (4)
\]

2.2.6. Lignocellulosic Composition

The lignocellulose composition of the RWS and SS samples was determined as previously described by Georing and Van Soest [31,32]. In this method, the percentages of cellulose, hemicellulose, and lignin are determined in terms of acid detergent fibre (ADF), neutral detergent fibre (NDF), and acid detergent lignin (ADL). The percentage of cellulose, hemicellulose, and lignin were calculated using Equations (5)–(8). The extractives (E) were calculated by difference.

\[
\text{Cellulose} = \text{ADF} - \text{ADL} \quad (\text{wt.} \%, \text{ dry base}) \quad (5)
\]

\[
\text{Hemicellulose contents} = \text{NDF} - \text{ADF} \quad (\text{wt.} \%, \text{ dry base}) \quad (6)
\]

\[
\text{Lignin contents} = \text{ADL} \quad (\text{wt.} \%, \text{ dry base}) \quad (7)
\]

\[
\text{Extractives} = 100 - \text{Cellulose} - \text{Hemicellulose} - \text{Lignin} \quad (\text{wt.} \%, \text{ dry base}) \quad (8)
\]

2.2.7. Inductively Coupled Plasma Optical Emission Spectrometry Analysis

The concentration of eight elements (Si, Fe, Ca, Mg, Na, K, Cd, and Pb) that may affect biomass quality for combustion purposes were quantified by a PerkinElmer® Avio® 500 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Waltham, MA, USA). The elements were extracted by nitric acid and perchloric acid solution. The supernatants were then analysed for elements using ICP-OES. All the elements were calculated
as the average of the three measurements and are expressed as dry matter. Ultrapure water was used as a blank, and it was introduced during the acid digestion of the samples. In addition, ICP standard solutions and a spiked sample were range alongside the samples. All recovery rates were within the range of 90–110%.

3. Results and Discussion
3.1. Feedstock Characterisation
3.1.1. Particle-Size Distribution and Bulk Density of Ground Samples

Table 1 shows the particle-size distribution of all the biomass samples, which all have a main particle size of 0.6 mm, followed by 0.3 mm. Comparing the size of the two biomasses (RWS vs. SS), RWS has a larger particle size than SS. At a particle size of 0.6 mm, the yield of RWS was 52.33 wt.% and SS was 37.95 wt.%. Combining these two materials slightly changed the particle-size distribution of the biomass. By increasing the ratio of bio-sludge from 25% to 50%, the yield of particle size at 0.6 mm decreased from 48.74 wt.% to 45.17 wt.%. Smaller particle sizes below 0.21 mm also increased slightly.

Table 1. Particle-size distribution of rubber sawdust, bio-sludge, and their blends.

| Size  | Particle-Size Distribution of Ground Biomass (wt.%) |
|-------|-----------------------------------------------------|
|       | Mesh mm | RWS | SS | RWS50:SS50 | RWS75:SS25 |
| 16    | 1.18    | 0.08 | 0.2 | 0.14 | 0.11 |
| 30    | 0.60    | 52.33 | 37.95 | 45.14 | 48.74 |
| 50    | 0.30    | 30.01 | 27.12 | 28.57 | 29.29 |
| 70    | 0.21    | 9.5  | 12.25 | 10.88 | 10.19 |
| 100   | 0.15    | 3.38 | 10.01 | 6.70  | 5.04  |
| 140   | 0.11    | 2.1  | 3.08 | 2.59  | 2.34  |
| 200   | 0.08    | 1.5  | 2.35 | 1.92  | 1.71  |
| Pan   | >0.08   | 1.1  | 7.04 | 4.06  | 2.58  |
| Total |         | 100.00 | 100.00 | 100.00 | 100.00 |

Biomass particle size is a key factor in the pyrolysis process, and it significantly affects heat and mass transfer from one particle to the other during pyrolysis. It also strongly influences the yield of the product, where the liquid or solid depends on the pyrolysis environment. Fine particle sizes are more favourable for the smart yield of biofuel products due to the heterogeneous oxidation ignition associated with the vapours produced from burning VM at a higher temperature [33]. Smaller particle sizes are also preferred for uniform heat transfer, where a lower heat transfer leads to a lower average temperature and yields less liquid [6]. Normally, the heat is more rapidly and efficiently transferred from one medium to the other in the end product. Therefore, biomass with larger particle sizes will affect the cost of preparation and feeding as well as storage and transportation [28,34].

Figure 1 shows the bulk density of ground RWS (277.62 kg/m$^3$), SS (963.94 kg/m$^3$), RWS50:SS50 (454.95 kg/m$^3$) and RWS75:SS25 (365.87 kg/m$^3$). RWS had a lower bulk density than SS, RWS50:SS50, and RWS75:SS25, while SS had the highest bulk density of the four samples. RWS had a lower bulk density (277.62 kg/m$^3$) than pelletised samples (652 kg/m$^3$) and extruded samples (334 kg/m$^3$), while SS had a higher bulk density than both pelletised and extruded samples [35]. Bulk density is an important parameter and plays a vital role in the physical characterisation of biomass for logistics purposes, as it affects the cost of transportation and safe storage [36]. Therefore, due to the lower bulk density, the RWS-biomass findings of our study make RWS more suitable for the production of biofuel and solid fuel than the higher bulk density of SS because lower bulk density biomasses are easier to handle, have lower transportation costs and are tapped into the reactor chamber for decomposition. In particular, the bulk density of biomass can directly affect the volume of biomass present in the reactor chamber and also influences heat-transfer behaviour during the pyrolysis process. RWS biomass had a lower bulk density than SS. However, RWS was a lighter and lower bulk density biomass because
of its fibrous and bulky nature, while SS had a much higher bulk density because of its sandy nature. By comparing coal bulk density with that of lignocellulose biomass, it can be observed that lignocellulosic biomass has a lower bulk density than coal [15,29].

![Biomass feedstocks](image)

**Figure 1.** Biomass feedstock materials of RWS and SS.

### 3.1.2. Proximate and Ultimate Analysis

RWS contained 5.38 wt.% moisture, 77.47 wt.% VM, 17.50 wt.% FC, and 2.01 wt.% ash, while SS contained 6.60 wt.% moisture, 53.84 wt.% VM, 8.32 wt.% FC, and 33.77 wt.% ash (Table 2). Proximate analysis is important in experimental studies. There was a slight difference in the mean moisture value between RWS and SS. The moisture content of both materials was below 10% for pyrolysis, an acceptable amount of moisture in biomass. Furthermore, the proximate analysis provided rapid and higher combustion temperatures (7 min at 950 °C) to improve the VM value [37]. After drying in a dryer in a solar greenhouse, the moisture content of the feedstock materials decreased. The lower amount of water in the biofuel liquid is not only because of the moisture content of the biomass but is also because of the pyrolysis parameters that influence the reactor, residence time, and reactor temperatures [28]. Pyrolysis can reduce the amount of VM in a sample after biodegradation because the vapour liquid changes into bio-oil and the FC directly increases the biochar yield. Typically, due to the evaporation of oily compounds, more ash is contained in the biochar [38]. The proximate properties of this study were compared with those of other studies. The moisture content of RWS (5.38 wt.%) and SS (6.60 wt.%) was lower than the moisture content of corn straw (7.55 wt.%), whereas the VM and FC content of RWS (77.47 wt.% and 17.50 wt.%, respectively) were slightly lower than that of the corn-straw feedstock [38]. However, the VM content of RWS (77.47 wt.%) was higher than that of phylodes (69.03 wt.%) and trunks (67.66 wt.%) [39]. Therefore, the results of our study demonstrated better percentages of organic compounds and could produce a suitable amount of liquid yield.
Table 2. Proximate and ultimate analyses of RWS, SS, and their blends.

| Properties                  | Type of Biomass Sample | RWS                | SS                | RWS50:SS50         | RWS75:SS25         |
|------------------------------|------------------------|--------------------|-------------------|--------------------|--------------------|
| **Proximate analysis (wt.%, as-received basis)** |                        |                    |                   |                    |                    |
| Moisture content (MC)        | 5.38 ± 0.03            | 6.60 ± 0.49        | 5.99 ± 0.24       | 5.68 ± 0.12        |
| Volatile matter (VM)         | 77.47 ± 0.44           | 53.84 ± 0.67       | 65.66 ± 0.47      | 71.56 ± 0.43       |
| Fixed carbon (FC)            | 17.50 ± 0.23           | 8.32 ± 0.05        | 12.91 ± 0.09      | 15.21 ± 0.16       |
| Ash                          | 2.01 ± 0.03            | 33.77 ± 0.05       | 17.89 ± 0.02      | 9.95 ± 0.02        |
| **Ultimate analysis (wt.%, as-dry basis)** |                        |                    |                   |                    |                    |
| Carbon (C)                   | 48.49 ± 0.04           | 32.29 ± 0.03       | 40.42 ± 0.02      | 44.50 ± 0.03       |
| Hydrogen (H)                 | 7.15 ± 0.01            | 4.06 ± 0.01        | 5.60 ± 0.00       | 6.38 ± 0.00        |
| Nitrogen (N)                 | 0.18 ± 0.00            | 6.14 ± 0.01        | 3.15 ± 0.00       | 1.67 ± 0.00        |
| Sulphur (S)                  | 0.03 ± 0.00            | 1.62 ± 0.03        | 0.83 ± 0.01       | 0.43 ± 0.01        |
| * Oxygen (O)                 | 41.99 ± 0.04           | 19.23 ± 0.22       | 30.62 ± 0.13      | 36.31 ± 0.09       |

* Oxygen calculated by difference.

Table 2 shows the ultimate analysis of RWS and SS. The C, H, N, S and O contents of RWS were 48.49, 7.15, 0.18, 0.03, and 41.99 (wt.%), respectively, and 32.29, 4.06, 6.14, 1.62, and 19.23 (wt.%), respectively, in SS. RWS had the highest C content, which possibly led to a higher HHV. As H is required for the production of biofuel or liquid products and as RWS had a higher H content than SS, RWS could yield more liquid. However, the S content of SS was higher than that of RWS. SS is considered a useful nutrient, and in the form of a fertiliser in a biochar yield, it can aid plant growth [40]. C and H are both principal components for producing bioenergy, especially biofuel or liquid yield with a lower O content [39]. Moreover, in biomass, a higher C and H content and a lower O content is immensely favourable for biofuel or liquid products because C and H can be converted into aromatic compounds that produce fuel or liquid [28]. RWS was found to have a higher C content (48.49 wt.%) than empty fruit bunches (40.63 wt.%) and fibre (42.93 wt.%), but both RWS and SS had a lower C content than shells (49.01 wt.%). RWS also had a slightly higher H content (7.15 wt.%) than empty fruit bunches (6.11 wt.%), fibre (6.09 wt.%), and shells (6.18 wt.%), while SS had a lower H content than RWS. SS had a higher N (6.14 wt.%) and S (1.62 wt.%) content than RWS (0.18 wt.% and 0.03 wt.%, respectively). SS also had a higher N content (6.14 wt.%) than empty fruit bunches (1.23 wt.%), fibre (1.15 wt.%), and shells (1.15 wt.%). Both RWS (41.99 wt.%) and SS (19.23 wt.%) had a lower O content than empty fruit bunches, fibre, and shells [41].

3.1.3. HHV and LHV Energy Comparison with Fossil Fuels

Figure 2 shows the HHV and LHV of the biomass samples. HHV and LHV are two important and well-known energy parameters in the context of calorific heat value (CHV) and latent heat value (LHV), which measure the total heat present in biomass. The HHV of RWS, SS, RWS50:SS50, and RWS75:SS25 were 21.01, 13.98, 17.01, and 19.01 MJ/kg, respectively. HHV and LHV are a result of biomass degradation and play a vital role in the heating rate, which is an indicator of the energy potential of the solid materials in the biomass [36]. However, high C, H, FC, and VM content present in biomass yields higher energy and result in a higher HHV [28]. However, biomass feedstock with higher FC and VM content and less ash content will provide a higher heating value because poor HHV impacts the speed of the heating rate and, thus, decreases the desired yield [42]. The HHV of RWS (21.01 MJ/kg) was higher than that of SS (13.98 MJ/kg), RWS50:SS50 (17.01 MJ/kg), and RWS75:SS25 (19.01 MJ/kg). The HHV of RWS, SS, RWS50:SS50, and RWS75:SS25 was higher than the HHV of other studies, such as that of the trunk (17.85 MJ/kg), branches (190.3 MJ/kg), and bark (20 MJ/kg), but lower than for phyllodes (21 MJ/kg) [39]. In comparison to petroleum feedstock fuels (Figure 3), such as natural gas (50.84 MJ/kg), gasoline (46.94 MJ/kg), diesel (45.60 MJ/kg), and kerosene (45.99 MJ/kg), the HHV of...
RWS, SS, RWS50:SS50, and RWS75:SS25 was lower than that of petroleum feedstocks [43]. This could be due to the higher concentration of undesirable properties (higher water content) in the biomass products than in the petroleum feedstocks. Heat transfer would be compromised in the presence of high quantities of water, and the mass would not burn very well [44]. However, as petroleum feedstocks, unfortunately, directly contribute to GHG emission and rapidly cause pollution, the production of alternative biofuel is acceptable for reducing uncontrolled atmospheric pollution.

![Figure 2. Bulk density of biomass samples.](image)

![Figure 3. Comparison of higher heating values (HHV) and lower heating values (LHV) of biomass feedstocks (RWS, SS, RWS50:SS50 and RWS75:SS25) and petroleum feedstocks (kerosene, diesel, gasoline, and natural gas).](image)
The LHV of RWS, SS, RWS50:SS50, and RWS75:SS25 was 17.66, 11.65, 13.65, and 16.81 MJ/kg, respectively (Figure 3). LHV is the part of the burning process that occurs inside the hot reactor as water is converted to steam, resulting in vapour formation and condensation, which results in a higher LHV. LHV is calculated from HHV using the difference formula; it is the energy released by VM as it evaporates and changes from a gas into a liquid fuel. The LHV of RWS, SS, RWS50:SS50, and RWS75:SS25 was higher than for both the dry (10.94 MJ/kg) and wet (9.21 MJ/kg) samples of Posidonia Oceanica biomass [45]. However, it was lower than the LHV of petroleum feedstocks, such as natural gas (45.86 MJ/kg), gasoline (44.15 MJ/kg), diesel (42.91 MJ/kg), and kerosene (43.69 MJ/kg). As biofuel derived from biomass has a large quantity of impurities (chemical compounds) and a high O content, it causes corrosion and does not support direct engine ignition prior to upgrading, whereas lower grade biofuels can be used in boiler engines; however, this is an improvement on fossil fuels and is also considerably more environmentally friendly [46].

A van Krevelen diagram was used to illustrate the H/C and O/C atomic ratios of RWS, SS, RWS50:SS50, and RWS75:SS25 and to compare them with various types of coal (lignite, sub-bituminous, semi-anthracite, anthracite) (Figure 4). The H/C and O/C atomic ratios were determined from the elemental composition and were converted from the as-received form to dry and then from dry to ash-free. The atomic ratio of RWS, SS, RWS50:SS50, and RWS75:SS25 was 1.50, 1.75, 0.04, and 0.65, respectively. The main purpose of H/C and O/C atomic ratios is to evaluate the degree of hydrogenation and deoxygenation of elements involved in the process as well as to provide information about the thermal efficiency of the combustible materials [47]. While the atomic H/C and O/C ratios of raw biomass depend on the fluctuation of the thermal degradation of the sample, decreasing H, C, and O ratios are due to the loss of the hydroxyl groups as well as the unstable thermal behaviour of organic compounds and the deoxygenation, dehydration, and dehydrogenation reactions [48]. Setter and Borges [49] believe that the lower atomic H/C and O/C ratios of biomass signify the transforming thermal efficiency degradation of the feedstock due to higher aromatic and carbonaceous formation at temperatures above 400 °C. The H/C, and O/C atomic ratios of RWS (1.76 and 0.65), SS (1.50 and 0.45), RWS50:SS50 (1.65 and 0.57), and RWS75:SS25 (1.71 and 0.61) were higher than that of coal lignite (1.08 and 0.22), sub-bituminous (0.83 and 0.17), semi-anthracite (0.45 and 0.04), and anthracite (0.34 and 0.07) [50]. The findings on atomic ratios in this study were also compared with the results of other studies on methane (4.0 and 0.1), gasoline (2.1 and 0.2), and kerosene (2.1 and 0.3), which were slightly higher than our results [51]. Therefore, higher H and C ratios can increase the final yield of biochar and biofuel.

3.1.4. Lignocellulosic Composition

The lignocellulosic composition of RWS, SS, RWS50:SS50, and RWS75:SS25 was 57.12, 5.30, 30.09, and 45.49 wt.% of cellulose, 19.10, 8.32, 13.70, and 14.47 wt.% of hemicellulose, 13.12, 32.13, 21.20, and 18.34 wt.% of lignin, and 10.66, 54.25, 35.01, and 21.60 wt.% of extractives, respectively (Figure 5). Lignocellulosic biomass may have an impact on kinetic and product yields. Qu et al. [52] reported that cellulose content during pyrolysis can contribute to the production of a higher bio-oil or liquid yield compared to that of hemicellulose due to the high content of volatile components. Additionally, short rotation coppice (SRC) and eucalyptus leaves contain higher quantities of cellulose than other sources of biomass [53]. However, the hemicellulose content of forestry residue is lower (22% to 33%) than that of crops (31% to 38%). It is difficult for lignin to decompose during pyrolysis or combustion, as it requires temperatures above 1200 °C to break down, which is higher than the temperature required for the breakdown of cellulose and hemicellulose. Moreover, forestry biomass contains more lignin than agricultural biomass [53], while RWS contains very high amounts of cellulose and hemicellulose. This indicates a higher amount of VM in RWS, which facilitates the higher yield of biofuel and liquid products [54]. Cellulose is more volatile than hemicellulose during conversion via pyrolysis [55]. Quan and Gao [56]
state that pyrolysis at 500 °C with higher amounts of hemicellulose, cellulose, and lignin is capable of producing a higher liquid-product or bio-oil yields of 18.67, 30.83, and 0.5 wt.%, respectively. In addition to the bio. Furthermore, the lignocellulosic composition of biomass affects the liquid yield, as it has great potential for producing transportation fuel on a very large scale [57]. Biomass containing higher amounts of cellulose also increases bio-oil or liquid yields, such as esters, ethanol, aldehydes, acids, phenol, alcohols, and other organic compounds [15]. The present study discovered that RWS (57.12 wt.%) not only had a higher cellulose content than SS (5.30 wt.%) but also a higher cellulose content than the results of other studies, such as that of beech woodchips (40 wt.%), spruce woodchips (39.89 wt.%), and eucalyptus (42 wt.) [53]. However, RWS (19.10 wt%) contained less hemicellulose than beech woodchips (35 wt.%), spruce woodchips (39.89 wt.%), and eucalyptus (38.12 wt.%). SS was found to contain the highest lignin (32.13 wt.%) and had the highest extractive composition (54.25 wt.%) of all biomasses studied [53].

Figure 4. A van Krevelen diagram of the H/C vs. O/C ratios of biomass feedstocks (RWS, SS, RWS50:SS50, and RWS75:SS25), various types of coal (lignite, sub-bituminous, semi-anthracite, and anthracite), and petroleum feedstocks (kerosene, diesel, gasoline, and natural gas).

Figure 5. Lignocellulose composition of RWS, SS, and their blends.
3.1.5. Thermal Degradation Behaviour

Figure 5 shows the thermal degradation behaviour, TGA and DTG, of RWS, SS, RWS50:SS50, and RWS75:SS25. These samples were found to thermally degrade in the presence of N₂, an unreactive gas used to purge the equipment between 50 °C and 1000 °C at a heating rate of 10 °C/min [58]. Thermal degradation has four main phases. In the first phase, the temperature ranges between 50 °C and 100 °C and increases to between 100 °C and 250 °C in the second phase. In the third and fourth phases, the temperature ranges between 250 °C and 550 °C (Figure 6a,b). The first stage of RWS thermal degradation began with the decomposition of the lignocellulose, which resulted in a decrease in weight and moisture content due to evaporation. In the second phase, the SS decomposed at a slower rate due to its sandy nature and lower VM contents, which evaporated to form condensable vapours. Although several studies report that SS contains higher amounts of organic compounds, such as carbohydrates, proteins, lipids, and saccharides [59], it also contains some non-combustible materials, such as metals and silicates, which are found in the end product as biochar or ash as they do not decompose even at higher temperatures [58]. During the third phase, RWS began to decompose and lose more weight between 250 °C and 450 °C and produced oils that formed vapours as the remaining cellulose and hemicellulose contents broke down. Finally, at the fourth stage, some parts of the remaining lignin decomposed between 500 °C and 550 °C. Although the peaks of the TGA and DTG curves were almost identical, the peak of the RWS TGA curve was higher than the DTG curve. To increase the heating rate, the biomass particle size should be smaller for reactions at pyrolysis temperatures because intermediate-sized particles are more favourable for pyrolysis. However, if the reaction time decreases, then the degree of reaction also decreases.

3.1.6. ICP-OES Analysis

Table 3 shows some of the major and minor elements found in RWS, SS, RWS50:SS50, and RWS75:SS25. RWS contained Si (1450 mg/kg), Fe (190.68 mg/kg), Ca (4796.33 mg/kg), Mg (1131.33 mg/kg), Na (60.49 mg/kg) and K (3052.67 mg/kg), while Cd and Pb were not detected (ND). SS contained Si (24,203.33 mg/kg), Fe (85,018 mg/kg), Ca (27,834.67 mg/kg), Mg (7766.67 mg/kg), Na (7625 mg/kg), K (9144.33 mg/kg), Cd (24.47 mg/kg), and Pb (6.63 mg/kg). The concentration of all these major and minor elements increased in RWS and SS as the pyrolysis temperature increased [60]. Heavy metals influence the gaseous emissions and composition of the ash content. SS had more major and minor elements than RWS and the co-pyrolysis blended biomass (RWS50:SS50 and RWS75:SS25). RWS had lower concentrations of elements and heavy metals, while RWS50:SS50 and RWS75:SS25 had higher concentrations of major elements and heavy metals. SS had higher amounts of the toxic elements Cd and Pb, which are both very harmful to human life, while these elements were not detected in RWS. Furthermore, pyrolysis and co-pyrolysis are both more interesting and beneficial thermochemical conversion processes for any type of biomass or residue as they can degrade the chemical bonds of a material. At higher temperatures, the existing trace elements and heavy metals break down further and form aqueous and gaseous media, while the remaining elements bond to form oxides, thereby reducing the toxicity of the heavy metals [25]. RWS and SS results correlated with the ultimate analysis and proximate analysis of other studies, with SS having a higher ash content and lower HHV [15]. Metals and alkali metals, such as Na, Ca, Mg, and K, are very important for pyrolysis because these alkalis come from the biomass feedstock and can react with other elements to form compounds that may, in turn, react with Si and accelerate pyrolysis. Alvarez and Amutio [61] reported that the presence of metals in raw biomass acts as an induction agent and enhances the process by creating catalytic movements during pyrolysis, which leads to a secondary reaction that produces a high yield of biofuel or liquid products as well as a higher concentration of tar fractions. Therefore, the influence of the abovementioned factors results in a lower biofuel or liquid-product yield but a slightly higher gas yield [62]. In the present study, RWS did not contain any heavy metals, while
SS had a small quantity. However, some of these heavy metals convert to gases, while the less toxic biochar may be used to absorb and remove dangerous toxic metals from water wells and for soil amendments by reducing leaching. Although RWS, SS, RWS50:SS50 and RWS75:SS25 contained less Pb than SRC (20 mg/kg), SS contained more Cd (24.47 mg/kg) than RWS and SRC [63]. SS also contained more elements, such as Fe (85,018 mg/kg), Ca (27,834.67 mg/kg), Mg (7766.67 mg/kg), and K (9144.33 mg/kg), than the SS studied by Ruiz-Gómez and Quispe [63], which only had Fe (66,800 mg/kg), Ca (22,990 mg/kg), Mg (6810 mg/kg), and K (5030 mg/kg). Therefore, the presence of the elements in biomass materials leads to faster conversions because they increase temperatures and are converted to vapor.

Figure 6. TGA (a) and DTG (b) of RWS, SS, RWS50:SS50, and RWS75:SS25.
Table 3. Inorganic elements found in RWS, SS, and their blends.

| Elements (mg/kg) | Biomass Samples |
|-----------------|-----------------|
|                 | RWS             | SS              | RWS50:SS50 | RWS75:SS25 |
| Si              | 1450            | 24,203.33       | 12826.67   | 7138.33    |
| Fe              | 190.68          | 85018           | 42,604.34  | 21,397.51  |
| Ca              | 4796.33         | 27,834.67       | 16,315.5   | 10,555.92  |
| Mg              | 1131.33         | 7766.67         | 4450       | 2790.17    |
| Na              | 60.49           | 7625            | 3842.75    | 1951.62    |
| K               | 3052.67         | 9144.33         | 6098.5     | 4575.59    |
| Cd              | ND              | 24.47           | 12.24      | 6.12       |
| Pb              | ND              | 6.63            | 3.32       | 1.57       |

ND = Not detected.

4. Conclusions

In the present study the physicochemical properties of rubberwood sawdust (RWS), sewage sludge (SS), and their blends were investigated for a potential application in the production of biofuel. Both RWS and SS showed high volatile matter (55–77%) that can be used for biofuel production. However, the bulk density of rubberwood sawdust was relatively low whereas SS contained some toxic metals. Therefore, combining these two materials would give a better quality of materials for pyrolysis and it also can reduce environmental impacts from heavy metals contamination (Cd, Pb) leaching from sludge. The estimated HHV and LHV of blending RWS and SS materials was about 17–18 MJ/kg indicating these two local wastes could serve as sustainable fuel sources.

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