

Characterization of Energy Content in Food Waste by Using Thermogravimetry Analyzer (TGA) and Elemental Analyzer (CHNS-O)

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Abstract - Recently, food waste generation has become a serious issue and become a hot topic among the superiors in order to handle the waste from going to landfill. There are many researches that have been done regarding to the how to handle this waste efficiently and effectively. Thus, this research is interested in helping the world to convert the waste into an energy sources effectively by analyzing the characteristics that could be presented in each of the food waste. For this research, the food waste samples that have been analyzed are tofu, apple, carrot, corn, chicken, biscuit, rice and meat. This analysis is conducted as the very first step in encouraging the ways of handling such waste before implementing the waste transformation into an energy sources process in order to identify and conclude whether the waste is suitable for the transformation process or not. The methods to be used are by conducting a proximate analysis and also an ultimate analysis. These two analyses will show several contents that may be presented in each of the food waste sample. A proximate analysis will observe the percentages of the moisture content, volatile matter content, ash content as well as the fixed carbon content while an ultimate analysis will provide the percentages of carbon, hydrogen, nitrogen, sulfur as well as oxygen element in that food waste sample. In conjunction with that, it is needed to run in a thermogravimetry analyzer (TGA) in order to study the proximate analysis and also for the ultimate analysis; a CHNS-O elemental analyzer can be used for that purpose. The results from the proximate analysis will be presented as in TGA-DTG curves while the ultimate analysis only in numbers. The TGA experiment is discussed further by providing another graph plotting the weight loss of the samples in percent (wt%) versus temperature (°C). Meanwhile, the elements that were recorded by conducting the ultimate analysis is used in defining the higher heating value (HHV) depending on various equations. Among all of the samples, it can be observed that the most efficient 'waste-to-energy' sample is the protein-based food because this food has the highest amount of volatile matter with the lowest amount of ash content and fixed carbon content. Plus, protein food gives the highest percentages of carbon and hydrogen elements in order to help the combustion process going perfectly in order to convert it into an energy sources.

Keywords – food waste, thermogravimetry analyzer (TGA), elemental analyzer (CHNS-O), proximate analysis, ultimate analysis, waste-to-energy, higher heating value (HHV).

INTRODUCTION

Nowadays, there are many researches have been done in finding the alternatives for renewable energy in order to reduce the issue on energy crisis. Need to concern that energy demand will be continuously increased dramatically about 48% from until 2040 as described in the report of United States of America Energy Information Administration 2016. In conjunction with that, the fossil fuel energy needs to be replaced with other alternatives sources of renewable energy as this energy sources continuously depleting as time goes by. Not only that, the combustion of fossil fuel energy also gives many bad impacts to the environment. Along these years, researchers have been diagnosing to find any possible renewable energy from various sources such as solar, geothermal and biomass. The conservation law of energy stated that energy cannot be created nor destroyed, however it can be converted from one form to another form. Sources of energy can be found as in renewable source or non-renewable source. Agricultural wastes are the examples of renewable source of energy while coals are the example of non-renewable source of energy. Renewable energy source is the material that can generate energy, which is the material, could be added easily and non-renewable source of energy is the one that cannot be added easily (U.S. Energy Information, 2018).

One of the biggest advantages of using renewable energy sources is that it is less hazardous since it does not comply with some complex equipment and process that could emit pollutants.

However, there is only a little research on defining that food waste (FW) could also be one of the renewable energy sources. FW is an edible food that was collected from the human consumption and some of it is being left uneaten and discarded from the food chain (Ghafar, 2017). FW mainly consists the highest volatile matter compound rather than another wastes and also categorized of the municipal solid waste (MSW) due to unsuitable to be consumed completely which later being disposed to the landfill. The impacts of this activity to the environment is that the FW is catastrophic climate change and this problem will kept continuing in the next 25 years (Melikoglu et. al., 2013). Majority of the authorities will be practicing the landfill disposal without any further treatment that can be related to the FW issues.

As high as 1.3 billion tons of MSW were generated every single year from all countries and was predicted to be doubled in the amount of generated MSW by 2025 due to rapidness of the human's growth and technologies development based on the report written by Gary Gardner in July 24, 2012 (Gardner, 2012) . About 38.1% of the overall MSW generated per year was collected from the kitchen or food waste, where this is the highest value among another type of wastes. Generally, there is a wider gap of the waste generated percentage between the food waste and agricultural waste, which means that food wastes are frequently being, disposed each day rather than agricultural wastes. Because of the problems, there is an increased in research finding related to FW. In order to overcome the issues, researches on the collection, minimization, treatment and energy recovery have been discovered and implemented (Schott et. al., 2015)(Halloran et. al., 2014).

It was proposed that the food waste generally can be converted into an energy source, where it can provide energy to other areas such as for agricultural and industrial areas to be operated and used in daily activities. There are high chances of the costs for the operation or costs for remodeling new substances can be reduced instantly if the waste can be converted into an energy source and replaced the existing new produced energy, which is costlier and more harmful to the environment. The aim must be achieved by identifying the FW characteristics by conducting the proximate analysis and ultimate analysis. Characterization of energy content in food waste is the determination of that food waste capability to become a renewable energy source.

Basically, the needs to analyze how much of fixed carbon (FC), moisture content (MC), volatile matter (VM) and ash content (AC) in a food waste sample can be run through the Thermogravimetry Analyzer (TGA). Next, the amount of element components that contained in the

FW can be observed by running an ultimate analysis through an elemental analyzer (CHNS-O Analyzer). The elements that can be found out by running through this analyzer are carbon (C), hydrogen (H), nitrogen (N), sulfur (S) as well as oxygen (O). The values from both analyses can be used to calculate the higher heating value (HHV) of that specified food wastes. HHV will indicates the energy content in FW and it is important in determining which industry is suitable for the specified wastes based on its needs in heating value to be operated. Hence, this research is giving a better understanding of FW properties by conducting the proximate analysis and ultimate analysis. Plus, this study also will prove the difference of the relationship between proximate analysis factors using TGA with energy content as well as the relationship between the ultimate analysis factors using CHNS-O with energy content.

METHODOLOGY

Feedstock materials

The materials to be used for this experiment were variety of FW; sweet corn, apple, carrot, white rice, biscuit, tofu, chicken and beef. As for the preparation of the FW sample, digital weight is used to weigh the sample before running into the analyzers for a specified weight as well as the tin capsule to act as the holder for the food waste going into the CHNS-O analyzer. The samples were needed to be prepared in two forms; wet and dry sample before running in the analyses. The dry sample is prepared by drying the FW samples in a conventional oven at 50°C placed in a porcelain crucible. HHV for each sample can be calculated from both proximate analysis and ultimate analysis by using the following correlations:

Table 1
Summary of correlations to be used in calculating HHV of FW.

Eqn .	Correlation	Based on	Unit	Ref.
Eqn. (1)	$HHV = 0.1846 VM + 0.3525 FC$	Proximate analysis	MJ/kg	(Nhuchhen & Afzal, 2017)
Eqn. (2)	$HHV = -1.675 + 0.3137C + 0.7009H + 0.0318O$	Ultimate analysis	MJ/kg	(Sheng & Azevedo, 2005)
Eqn. (3)	$HHV = 354.68 C + 1376.29 H - 15.92 Ash$	Proximate & Ultimate analyses	kJ/kg	(Jahirul, et. al., 2012)

	124.69 (O + N) + 71.26			
Eqn. (4)	HHV = 0.3491C + 1.1783H + 0.1005S + 0.1034O + 0.0151N + 0.0211Ash	Proximate & Ultimate analyses	MJ/kg	(Channiwal & Parikh, 2002)

Proximate Analysis

Proximate analysis can be determined by running the experiment on TGA which consists of the percentages of moisture content, volatile matter, fixed carbon and ash content according to D1762-84 (ASTM, 2007). The analysis is run until 1100°C with a constant heating rate of 20°C/min, where the first step is conducted from 25°C to 950°C in 100 mL/min of nitrogen gas flow to identify the percentages of moisture content and volatile matter. Meanwhile, the second step is conducted from 950°C to 1100°C with heating rate of 20°C/min in 100 mL/min of air flow to observe the behavior of the samples' ash content. Basically, the sample is heated until 160°C maximum for 2 hours to identify the moisture content just like in an oven dry process while in order to observe the volatile matter, it is needed to heat up the sample until 950°C for about 11 minutes. Finally, the ash content can be determined by adding up heat source further at least 2 hours until the temperature reaches 1100°C. The value for the fixed carbon content can be calculated by subtracting a 100% with the total percentages of the rest three characteristics.

Ultimate Analysis

Ultimate analysis could be conducted when the feedstock is undergoes the experiment in the elemental analyzer. The ultimate analysis is performed using a Thermo Finnigan Flash EA 1112 Series Elemental Analyzer CHNS-O. The elements that can be analyzed are carbon, hydrogen, nitrogen and sulfur. Since most of the FW contains a larger amount of moisture content, it is needed to be dried overnight in a conventional oven at a constant temperature of 50°C. The preparing of the sample before running in the analyzer must be done precisely. Firstly, the sample is placed in a tiny tin capsule that was held by the tin capsule holder as presented in the Fig.1 below. Then, the capsule along with the sample is needed to be weighed by using electronic beam balance at maximum of 15 mg. After that, the capsule is closed tightly by clipping in the capsule together and is ensured that there is no hole in any angle. Finally, the closed tin capsule is ready to run by the elemental analyzer. Noted that the

oxygen element could not be recorded directly from the analyzer due to the interference of inorganic oxides that presented in the ash (Ronsse et. al., 2013)



Fig. 1: The magnified view of the tin capsule to place the sample that was already being prepared in a powder form.

RESULTS AND DISCUSSION

All of the FW were collected and prepared in order to be conducted in the two different analyzers, which are thermogravimetry analyzer (TGA) and elemental analyzer (CHNS-O). The characteristics of the sample that can be outlined at the end of this research are carbon, hydrogen, nitrogen, sulfur and oxygen content as well as the moisture content, volatile matter, ash content and fixed carbon. Plus, the energy content value for each of the sample also can be calculated by referring to the correlations that have been highlighted before.

Proximate Analysis

Fig. 2 and Fig. 3 below show the TG plot for the weight loss (wt%) of the dry FW samples as well as the weight loss (wt%) of the wet FW samples versus temperature of the proximate analysis (°C), respectively. Generally, there are 3 phases presented in a proximate analysis by using TGA. Phase I, which obtained from the temperature range of 25°C to 160°C represent the phase to observe the moisture content in each of the sample due to the occurrence of dehydration reaction. Phase II represent the thermal decomposition stages of the reaction in order to identify the volatile matter content of the sample while phase III represent the solid residue left after the combustion reaction successfully occurred. In addition, the values for the fixed carbon content is calculated after subtracting total amount of the moisture content, volatile matter as well as the ash content. This calculation is parallel to the definition of the fixed carbon itself, which described as the solid residue that left after volatile matter has been removed when it is being heated at a higher temperature (Scaroni et. al., 2019).

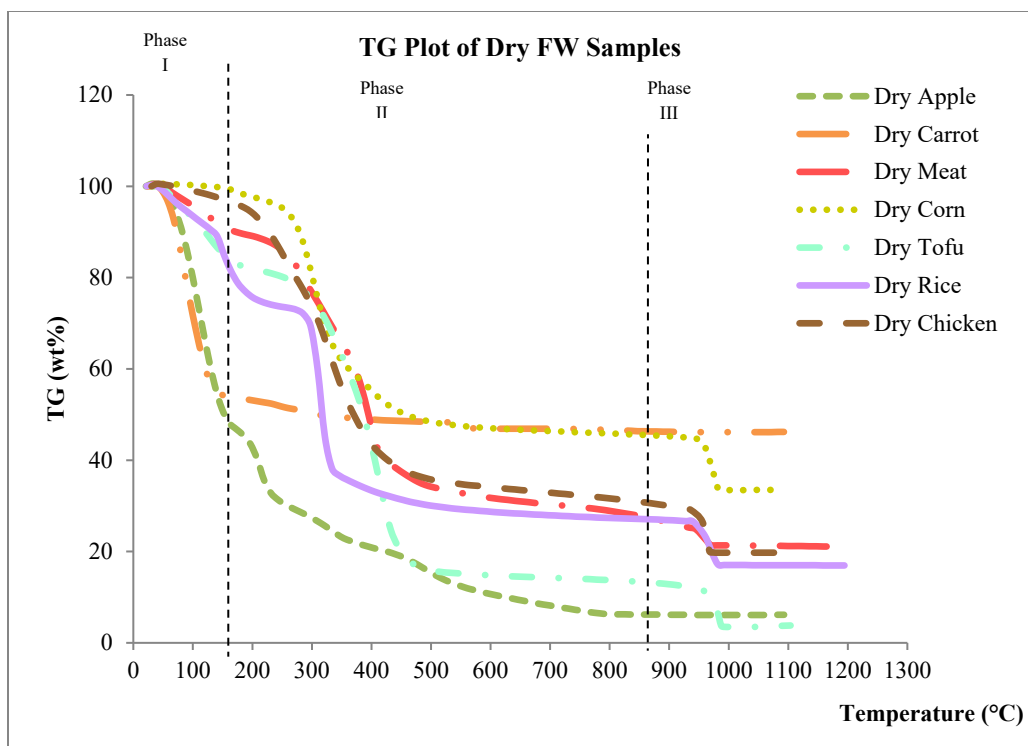


Fig. 2: The TG plot of dry FW samples with heating rate 20°C/min.

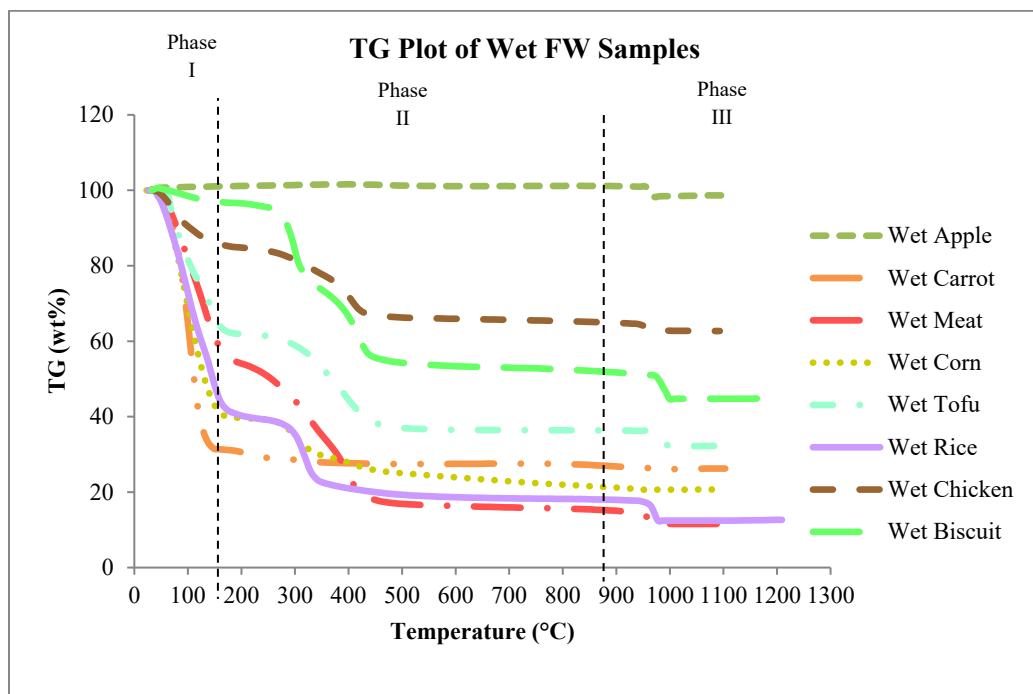


Fig. 3: The TG plot of wet FW samples with heating rate 20°C/min.

From the proximate analysis that has been done, wet-formed sample does contain more moisture since it

does contain a lot of moisture rather than the dry-formed sample. Thus, the weight loss in wet samples in Fig. 3

seems to be steeper than in the dry samples. Besides, the dry samples contained more volatile matter due to the easy-to-combust characteristics which produced from the changing of the sample's state from solid form into vapor form. This can be proved from Fig. 2 & Fig. 3 which the wet samples having a rapid reduction of the weight loss than the dry samples. Volatile matter is basically a state where the sample cannot withstand by itself and tend to change its form rapidly when a specified condition is introduced to the sample.

Table 2 concluded the all of the contents in each of the FW sample. Even some the results from this experiment did not proved the best percentages of the content in each of the sample, majority of the sample did run perfectly in identifying the contents in the FW. The imperfect results such as from the dry sweet corn, wet sweet corn and wet meat/beef were identified and concluded due to several factors such as in the preparation step, the sample did not stored in a crucible pot especially for the wet sample before going into the analyzer. This mistake will affect the purity of the sample because of the

Next, the ash content is the residue that left after the combustion has been took place completely. The lower the amount of the ash content, the better the sample because it indicates that the sample can be combusted perfectly without produced more residues that is not gives any benefits to the combustion process. Meanwhile, the samples that have a high percentage of fixed carbon is needed to be burned much longer than the low amount to ensure that all of the atoms could be combusted completely before converting into one of the renewable energy sources.

sensitivity of the food towards air surrounding and the temperature of the surrounding. Generally, wet FW samples contain much higher moisture content and lower volatile matter content. Even all of the dry FW samples exhibited much higher volatile matter, the dry meat sample resulted lower volatile matter content rather in wet meat sample. This is due to the presence of fats in the meat that contributed to higher volatile matter and lower ash content. The highest percentage of fixed carbon among all of the FW samples is dry white rice sample.

Table 2

The summary of the proximate analysis resulted from the thermogravimetry analyzer (TGA).

Food waste samples	Food classes	Type of sample	Moisture content (%)	Volatile matter (%)	Ash content (%)	Fixed carbon (%)
Sweet Corn	Carbohydrate, Fat, Protein, Dietary Fiber	Wet	39.9	12.6	47.8	-0.3
		Dry	33.6	68.3	16.4	-18.3
Apple	Carbohydrate, Dietary Fiber, Protein, Fat	Wet	1.0	0.1	98.7	0.2
		Dry	47.3	46.6	6.1	0
Carrot	Carbohydrate, Sugar, Fiber, Fat	Wet	66.4	5.0	26.2	2.4
		Dry	45.0	8.3	46.2	0.5
White Rice	Carbohydrate, Protein, Fat, Dietary Fiber, Sugar, Calcium	Wet	53.9	25.0	12.6	8.5
		Dry	11.6	60.1	17.0	11.3
Biscuit	Carbohydrate, Fats, Protein, Cholesterol, Sodium	Wet	2.8	46.1	44.8	6.3
Tofu	Protein, Fat, Calcium, Iron, Carbohydrate, Fiber	Wet	32.7	29.9	32.3	5.1
		Dry	14.0	73.4	3.7	8.9
Chicken	Protein, Fat (include saturated fat), Cholesterol, Sodium	Wet	13.8	21.5	62.7	2.0
		Dry	3.1	67.3	19.7	9.9
Meat	Protein, Fat, Vitamin B12, Zinc, Iron, Cholesterol	Wet	29.5	75.7	12.8	-18
		Dry	8.2	66.0	21.1	4.7

Ultimate Analysis

All of the FW samples are needed to be dried first before undergoing the ultimate analysis in the elemental analyzer since this equipment is very sensitive to the sample that contain high amount of moisture content. Only then, the FW samples can be combusted perfectly in the tubular reactor that is connected together. To fulfill the requirement, it is suggested that all of the sample must be

dried first in an oven under 50°C for a day to reduce its moisture content and also to be able being combusted in the analyzer. Fig. 4 below shows the example of the ultimate analysis resulted from the experiment that was analyzed under elemental analyzer (CHNS-O) for dried tofu sample. Meanwhile, Fig. 5 shows a set of bar chart for the summarization of the elements contained in each FW samples.

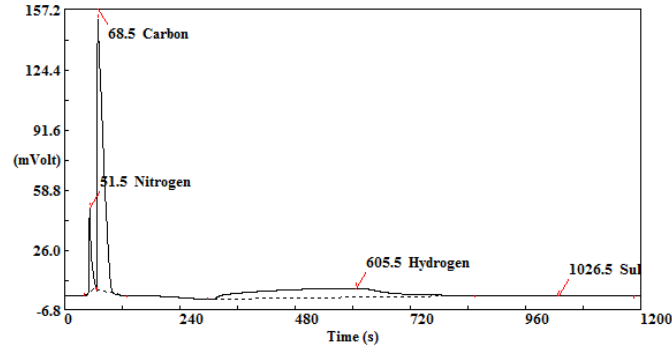


Fig. 4: The graph above shows the percentages of each element that existed in the sample.

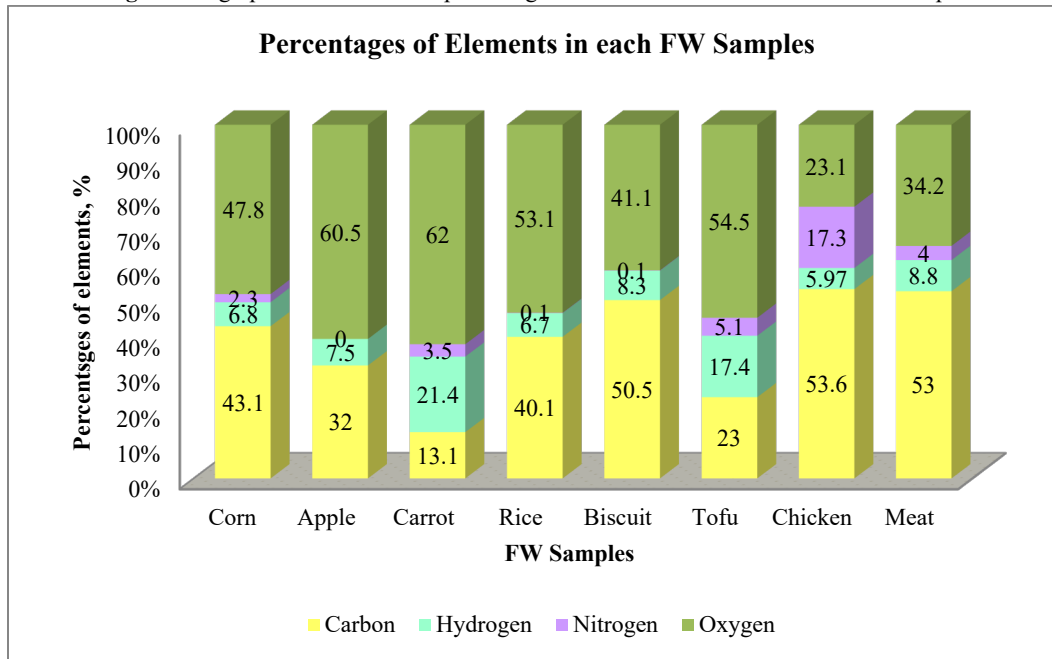


Fig. 5: The summarization of the elements contained in each FW samples.

An ultimate analysis can show the percentages of elements that are presented in a sample in details. These elements are important in defining and calculating the high heating value for each so that it can help in choosing the most suitable sample that can be used as the new energy sources based on its chemical characteristics.

Carbon elements in food are very important as it is the main component that can lead others to function properly. All of the food we eat must have carbon dioxide either the food is plant-based or animal-based. A hydrocarbon element is very helpful in initiating a combustion process when it combines with oxygen element in the air. This shows on why these three elements give a very big impact on how to choose the best sample to reproduce as the new energy sources in energy industry. The higher the percentages of these three elements, the better the combustion will take place. Combustion is important in producing energy because the energy can be

converted into another form of energy when heat is introduced.

Meanwhile, the nitrogen element needed to be in a small amount only because this element does not easily combust. It can only be burned when it reacts with additional elements that can help to initiate the element to be reactive. However, the combustion did not occur because of the nitrogen existence but because of the supported element existence (Summers, 2018). This situation is the same with the sulfur element characteristics. The sample that contains the lowest percentages of nitrogen and sulfur element should be chosen as the new energy sources.

As can be clearly seen in Fig. 5, carbon element is the highest among other elements with 53.6% in chicken sample. The lowest carbon content is from the carrot sample which proved that this FW sample does not suitable to be one of the renewable energy sources. With the high

amount of ash content in the carrot, it can be used as a good composting system that will produce a high quality of end product (Asquer et. al., 2017).

Table 3 below shows the summarization of those elements in each of the FW samples in an ultimate analysis process. Noted that this FW does not have any sulfur contained due to the fact that sulfur existed can build amino

acids that later will cause harm to the skin, bones and nerve cells' healthy development (Wagner, 2017). This is a very good reason on why FW can be chosen as the renewable energy source. Not only that, protein-based food contains higher percentages of nitrogen than the others because it has amino acids presented in the molecules that later will be catabolized into energy and ammonia (Corleone, 2019).

Table 3

The summary of the ultimate analysis resulted from the elemental analyzer (CHNS-O).

Food waste samples	Food classes	Carbon, C (%)	Hydrogen, H (%)	Nitrogen, N (%)	Sulfur, S (%)	Oxygen, O (%)
Sweet Corn	Carbohydrate, Fat, Protein, Dietary Fiber	43.1	6.8	2.3	0	47.8
Apple	Carbohydrate, Dietary Fiber, Protein, Fat	32.0	7.5	0	0	60.5
Carrot	Carbohydrate, Sugar, Fiber, Fat	13.1	21.4	3.5	0	62
White Rice	Carbohydrate, Protein, Fat, Dietary Fiber, Sugar, Calcium	40.1	6.7	0.1	0	53.1
Biscuit	Carbohydrate, Fats, Protein, Cholesterol, Sodium	50.5	8.3	0.1	0	41.1
Tofu	Protein, Fat, Calcium, Iron, Carbohydrate, Fiber	23.0	17.4	5.1	0	54.5
Chicken	Protein, Fat (include saturated fat), Cholesterol, Sodium	53.6	5.97	17.3	0	23.2
Meat	Protein, Fat, Vitamin B12, Zinc, Iron, Cholesterol	53.0	8.8	4.0	0	34.2

Higher Heating Value (HHV)

HHV is also known as calorific value used to observed the value of the energy contained in the sample. It is observed as the amount of the heat that been released during the combustion and is measured in the unit of energy per mass of the substance. HHV is a very important indicator on which the sources that more beneficial to be combusted to form an energy. When combustion is occurred, water will be produced and the amount of the water produced is depending on the amount of the hydrogen existed. The resulted water will be converted into vapor form due to the high temperature that was introduced onto it as the latent heat of vaporization (Aminatural, 2015). To be simplified, this value calculating the water component in liquid state at the end of the combustion.

In this context, HHV value can be calculated from the results by proximate analysis as well as by ultimate analysis by using different correlations as stated above. The calculated is recorded as in Table 4 below

which depending on the correlations used. All of the correlations exhibited a vary values for each FW sample. Eqn. (1), (3) and (4) is depending on the proximate analysis while Eqn. (2), (3) and (4) is derived from the ultimate analysis. Clearly, there is a slightly difference in HHV between those correlations which is convincing to be practiced for other FW samples.

As tabulated in Table 4, the sample that contains the highest amount of HHV based on the ultimate analysis is from the protein-based samples, which in this case are chicken and meat samples while the highest HHV based on the proximate analysis is biscuit sample due to the contribution of volatile matter as well as fixed carbon. Not only that, the correlation that accounted the amount of the ash content is much preferable because of the requirement to convert the substance into the energy sources. It also is considered as the renewable energy sources that do not released the carbon dioxide to the environment.

Table 4

Summary of the HHV calculated from the proximate analysis and ultimate analysis.

Food waste samples	Eqn [1] (MJ/kg)	Eqn [2] (MJ/kg)	Eqn [3] (MJ/kg)	Eqn [4] (MJ/kg)
Sweet Corn	6.157	18.132	18.209	17.735
Green Apple	8.602	15.544	14.102	13.624
Carrot	1.708	19.405	25.267	22.350
White Rice	15.078	17.289	16.611	16.043
Biscuit	10.731	21.291	23.555	22.213
Tofu	16.687	19.469	24.686	22.741
Chicken	15.913	20.060	21.944	22.674
Meat	13.840	22.207	25.882	24.829

CONCLUSION

In conclusion, there are several food wastes that can be accounted as the new energy sources after doing the analyzing steps to state all of the characteristics that the wastes have. The characteristics for each food waste sample can be observed by the physical properties and chemical properties contained by analyzing in terms of proximate analysis and ultimate analysis. From the proximate analysis, the sample could give the values for the percentages of the moisture content, volatile matter, ash content and fixed carbon. Meanwhile, the percentages of carbon element, hydrogen element, nitrogen element, sulfur element and oxygen element can be observed from the ultimate analysis experiment. From the calculated HHV based on the proximate analysis, the most suitable food waste sample that can be used as the new feedstock for energy sources is the protein-based food such as tofu, chicken and meat/beef either it is in wet or dry form. Plus, this result also has been supported by observing the calculated HHV by using the ultimate analysis' correlations that emerged that the protein-based foods have the highest

HHV. The higher the amount of HHV, the better the substance can be burned under specified condition. Another reason is that these foods are relatively having the higher amount of carbon and hydrogen elements that will help in combustion process. The dry protein-based food sample also can be chosen because it has the highest amount of volatile matter with the lowest amount of ash content as well as fixed carbon content. The food that produced only small amount of solid residue should be chosen in order to ensure that the combustion is perfectly reacted.

ACKNOWLEDGMENT

First and foremost, I would like to express my sincere appreciation to my supervisor, Ir. Normadyzah binti Ahmad, for her support, encouragement and consideration during completing this research project. Without her support, this research project would not being completed as shown here. Not to forget, a very special thanks to my co-supervisor, Pn. Fazni Susila, for her co-operation in providing a platform for me to complete my experiment successfully.

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