Evaluation of Thermochemical Characteristics and Pyrolysis of Fish Processing Waste for Renewable Energy Feedstock

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Abstract: The necessity of energy is continuously increasing, whereas fossil fuel sources are gradually depleting. To mitigate this problem, fish processing waste of the bluespotted stingray (Neotrygon kuhlii), available in the Borneo region, was investigated for an alternative feedstock of bioenergy production. The fish wastes are hazardous for the environment, whereas the biodiesel from fish waste is pollution-free and produces less contaminant gas and carbon dioxide than fossil fuel. From the proximate analysis, the moisture content, volatile matter, fixed carbon, and ash content of the fish waste were achieved as 4.88%, 63.80%, 15.03%, and 16.29%, respectively. The proportion of carbon, hydrogen, nitrogen, sulfur, and oxygen was found as 42.06%, 5.99%, 10.77%, 0.91%, and 40.27%, respectively, from the ultimate analysis. The calorific value was 21.53 MJ/kg, which would be highly effective in biofuel production. The morphology analysis results of the biomass are favorable for renewable energy sources. The major bondage between carbon and hydrogen and oxygen was found using Fourier transform infrared spectroscopy. The thermogravimetric analysis and derivative thermogravimetry revealed that the highest weight loss occurred at 352 °C temperature with a decomposition rate of 4.57 wt.%/min in pyrolysis circumstances, and at 606 °C temperature with a decomposition rate of 3.77 wt.%/min in combustion conditions. In the pyrolysis process for 25 °C/min heating rate, the yield of biochar, bio-oil, and bio-syngas was found as 33.96, 29.34, 23.46% at 400 °C, 33.87% at 500 °C, and 18.32, 21.34, 42.37% at 600 °C, respectively. The characteristics and pyrolysis yields of fish waste are suitable for being an effective renewable energy source.

Keywords: fish processing waste; pyrolysis; HHV/GCV; FTIR; SEM/EDX; TGA/DTG

1. Introduction

The total energy consumption in the modern world has increased significantly for the present urbanization and civilization, which will be doubled in the future. The lifeblood of energy is fossil fuel, which is depleting over time and increasing the amount of greenhouse gases emitted to the environment during burning. Fossil fuel is sadly the single most unifying force of the world, the attention of which will be forced to turn to renewable energy sources [1,2]. Fortunately, scientists and engineers from all over the world did not wait for this crisis to happen and have given extensive consideration to biofuel as an alternative fuel to produce renewable energy that can partially or even completely replace fossil fuels [3]. Biofuels are less-toxic, degradable, have a lower sulfur capacity, and produce renewable energy with minimum carbon dioxide and greenhouse gas emissions to the...
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2. Materials and Methods

2.1. Sample Preparation

*Neotrygon kuhlii* fish wastes were accumulated from the local fish market in Brunei Darussalam. The wastages were thoroughly cleaned with water to remove the sand and debris. Once the cleaning process was accomplished, the fish wastes were dried in direct sunlight for few days. After sun drying, the feedstock was oven-dried at 100 °C for 12 h. Normally, the oven temperatures are maintained at 100–110 °C for 12–24 h to minimize the excess moisture and pungent smell from animal waste samples [16,28,29]. The dried samples were crushed in a blending machine and were kept in airtight bags for further analysis. Figure 1a,b represents the *Neotrygon kuhlii* fish and its wastes, respectively.
sunlight for few days. After sun drying, the feedstock was oven-dried at 100 °C for 12 h. Normally, the oven temperatures are maintained at 100–110 °C for 12–24 h to minimize the excess moisture and pungent smell from animal waste samples [16,28,29]. The dried samples were crushed in a blending machine and were kept in airtight bags for further analysis. Figure 1a,b represents the Neotrygon kuhlii fish and its wastes, respectively.

Figure 1. (a) Neotrygon kuhlii (bluespotted maskray) fish and (b) sun drying of fish wastes.

2.2. Proximate Analysis

For any biomass, the proximate analysis represents the percentages of moisture content (MC), volatile matter (VM), fixed carbon (FC), and ash content (AC). The American Society of Testing Materials (ASTM) standards were utilized to conduct this analysis on a 1 g sample of fish waste. All of the tests were carried out twice for the dried sample, and the average findings are presented below. Equation (1) was used to calculate the moisture content using the ASTM D3173-11 standard [30]:

\[
\text{Moisture content (wt%)} = \frac{\text{Sample weight before heating} - \text{Sample weight after heating}}{\text{actual sample weight}}
\]  

(1)

For measuring the volatile matter (VM) percentage of the biomass sample, ASTM D 3175-07 method was used in Equations (2) and (3),

\[
\text{Total loss (weight)} = \frac{\text{sample weight before drying} - \text{sample weight after drying}}{\text{Weight of raw biomass}}
\]

(2)

\[
\text{Volatile matter (wt%)} = \frac{\text{Total loss} - \text{Moisture content (MC)}}{\text{Total loss}}
\]

(3)

The ash content (AC) % was calculated using the ASTM D 3174-04 technique in Equation (4)

\[
\text{Ash content (wt%)} = 100 - \frac{\text{sample weight before heating} - \text{sample weight after heating}}{\text{actual weight of raw biomass}}
\]

(4)

Equation (5) was used to calculate the fixed carbon (FC) content

\[
\text{Fixed carbon (wt.%) = 100} - (\text{MC} + \text{VM} + \text{AC})
\]

(5)

2.3. Ultimate Analysis

The weight percentages of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in the dried fish waste were studied in the ultimate analysis. This experiment was carried out at Prince of Songkla University (PSU) in Thailand using a CHNS analyzer of Flash Series (EA 1112) manufactured by Thermo Quest, Italy. Equation (6) was used to compute the proportion of oxygen (O) [31],

\[
\text{Oxygen (wt.%)} = 100 - \{\text{C (wt.%) + H (wt.%) + N (wt.%) + S (wt.%)}\}
\]

(6)
2.4. Calorific/Heating Value

The gross calorific value (GCV), also known as the higher heating value (HHV), of the biomass sample was investigated using a bomb calorimeter (C-200 series) made by P.A. Hilton, Stockbridge, UK. The results were analyzed using ASTM D 5468-02 techniques. The heating or calorific values are usually computed as the energy available per unit mass (MJ/kg) for solid fuels.

2.5. Morphology Analysis (SEM/EDX)

The morphology of the fish waste was examined using the scanning electron microscope (SEM) of a Schottky Field Emission SEM (JSM-7610F), made by JEOL, Tokyo, Japan. The images of the sample were taken at 25×, 100×, 1000×, 5000× magnifications. For measuring the inorganic components and the atomic proportion of fish waste, energy-dispersive X-ray (EDX) analyses were undertaken using the same machine with no carbon coating.

2.6. Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of the fish waste were investigated using a Fourier transform infrared spectrometer made by Perkin Elmer of Spectrum (Two series), USA. All spectrums were attained from the wavenumbers of 4000 to 500 cm$^{-1}$, with a 1 cm$^{-1}$ step size.

2.7. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG)

A thermogravimetric analyzer (TGA7 series) from Perkin Elmer, USA was used to perform the thermogravimetric analysis (TGA) and the derivative thermogravimetry (DTG) of the fish waste in the Scientific Equipment Center, PSU. The experiment was carried out for both pyrolysis and combustion conditions for 50–900 °C temperatures with 10 °C/min heating rate. In the heating chamber, pure nitrogen (N$_2$) gas was passed to establish the pyrolysis condition, while oxygen (O$_2$) gas was used to sustain the combustion situation. The TGA and DTG curves were investigated to evaluate the decomposition trend of the fish processing waste.

2.8. Pyrolysis Process

The pyrolysis process was executed by a horizontal tube furnace (fixed bed) manufactured by Carbolite Gero (300–3000), UK. The experiments were accomplished for 30 g fish waste for three different temperatures of 400, 500, and 600 °C with a 25 °C/min heating rate and 0.5 L/min nitrogen gas flow rate. The procedure was sustained up to 1 h after obtaining the last temperature. The bio-oil was accumulated from the flask and the biochar was from the reactor. The proportion of bio-syngas was determined using Equation (7). Figure 2 illustrates the pyrolysis setup for this study.

$$\text{bio-syngas (wt.)} = \text{Raw Sample (wt.)} - \left( \text{Biochar (wt.)} + \text{Bio-oil (wt.)} \right)$$  \hspace{1cm} (7)
3. Results and Discussion

3.1. Proximate Analysis

The percentage of moisture content, volatile matter, fixed carbon, and ash content of the fish waste were determined using the proximate analysis. Table 1 reflects the proximate analysis of the dried *Neotrygon kuhlii* fish waste of this study and other relevant wastes. This analysis is important to reveal the chemical characters of the biomass.

Table 1. Proximate analysis of fish waste (*Neotrygon kuhlii*).

| Fish Waste                  | Moisture Content (%) | Volatile Matter (%) | Fixed Carbon (%) | Ash Content (%) | Reference |
|-----------------------------|----------------------|--------------------|-----------------|----------------|-----------|
| *Neotrygon kuhlii*          | 4.88                 | 63.80              | 15.03           | 16.29          | This Study |
| De-oiled fish waste         | 7.55                 | 74.94              | 17.19           | 7.87           | [19]      |
| Goat dung                   | 4.80                 | 83.45              | 6.74            | 3.79           |           |
| Cow dung                    | 7.78                 | 85.23              | 4.45            | 4.90           |           |
| Fish waste                  | 7.83                 | 84.10              | 6.45            | 2.23           | [33]      |
| Poultry waste with sawdust  | 5.76                 | 82.34              | 6.12            | 3.45           |           |
| Poultry waste with sand     | 4.24                 | 80.34              | 7.90            | 2.10           |           |

* Dry basis.

The moisture content of the solid biomass is determined as the amount of water accessible in the dry sample. When the moisture content in biofuel is high, it has an undesirable influence on pyrolysis reaction, which reduces the quality of the product [34]. The value should be less than 10% for the effective thermochemical degradation in the pyrolysis process. The moisture content in this work was found as 4.88%, which is lower than the moisture content of de-oiled fish waste [19], cow dung, fish waste, and poultry waste with sawdust [33]. Because these biomasses have a low moisture content, they may be suitable for manufacturing biochar, bio-oil, and bio-syngas.

The volatile matter of biomass is the part that has been driven off as the gases element, including moisture content, by the heating temperature of 950 °C for 7 min [35]. Volatile matter mainly consists of hydrocarbons, carbon dioxide, hydrogen gas, and some tars. The reactivity of the biomass in the thermochemical procedure depends on the proportion of the volatile matter. If the percentage of VM is high, the reactivity will be high [32]. The percentage of volatile matter in this study was 63.80%, which is comparable to other research [33].

Fixed carbon is the amount of carbon that remains after the volatile matter is discharged, omitting ash and moisture content [36]. The fixed carbon of this fish waste was calculated as 15.03% using the subtracting technique. These values are higher than the values of goat dung, cow dung, fish waste, poultry waste with sawdust, and poultry waste with sand [33]. The higher VM reacted to their low fixed carbon content, revealing that the majority of the fuel is burned in the gaseous state during burning. Plant material with a higher fixed carbon content has a higher energy value [37].

In this investigation, the amount of ash was found as 16.29%. When the ash level of the biomass is high, the mineral content of the biomass is also high [38]. In the pyrolysis process, ash content demonstrated the catalytic activity for the pyrolyzed product [34].

3.2. Ultimate Analysis

The ultimate analysis of the fish waste was specified with the atomic ratio of hydrogen to carbon (H/C) and oxygen to carbon (O/C). The weight percentage of carbon, hydrogen, nitrogen, and sulfur for this dried sample was achieved as 42.06%, 5.99%, 10.77%, and 0.91%, respectively (Table 2). The weight percentage of oxygen was calculated by deduction, which was 40.27%. These values are similar to the values for de-oiled fish waste [19] but different from the lamb, poultry, and swine [23].
Table 2. Ultimate analysis of *Neotrygon kuhlii*.

| Sample                  | Carbon (wt.%) | Hydrogen (wt.%) | Nitrogen (wt.%) | Sulfur (wt.%) | Oxygen (wt.%) | Reference       |
|-------------------------|---------------|-----------------|-----------------|--------------|--------------|----------------|
| *Neotrygon kuhlii* *    | 42.06         | 5.99            | 10.77           | 0.91         | 40.27 **     | This study      |
| De-oiled fish waste     | 47.86         | 7.70            | 9.46            | -            | 34.98        | [19]           |
| Lamb                    | 74.63         | 12.11           | 0.15            | 0.27         | 12.50        | [23]           |
| Poultry                 | 63.25         | 11.26           | 1.03            | 0.23         | 23.64        | [23]           |
| Swine                   | 65.38         | 11.31           | 0.58            | 0.09         | 21.99        | [23]           |

* Dry basis, ** calculated from deduction.

The hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios were found to be 1.607 and 0.848, respectively. The H/C and O/C ratios are necessary to determine the elemental makeup of any feedstock. When using biomass as a heating fuel, the amount of carbon is the most important factor [39]. The heating value of solid biomass will be higher if the carbon content is higher and the oxygen concentration is lower. Because the samples contain relatively little sulfur, they will generate more biofuel [38]. The H/C and O/C ratios were used to determine the energy content of the feedstock on the basis of oxygen–carbon and hydrogen–carbon bonds. Lower H/C and O/C ratios indicated a larger energy content, indicating that the material might be utilized as a solid fuel [36].

### 3.3. Calorific Value (Heating Value)

A bomb calorimeter is a device that is used to determine the energy of burning. The reaction takes place in a confined chamber known as the appropriate calorimeter, at a steady temperature, in regulated thermal contact with its surroundings, the jacket. One of the significant processes to justify the capacity of the sample as a useful energy source is the calorific value or higher heating value (HHV) [6].

In Table 3, the HHV of *Neotrygon kuhlii* fish waste was revealed to be 21.53 MJ/kg. The HHV of this fish waste is competitive with the values of de-oiled fish waste (20.99 MJ/kg) [19], salmon fish (16.01 to 23.14 MJ/kg) [40], *Pelates octolineatus* (12.83 KJ/g) [41], *Gasterosteus aculeatus* (8.16 MJ/kg), and *Tilapia nilotica* (21.72 MJ/kg) [42]. The literature illustrates that the calorific value rises for the high number of carbon (C) and hydrogen (H) but decreases for the upper quantity of nitrogen (N) in the biomass. The HHV/CV also drops with the growth of ash content. If biofuel derived from *Neotrygon kuhlii* is manufactured appropriately, the biofuel can also be mixed with fossil fuel or can be replaced with minimum cost and arrangements [43].

Table 3. Calorific value of fish waste.

| Biomass Sample               | HHV/GCV Unit | Reference |
|------------------------------|--------------|-----------|
| *Neotrygon kuhlii* waste     | 21.53 MJ/kg  | This study|
| De-oiled fish waste          | 20.99 MJ/kg  | [19]      |
| Salmon fish                  | 16.01 to 23.14 MJ/kg | [40] |
| *Pelates octolineatus*       | 12.83 KJ/g   | [41]      |
| *Tilapia nilotica*           | 21.72 MJ/kg  | [42]      |
| *Gasterosteus aculeatus*     | 8.16 MJ/kg   | [42]      |

### 3.4. Morphology Analysis (SEM/EDX)

In any biomass, the scanning electron microscopy for the morphological analysis and the energy-dispersive X-ray (EDX) for the elemental characteristics are some of the most useful techniques. The SEM micrographs of *Neotrygon kuhlii* fish waste at 10×, 100×, 1000×, and 5000× magnifications are presented in Figure 3a–d. The images revealed various fiber patterns and rough surfaces due to the various chemical compositions of the biomass [6].
Figure 3. SEM images of Neotrygon kuhlii fish waste for (a) 25×, (b) 100×, (c) 1000×, and (d) 5000×, resolutions.

Table 4 shows the constituent compositions of the biomass, as well as the atomic weight percentages determined by EDX where the main components were carbon (73.86%) and oxygen (21.55%). Other primary elements of biomass, magnesium (Mg), aluminum (Al), sodium (Na), sulfur (S), phosphorous (P), and calcium (Ca) [44] were also found in this fish waste. Magnesium (Mg) and sodium (Na) can produce ionic and covalent bonds with other organic elements, which also vaporize at high temperatures. Sulfur (S) and aluminum (Al) are fairly stable at low temperatures and produce complex chemical molecules [45].

Table 4. EDX results for Neotrygon kuhlii fish waste.

| Element       | Atomic (%) |
|---------------|------------|
| Carbon (C)    | 73.86      |
| Oxygen (O)    | 21.55      |
| Magnesium (Mg)| 0.05       |
| Sodium (Na)   | 0.14       |
| Phosphorus (P)| 0.97       |
| Aluminum (Al) | 0.22       |
| Sulfur (S)    | 0.31       |
| Calcium (Ca)  | 2.90       |

To calculate the grade of aromaticity and polarity of biomass, the O/C ratios (0.219) were utilized. The surface becomes less hydrophilic as the O/C ratio decreases. In comparison to earlier studies [46], the O/C in this study is better. The CHNS analyzer is shown
to be incapable of measuring oxygen levels, but the EDX approach can simply compute oxygen levels by elemental examination [47].

3.5. FTIR Analysis

Fourier transform infrared spectroscopy was used to investigate the relationship between the structure of the chemical components of biomass. Figure 4 depicts the FTIR analysis graph with the wavenumbers from 4000 to 500 cm$^{-1}$ and Table 5 describes the lists of functional groups based on standard literature codes [48,49]. For this feedstock, the transmittance was found at 3292 cm$^{-1}$ wavenumbers, mostly occurring for the bending of the O-H group in the moisture [50]. The detected peaks in the wavenumber of 3014 cm$^{-1}$ were for the enlarged C-H bond in the aliphatic organic compounds [51]. The bending occurred at 2956, 2924, and 2853 cm$^{-1}$ wavenumbers for C-H stretching from methyl (−CH$_3$) groups, methylene (−CH$_2$) asymmetric, and methylene (−CH$_2$) symmetric lipids [49]. Peaks found at 1656 cm$^{-1}$ happened due to the stretching of C=O in proteins. The C-N and N-H stretching was at 1543 cm$^{-1}$ due to Amide II of proteins [48]. The peak at 1456 cm$^{-1}$ for methylene (−CH$_2$) and methyl (−CH$_3$) was due to stretching of lipids [52].

Figure 4. The Fourier transform infrared results of fish wastes.

Table 5. List of functional groups of Neotrygon kuhlii fish waste.

| Functional Group                                         | Wavenumber (cm$^{-1}$) | Ref. |
|----------------------------------------------------------|------------------------|------|
| O-H stretching of water                                   | 3292                   | [48] |
| C-H of cis-alkene -HC@CH-                                | 3014                   | [51] |
| C-H stretching for methyl (−CH$_3$) groups of lipids     | 2956                   | [49] |
| C-H from methylene (−CH$_2$) asymmetric stretching of lipids | 2924                   | [53] |
| C-H from methylene (−CH$_2$) symmetric stretching of lipids | 2853                   | [49] |
| C=O stretching of Amide I of proteins                    | 1656                   | [48] |
| N-H bending and C-N stretching of proteins               | 1543                   | [48] |
| Methylene (−CH$_2$) and methyl (−CH$_3$) vibration of lipids | 1456                   | [52] |
| Carboxylate group (COO−) symmetric stretching            | 1404                   | [49] |
| C-O stretching vibration bonds in the ester              | 1236                   | [50] |
| Methylene (−CH$_2$) bending of lipids, C-O stretching    | 1167                   | [52] |
| C-O-C asymmetric stretching of lipid esters              | 1101                   | [51] |
| C-O stretching for lipids and proteins                   | 1043                   | [51] |
| CH aromatic stretching vibrations                         | 873                    | [50] |
| CH$_2$ deformation vibration                             | 700,607                | [50] |
The peak at 1404 cm\(^{-1}\) is the carboxylate group (COO-) symmetric stretching [49]. The peak found at 1236 cm\(^{-1}\) is for C-O stretching vibration bands in the ester [50]. The peak appearing for wavenumber 1167 cm\(^{-1}\) represents the bending of the \(-\text{CH}_2\) stretching of lipids, C-O vibrations [52]. The crest for 1101 cm\(^{-1}\) wavenumber was mainly for C-O-C asymmetric stretching of lipid esters [51]. The bond, C-O stretching, happened in lipids and proteins with 1043 cm\(^{-1}\) wavenumbers [51]. The CH aromatic stretching vibrations occurred at 873 cm\(^{-1}\) wavenumbers, and the CH\(_2\) deformation vibration occurred at the wavenumbers of 700 and 607 cm\(^{-1}\) for the aromatic rings feedstock [50].

### 3.6. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG)

The understanding of chemical kinetics through thermogravimetric analysis is highly important to analyze the reactions that occur in the thermochemical processes [54]. Thermogravimetric analysis and derivative thermogravimetry were used to measure the thermochemical properties of biomass samples in the pyrolysis and the combustion conditions. Figure 5 represents the TGA and the DTG curves for the fish waste samples under the pyrolysis setting. Table 6 shows the thermal degradation of the feedstock in pyrolysis conditions with the necessary temperatures for weight loss.

![Figure 5. The TGA and DTG curves for fish waste in the pyrolysis situation.](image)

Table 6. Different stages of temperature in the pyrolysis circumstance.

| Item         | Weight Loss (%) | Residue (%) | Peak Temperature (°C) | Peak DTG (wt. %/min) |
|--------------|-----------------|-------------|-----------------------|----------------------|
| Fish waste   | 3.56            | 55.72       | 9.94                  | 352                  | 4.58                |

For the pyrolysis condition, the first degradation occurred in the first stage at temperatures ranging from 50 to 200 °C, mostly because of the removal of moisture and light volatiles present in the biomass. The weight loss at this stage was determined to be 3.56%, which is similar to the proximate analysis findings. The elimination of extractable components in the sample happened in the second stage, which took place at temperatures ranging from 200 to 450 °C [55]. The major decomposition occurred in this stage with 55.27% due to the breakdown of macromolecules, guanine, and other organic materials [56]. This is a sign of the natural breakdown of the waste residue via thermal processing, which might be an ideal precursor for pyrolysis processes.

Figure 6 depicts the TGA and DTG curves of fish waste samples under the combustion conditions with the necessary temperatures for weight loss.
43.99% in the second step [57]. The peak was obtained from the DTG curve at a temperature of 315 °C with a decomposition rate of 3.22 wt.%/min during this phase. The formation of benzenic circles was produced at a temperature of more than 380 °C towards the polycyclic organization of char [58].

Figure 6 depicts the TGA and DTG curves of fish waste samples under the combustion condition.

Table 7. Different stages of temperature for the combustion situation.

| Item            | Stage (i) 50–200 (°C) | Stage (ii) 200–450 (°C) | Stage (iii) 450–900 (°C) | Residue (%) | Peak Temperature (°C) | Peak DTG (wt.%/min) |
|-----------------|------------------------|-------------------------|--------------------------|-------------|-----------------------|---------------------|
| Fish waste      | 4.64                   | 43.99                   | 35.34                    | 16.03       | 315/606               | 3.22/3.77           |

The third stage resulted in a weight loss of 35.34% at 606 °C temperature with 3.77 wt.%/min degradation rates. More residual organics of the fish feces were released in this stage, resulting in higher weight loss [57]. The residual was determined to be 16.03% after 900 °C, primarily owing to the ash of the sample. The inorganic components contributed to the increased residue for the fish scale [59]. The thermochemical breakdown pattern demonstrated that this waste biomass might be employed as a good feedstock for biofuel generation.

3.7. Pyrolysis Yield

Pyrolysis is a method of thermal decomposition of biomass in the deficiency of oxygen with or without a catalyst at moderate temperatures. Materials are oil, gas, and char pyrolysis. To decrease secondary reactions and increase the yield of the liquid, short residence times are required. Specific forms of pyrolysis are being utilized while the target material or product characteristics are dissimilar, such as slow or fast pyrolysis. Carbon monoxide, carbon dioxide, and methane are the significant components in the gaseous material. The char consists of pure carbon and hydrogen. It comprises the majority of all metals for the sources of biomass. The liquid (oil) after pyrolysis is the composition of esters, organic acids, alcohols, sugars, ketones, phenols, aldehydes, syringols, alkenes, and oxygenate compounds [60].

Table 8 represents the production percentages of the biochar, the bio-oil, and the bio-syngas of Neotrygon kuhlii fish waste for three different pyrolysis temperatures (400, 500, and 600 °C). The production of biochar was decreased from 33.96 to 23.46% when the pyrolysis temperature was raised from 400 to 600 °C, which is similar to the literature (37.5% and 25.6% for 400 and 600 °C) [61]. Biochar development is the procedure of breaking light
bonds and the development of denser arrangements [32]. The biochar can be used as an alternative to chemical fertilizers for soil improvement due to its stable nature [62].

Table 8. Production yield of Neotrygon kuhlii fish waste.

| Temperature (°C) | Biochar (%) | Bio-Oil (%) | Bio-Syngas 1 (%) |
|------------------|-------------|-------------|------------------|
| 400              | 33.96       | 47.72       | 18.32            |
| 500              | 29.34       | 49.32       | 21.34            |
| 600              | 23.46       | 33.87       | 42.67            |

1 Calculated from deduction.

The result revealed the comparable production effectiveness for bio-oil, which can approve the potentiality of the biomass as a bioenergy. The yield of bio-oil was increased from 47.72 to 49.32%, for the temperature rise of 400–500 °C, whereas it fell to 33.87% at 600 °C temperature. The values are higher than the bio-oil yield (17.08 wt.%) from the liquid fraction process [63]. The bio-oils from animal waste contain mainly alkanes, alkenes, aromatics, aldehydes, ketones, and carboxylic acids, whereas the lignocellulosic biomass formed mostly phenols, furanes, benzenediols, and their compositions [23]. The bio-oil can be upgraded by dropping the oxygen and alkali content from the pyrolysis oil for specific applications [50]. For the production of biofuel with a higher ratio, the pyrolysis process became the most promising procedure to convert the biomasses. Bio-oil is important in terms of energy safety, ecological aims, foreign currency savings, and socio-economic purposes in countryside areas [28]. These results prove that this fish waste can be used as an effective source of biofuel.

The bio-syngas production for this fish waste was raised by 18.32%, 21.34%, and 42.67% for the pyrolysis temperature increases of 400, 500, and 600 °C, respectively. The bio-syngas yield was higher due to the formation of non-condensable gases through secondary cracking of the pyrolytic vapors at higher temperatures [17]. These trends are similar to the values found in the literature [19,61]. The main components of the bio-syngas are hydrogen, methane, carbon dioxide, and carbon monoxide, which can be used as fuel. Hydrogen gas can be used to make the heat energy or can be utilized in a fuel cell for producing green energy (electricity). This gas can also minimize the dependence on petroleum and monitor the pollution of greenhouse gas emissions [3,64]. Therefore, it can be concluded that this fish processing waste can be an effective source of bio-syngas with biochar and bio-oil from the pyrolysis procedure to use as fuel.

4. Conclusions

The findings of this research illustrated that the fish processing waste from the bluespotted stingray (Neotrygon kuhlii) might be a promising source of biofuel through the pyrolysis process. The proximate analysis of the feedstock postulated that the reduced moisture content, high volatile matter, and suitable fixed carbon contents are highly effective in generating the superior quality of biofuels. The feedstock contains a moderate amount of ash which can also be used as a catalyst in the catalytic pyrolysis process. The lower O/C atomic ratio (0.219) and a small quantity of sulfur (0.91%) demonstrated the upgraded bioenergy production with lower SOx gas emission to the atmosphere. The higher calorific value (21.53 MJ/kg) of this fish waste revealed that this feedstock is an effective renewable energy source. The SEM analysis gave an indication of the higher micronutrients and macronutrients in the biochar to use for the filtration and soil amendment purposes. The EDX result also represented an enhanced percentage of carbon and oxygen content in this fish waste. In the FTIR, the significant bondage between hydrogen, carbon, and oxygen in this fish waste established the potentiality of bioenergy. The thermal breakdown of this waste biomass followed the same pattern as the other biomass in the TGA and DTG curves, where the maximum degradation occurred at the second stage for both pyrolysis and combustion conditions. Finally, the yield of the pyrolytic products proved that this fish waste would be a promising source of bioenergy where the maximum
amount of biochar was produced at 400 °C, the bio-oil at 500 °C, and the bio-syngas at 600 °C. As a consequence, it can be stated that the Neotrygon kuhlii fish wastes found in the Borneo region have the potential to be an effective source of renewable energy through the thermochemical conversion process to save landfills, ecology, and the environment. Future research should analyze the chemical composition of bio-oil and bio-syngas for application in the field.

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Abbreviation and Nomenclature

| Abbreviation | Description |
|--------------|-------------|
| MC           | Moisture content |
| VM           | Volatile matter |
| FC           | Fixed carbon |
| AC           | Ash content |
| ASTM         | American Society of Testing Materials |
| C            | Carbon |
| H            | Hydrogen |
| N            | Nitrogen |
| S            | Sulfur |
| O            | Oxygen |
| PSU          | Prince of Songkla University |
| GCV          | Gross calorific value |
| HHV          | Higher heating value |
| UK           | United Kingdom |
| SEM          | Scanning electron microscope |
| EDX          | Energy-dispersive X-ray |
| FTIR         | Fourier transform infrared spectroscopy |
| TGA          | Thermogravimetric analysis |
| DTG          | Derivative thermogravimetry |
| N₂           | Nitrogen gas |
| O₂           | Oxygen gas |
| CO₂          | Carbon dioxide |
| °C           | Degree Celsius |
| °C/min       | Degree Celsius per minute |
| L/min        | Liter per minute |
| wt.          | Weight |
| MJ/kg        | Mega Jule per kilogram |
| wt.%/min     | Weight percentage per minute |
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