Torrefaction of fish waste (Sardinella fimbriata) in a fixed bed reactor: Yields and biochar characterization

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Abstract. Torrefaction is a promising process to upgrade biomass and produce solid biofuel. In this study, the fish by-product (\textit{Sardinella fimbriata}, a fish-processing waste from the food industry highly prevalent in the east coast region of Peninsular Malaysia was investigated in a fixed bed torrefaction reactor with varying reaction temperature (200, 250, and 300 °C) under a nitrogen atmosphere and single residence time (30 minutes). The distribution and yield of the biochar, bio-oil, and biogas were examined, and further characterization of the biochar was performed (proximate and ultimate, SEM, and FTIR analysis). The results indicated that with the increased torrefaction temperature, solid char yield decreases down to \textasciitilde 52 \% while bio-oil and biogas fluctuate between 7 - 28 \% and 21 – 27 \& respectively. The proximate and ultimate analysis of the torrefied solid char showed that the fixed carbon, carbon content increased while volatile matter, moisture, hydrogen, and oxygen content decreased with temperature rise. From the SEM analysis, the torrefaction temperature causes an increase in biochar porosity. Lastly, from the FTIR analysis, it can be seen that there are degradation and formation of certain functional groups such as O-H, C-H, C=C, C=O, C-O, and C-C with torrefaction temperature variations.

1. Introduction
Fish waste can be defined as a by-product of fish-processing or fish-based food production produced by households, fish markets, restaurants, and/or fish processing industries daily. Depending on the processing method, approximately 60 \% of the fish mass includes bones, head, viscera, fins, tail, and shells discarded as waste [1]. Not always properly disposed of and managed, these wastes can increase environmental pollution, thus adversely affecting human health. For that reason, it became crucial to discover alternative routes for the utilization of these waste materials by converting them into value-added product resources. Conversion of wastes into improved products in a thermochemical reactor like pyrolysis, gasification, and combustion has been the focus of research in the past few years. However, some wastes such as fish waste cannot be directly fed into those reactors due to their moisture content. Torrefaction is regarded as a pre-treatment method to improve the physical, chemical, and biochemical properties of raw biomass materials and produce solid fuels with better quality. Biomass can be torrefied with no (inert) or minimal oxidative atmosphere at a temperature range of 200 to 300 °C [2]. Many works of literature reported that MC, O, H, H/C, and O/C ratio, and VM decreased, while FC and C content of biomass increased due to the torrefaction process [2-5]. Furthermore, the lesser moisture
absorption capacity than raw biomass prevents the biological degradation of the torrefied biomass and supports its long-time storage. The literature review reveals that the study on the torrefaction of fish waste is rare. Therefore, in this study, the yields of solid char, condensable liquid, and gases produced from torrefaction of fish waste in a fixed bed reactor were examined. The proximate and ultimate analysis was conducted to investigate the components in the solid char produced by the process. Meanwhile, the Fourier transform spectroscopy (FTIR) analysis and scanning electron microscopy (SEM) analysis was used to study the chemical structure and surface morphology of the solid char, respectively.

2. Methodology

2.1. Material
The sample used in this study is fish waste (FW), fish heads, and bones from *Sardinella fimbriata*, obtained from a seafood-based industry in the town of Kuala Nerus, Terengganu, Malaysia. Before the torrefaction process, the samples were sun-dried with an average ambient temperature of 25 – 28°C for 24 hours during the daytime (9 am to 5 pm). The samples then were ground and sieved to the particle size less than 150 μm.

2.2. Torrefaction in a fixed bed reactor
The torrefaction experiment was carried out in a fixed bed reactor under a nitrogen flow of 50 ml/min for a temperature of 200, 250, and 300 °C. When the reactor's temperature reaches the set temperature, the reactor's tube with samples was quickly pushed into the reactor and kept for 30 minutes. Then, the reactor and samples were cooled down to room temperature by flushing the nitrogen gas. The reactor's generated volatile products were purged downward by the nitrogen stream and flow into the condenser. The condensation system was set up by submerging the filtering flask into an ice bath. Then, the vapours that condensed into liquid were collected and weighed. The yield \( Y_X \) of the solid char, condensable liquid, and gas product was estimated according to equation (1). Each experiment was repeated three times under the same conditions, and the uncertainty for all yields calculated less than ±1.5 %.

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Y_X (\text{wt} \%) = \frac{\text{weight of } X (g)}{\text{weight of raw sample (g)}} \times 100 \% \tag{1}
\]

2.3. Solid char characterization
The carbon (C), hydrogen (H), nitrogen (N), sulfur (S) content of the raw materials and the torrefied fish waste (TFW) solid char was performed using Vario MICRO Cube elemental analyzer. The oxygen (O) content was calculated by difference from the CHNS results, i.e. 100-C-H-N-S. JIS M8812 standards were used for the identification of their moisture content (MC), volatile matter (VM), and ash contents (AC). The fixed carbon (FC) contents then were determined by the difference, i.e. 100-MC-VM-AC. Surface functional groups of the biochars were analyzed using a SHIMADZU IRTracer-100 Fourier-transform infrared (FTIR) spectrometer. The scanning region of the IR spectrum was from 4000 to 400 cm\(^{-1}\). Surface morphologies of the biochar were also analyzed by Scanning Electron Microscope (SEM), and the equipment is JEOL JSM-6360LA at an accelerating voltage of 10 kV magnification of X500.

3. Results and Discussion

3.1. Torrefaction yields
The yield of solid char, condensable liquid, and gaseous obtained by torrefaction of FW is presented in Figure 1. The solid yield decreased by less than 10 % from torrefaction 200 to 250 °C. The yield of liquid decreased by ~3 % and gas increased by ~10 % under this temperature range. As the temperature further increased to 300 °C, the solid yield decreased to around 15 %, the liquid yield increased by 20
% and the gas decreased by about 5%. That may explain these results during lower torrefaction temperature; the weight loss could be mainly due to the removal of the constitutive water and light volatile in the raw FW. Meanwhile, when higher torrefaction temperature is provided, the degradation of chemical structure (due to the decomposition of proteins and carbohydrates) in the FW becomes intense, and more thermal cracking reaction occurred.

Figure 1. Yields of solid char, liquid, gas from torrefaction at different temperature

3.2. Proximate analysis
Figure 2 shows the proximate analysis of the TFW char in comparison to its raw materials. It can be seen that as the torrefaction temperature increased, the FC increased, the VM and MC decreased. This result is observed on torrefied solid chars from ponkan peel waste [3], Ulva intestinalis [4], and Acacia nilotica [5]. In the raw FW, the VM content is accounting for the largest portion of the feedstock. The reduction of this content with the severity of the torrefaction process can be explained by the rise in the rate of release of light volatile matter, i.e. light hydrocarbon like methane, ethane, etc., an increase in temperature[5]. In contrast, the increase in FC content as the torrefaction temperature increase indicates the solid char becomes less reactive but with higher calorific value [2]. It should also be noted that AC is the highest at the lowest torrefaction temperature (200 °C) and decreases afterwards with further increases in the temperature. The change in the AC content with the severity of temperature can be associated with the formation and condensation of mineral elements during the torrefaction process[6].

Figure 2. Proximate analysis of raw FW and TFW at different temperature
3.3. Ultimate analysis

The ultimate analysis of raw FW and solid char obtained from its torrefaction process is presented in Figure 3. In agreement with the increase of FC mentioned in Figure 2, C is increased with the increase of the torrefaction temperature. In contrast, H content dropped, which could be due to MC's loss (Figure 2) and hydroxyl groups. Meanwhile, the O content decreased with elevated torrefaction temperature due to CO₂, CO, and H₂O release. Consequently, the H/C and O/C ratio decreased from 3.09 to 0.81 and 0.58 to 0.34, respectively, as the torrefaction increased from 200 to 300 °C. Compared to the parent material, the lower H/C and O/C ratios of TFW suggest that dehydration and deoxygenation are the foremost reactions during the torrefaction process [7]. Lastly, the raw FW's N content is considered high compared to lignocellulosic biomass like sugarcane bagasse, rice husk, or empty fruit bunch; but comparable to biomass such as food wastes [8], and Acacia cincinnata [9]. This element is associated with amino acids and proteins in the material and possibly retention in the solid char after the torrefaction. A slight increase of N content was observed as the torrefaction temperature grew from 200 to 300 °C.

![Figure 3. Ultimate analysis of raw FW and TFW at different temperature](image)

3.4. FTIR analysis

The FTIR spectra in 4000 – 400 cm⁻¹ range for raw FW and solid char from the torrefaction process are presented in Figure 4. The broad peak between 3600 and 3000 cm⁻¹ that shown by the spectrum of raw FW is attributed to O-H stretching bonds, and indicates the existence of alcohol, phenol, water or carboxylic acid. The peak becomes weaker as the torrefaction temperature increases due to dihydroxylation and condensation reactions [10]. Also, weak aliphatic C-H stretching vibrations peak (~2900 cm⁻¹) is seen in raw FW representing the presence of hydrocarbon compound, alkanes. The disappearance of these peaks for TFW at every torrefaction temperature could be due to the decomposition of this aliphatic group compound of FW into methane, carbon dioxide, and other gases and the formation of a dense ring structure in the torrefied solid chars [11]. The peak at ~1650 cm⁻¹ owing to amide bonds and aromatic ring stretching (C=O, C-C stretching) can be noticeably observed in raw FW but reduced in intensity with the severity of torrefaction temperature. This can be explained by the properties of C=O bonds that are easy to rupture with possibly released CO and CO₂ during the torrefaction process [12]. The peak around 1450 cm⁻¹ that can be seen in the raw FW confirmed the presence of C-H groups in alkanes [11]. As can be observed, this peak is still present in the solid TFW at all torrefaction temperatures, which indicates that organic matter is barely affected by the thermal energy provided during the torrefaction temperature. Another high peak at about 1030 cm⁻¹ observed on the spectrum for raw FW, representing C-O stretching and C-O-C stretching [13]. These bands indicate that alcohols and ethers were abundantly present within the raw FW. However, the intensity decreased for solid TFW, suggesting the destruction of these structures during the torrefaction process. A small peak appeared after the torrefaction at around 870, indicating the appearance of C-H stretching attributed to the presence of adjacent aromatic hydrogen hydrocarbons in the torrefied solid char [14]. The peak does not show up in the raw FW, and intensity is more vigorous with the increase in the torrefaction.
temperature. This condition suggests that TFW has more aromatic compounds with higher stability than its raw material and as the torrefaction process gets severe.

![FTIR spectra of raw FW and TFW at 200, 250, and 300 °C](image)

Figure 4. FTIR spectra of raw FW and TFW at 200, 250, and 300 °C

3.5. **SEM analysis**

The SEM images of raw FW and TFW at different torrefaction temperatures are presented in Figure 5. It can be observed that as the torrefaction process gets severe, the pores on the surface of TFW become noticeably seen. These pores are the results of volatile matter released during the torrefaction conversion. The increase of porosity with the increased torrefaction temperature is also found by [15].

![SEM images](image)

Figure 5. SEM image of (a) raw FW, and TFW at (b) 200 °C, (c) 250 °C, and (d) 300 °C

4. **Conclusions**

The torrefaction of FW was carried out in a laboratory-scale fixed-bed reactor with process temperature being varied. It was found that solid yields decrease linearly with the increase in temperature. Meanwhile, the optimized yield for condensable liquid and gas is at a temperature of 250 °C and 300 °C, respectively. The FC and C content of TFW increased, while VM, H, and O content decreased as the torrefaction temperature increased to 300 °C. The solid char The FTIR results showed that the torrefaction process mainly removes the O-H bond. Also, the SEM observation revealed the development of porous structures after the torrefaction process. This study's results could help for preliminary understanding of the torrefaction mechanism for FW in terms of the yields produced and some of the properties of biochar produced by the process.

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