# TGA Analysis of Rubber Seed Kernel

**Noorfidza Yub Harun**                      Noorfidza.Yub_Harun@unb.ca
*Graduate Student*
*Faculty of Forestry and Environmental Management*
*University of New Brunswick*
*Fredericton, E3B 5A3, Canada*


**M.T. Afzal**                                        mafzal@unb.ca
*Associate Professor*
*Faculty of Forestry and Environmental Management*
*University of New Brunswick*
*Fredericton, E3B 5A3, Canada*


**Mohd Tazli Azizan**                        tazliazizan@petronas.com.my
*Graduate Student*
*Chemical Engineering Department*
*University College of London*
*Gower Street,*
*London, WC1E 6BT,*
*United Kingdom*

## Abstract

This project investigated the possibility of converting biomass wastes into solid fuels by undergoing torrefaction process. Rubber seed kernel was used to produce torrefied material and the factors affecting torrefaction were investigated. Samples of rubber seed kernel were dried, ground, sieved, heated and cooled to obtain the torrefied material.  It was found that minimum 30% of the moisture content was removed from its original value during torrefaction process. Almost 100% of the calorific value in all the samples can be retained or increased by up to 10% from the original waste calorific value. The proximate analysis was carried out using Thermo Gravimetric Analyzer (TGA) where rubber seed kernels exhibited high fixed carbon region at the respective temperature. At the optimum condition of temperature 280°C and particle size of 0.025 mm, the torrefied material produced is viable to be promoted at a larger scale.


**Keywords:** Torrefaction, Biomass, Temperature, Particle Size.

## 1. INTRODUCTION

Nowadays, the increasing demands on fossil fuel have awakened the oil and gas industry due to the limiting resources of its reserved. Apart from that, concerning the environmental effect, continuous and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by $CO_2$. In order to meet rapidly increasing energy demand as well as to conserve the world, alternative energy sources should be utilized effectively.

Of all alternative energy resources, biomass has a great potential today and in the future, since it is renewable, in contrast to the nature of the fossil fuels [3]. Biomass is seen as one of the best options that can provide a renewable fuel which can be utilized in a range of energy conversion technologies and also has the added advantage of being $CO_2$ neutral [7]. It is biodegradable and non-toxic. It has low emission profiles and thus is environmentally beneficial. There are many biomass resources available in the world and one of those is rubber seed kernel which is not edible. Rubber seed kernel can be converted into source of energy via biomass processes which are torrefaction and fast pyrolysis.

Peninsular Malaysia, comprising 12 of the 14 states in the Malaysian federation is among the world's most important rubber growing area. Rubber is also grown in Sabah (formerly North Borneo) and Sarawak, which, known together as East Malaysia. Altogether Malaysia produces almost 20% of the world's natural rubber. More than half Malaysia's rubber comes from thousands of privately owned small landholdings, which are usually about 2 hectares. The rest is grown on big estates owned by various companies; each can cover over a thousand hectares. Altogether, Malaysia has 1.7 million hectares of rubber plantation [19]

Torrefaction produces solid product of carbon sources material like biomass, retaining approximately 70% of the initial weight and 80%-90% of the original energy content [4]. As the temperature increases, biomass begins to be brown and gives off moisture, carbon dioxide, and large amount of acetic acid with some phenols [5].

This project studies the possibility of using rubber seed kernel to produce biofuel via torrefaction. As the annual rubber seed production in Malaysia is high, this makes the source unlimited and renewable throughout the years.

## 2. METHODOLOGY

The biomass waste of rubber seed kernel was obtained from a local supplier. It was dried at 110 °C for 2 hours, then grinded into smaller particles and finally sieved into two mesh sizes i.e. 250 and 500 μm, respectively. Each sample weighing 10 grams underwent torrefaction process where it was heated for 1.5 and 3 hours respectively in a special furnace called Fixed Bed Activation Unit at two different temperatures i.e. 240 °C and 280 °C, in the presence of inert nitrogen. The torrefied material was then cooled to room temperature and reweighed to determine the weight loss from the material due to the torrefaction process.

### 2.1 Sample Analysis

### 2.1(a) Moisture Content Analysis
The moisture content of material was analyzed by using Halogen Moisture Analyzer (HMA). It is an important indication and method to determine the moisture content loss of the biomass sample after undergoing torrefaction or pyrolysis process. The measurement was conducted two times, which are before and after the torrefaction or pyrolysis process.

### 2.1(b) Ultimate Analysis
The ultimate analysis was conducted by using Carbon Hydrogen Nitrogen Sulphur (CHNS) Analyzer. The samples were weighed around 1.5 milligrams to 2.0 milligrams in aluminium container prior entering the analyzer. The analyzer will then display the composition of that carbon, hydrogen, nitrogen, and sulphur contained within the material in percentage value. The oxygen composition is calculated by difference method.

### 2.1(c) Calorific Value Analyses

The calorific value of biomass sample before and after undergoing torrefaction or pyrolysis was determined using Bomb Calorimeter by IKA which technology approved by DIN 51900, ASTM 240D, ISO 1928 and BSI.

### 2.1(d) Weight Loss Analyses
The weight loss of the heated material is determined by weighing the initial and final mass of the sample before and after heating.

Percentage of weight loss = $\dfrac{A - B}{A}$ x 100

Where;
A: weight of the sample before heating, g
B: weight of the sample after heating, g

The moisture content is determined by establishing the loss in the weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample weight, and equipment specification. The percentage of moisture in the analysis sample is calculated as follows:

Percentage of moisture = $\dfrac{A - B}{B - C}$ x 100

Where;
A: mass of container and wet sample, g
B: mass of container and dry sample, g
C: mass of container, g

### 2.1(e) TGA Analyses
The proximate analysis conducted by using Thermal Gravitational Analyzer (TGA). The samples are weighed approximately 5mg to 10mg to fit the small pan of TGA. A set methodology was programmed to the TGA controller to ensure the result obtained aligned with the objectives. The method was set as followed:

  i.    Hold for 1 minute at 50°C
  ii.   Heat from 50°C to 800°C at 40.00°C/min with nitrogen flow rate of 20ml/min

Next, the TGA procedure was followed to complete the analysis. The outcome of the analysis will be displayed in term of decomposition regime graph, and then further analysis will be carried on. TGA is used to determine elements of:

  i.    Moisture content
  ii.   Volatile matter
  iii.  Fixed carbon
  iv.   Ash

## 3.  RESULT AND DISCUSSION

### 3.1   Sample Pretreatment

The drying process took place in an oven having muffle temperature of 110°C for more than two hours. The weight of the biomass sample is taken periodically every 15 minutes until the weight is constant. Figure 1 shows a gradual decrease in the weight of the sample is observed for the first two hours. After two hours, the rate of weight loss is lower and remains constant until 24 hours.
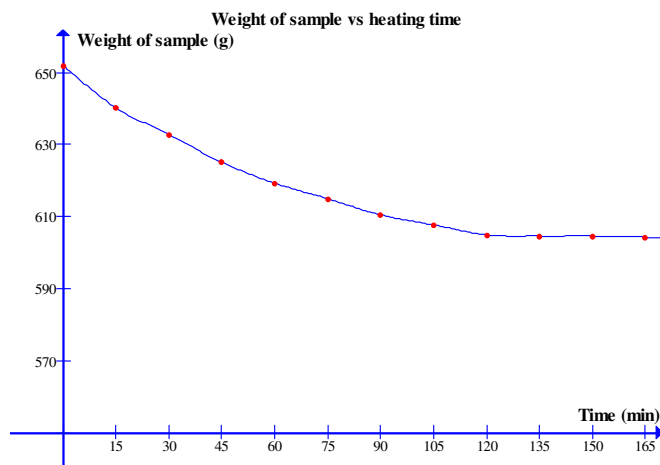
**Figure 1:** Weight of rubber seed kernel versus heating time

Referring to Alves and Figueiredo [19], when heat is applied into wood particles, it will begin to dry more intensely at the outer boundary with the increasing temperature. The bound and free water tend to move outwards by convection and diffusion, while some may migrate towards the inner, which is the colder part of the solid where condensation occurs. However, as the drying process proceeds, the penetration of heat into the deeper part of the wood particle and moisture movement to the surface becomes harder due to material resistance. This results in the rate decrease of drying.

This concept can also be applied to the pre-treatment process of rubber seed kernel via drying in the oven. This is because, the concept applied is similar in both cases where heat is applied to the wet raw material in order to remove the bound and free water; in this case; rubber seed kernel. The drying is considered finished when the weight of sample remains constant. During this time, it is assumed that all bound and free water have been released. The rate of weight loss gradually decreases because as time goes by, the moisture content in the raw material becomes lower and lower. Therefore, less water is removed from the sample from time to time throughout the drying period until the weight remains constant.

### 3.2    Sample Analysis

Sample analysis before heating is carried out using CHNS Analyzer. The equipment only evaluates the carbon, hydrogen, nitrogen, and sulphur composition of the material. The remaining composition of the material is oxygen which is determined by difference method. In this case, oxygen value is 50.25%. This is done to compare the composition of the sample before and after heating. From this analysis, the major components of rubber seed kernel initially are carbon and oxygen. This result will be compared with the composition obtained from the samples undergoing the heating process.

From CHNS analysis also, it is found out that hydrogen, nitrogen, and sulphur are minor components of rubber seed kernel. The percentages of those components are acceptable after comparison made with other torrefied biomass wastes used as solid biofuel production such as beech, willow, larch, and straw [9] as shown in the Table 1.

Apart from the CHNS analysis, the initial calorific value of the raw sample is also determined using bomb calorimeter before the heating process takes place which is 17218 J/g. From the first look also, rubber seed kernel is seen as a good viable source of alternative solid fuel as by nature.
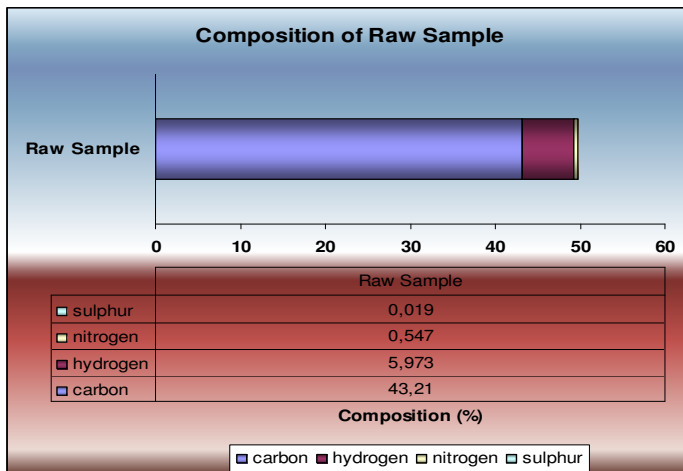
**Composition of Raw Sample**

| | Raw Sample |
|---|---|
| □ sulphur | 0,019 |
| □ nitrogen | 0,547 |
| ■ hydrogen | 5,973 |
| □ carbon | 43,21 |

**Composition (%)**

□ carbon ■ hydrogen □ nitrogen □ sulphur

**Figure 2:** Composition of fresh rubber seed kernel

| Biomass Type | % Carbon | % Hydrogen | % Nitrogen |
|---|---|---|---|
| Beech | 47.2 | 6.0 | 0.40 |
| Willow | 47.2 | 6.1 | 0.34 |
| Larch | 48.8 | 6.1 | 0.10 |
| Straw | 44.3 | 5.8 | 0.40 |
| **Rubber Seed Kernel** | **43.2** | **6.0** | **0.55** |

**Table 1:** Compositions of hydrogen and nitrogen of torrefied biomass wastes

### 3.3 Experimental Results
### 3.3(a) Color Changes
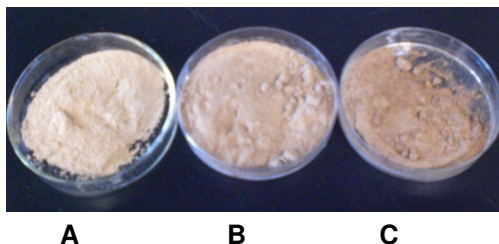


**A       B       C**
**Figure 3:** Colour change of samples

A is the sample taken before heating process takes place. B and C are samples observed when heated in the fix bed activation unit at temperature 240°C and 280°C respectively. From Figure 3, the colour of samples becomes darker as the temperature of heating increases. According to J. Bourgeois [5], he has proven from his research that as temperature increases, biomass begins to be browned off and gives off moisture, carbon dioxide and large amounts of acetic acid with some phenols. The colour turns into darker due to the increasing carbon content of the heating sample.

### 3.3(b) Effect of Duration, Temperature and Particle Size to Weight Loss
During torrefaction process where sample is heated at temperature range between 225°C to 300°C, two main reactions occur which are dehydration and carbonization. In general, higher process temperature and longer time period result in lower production of solid product as more biomass is converted to gas and liquid. This is proven by research done by Farah Dila [7] where longer reaction time from 1.5 hours to 4 hours produce higher liquid yield for pyrolysis process and lower product yield. This can also be applied to torrefaction. However, the portion of liquid

and gas produced during torrefaction is lower compared to pyrolysis due to the difference in temperature ranges.
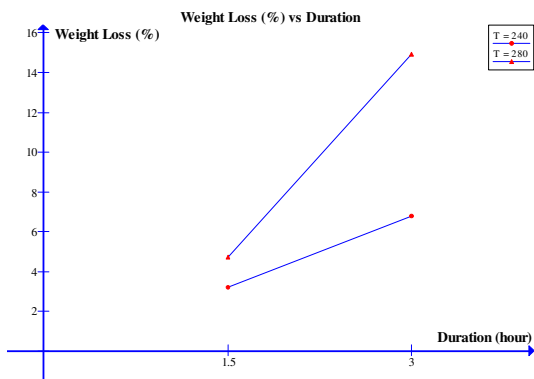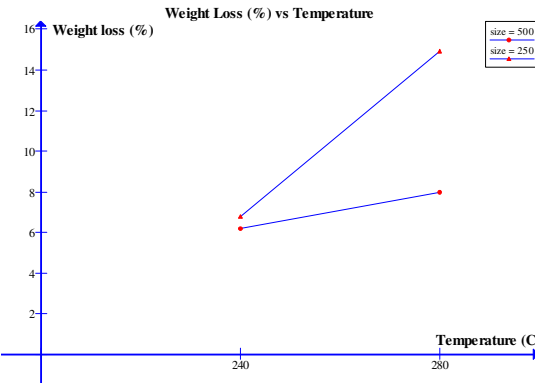


**Figure 4:** Effect of duration



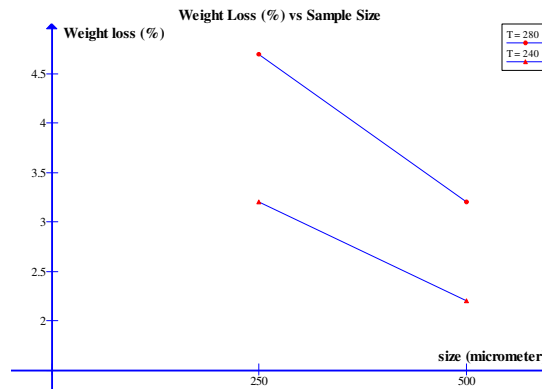**Figure 5:** Effect of Temperature



**Figure 6:** Effect of Size

By referring to Figure 4, heating time gives a massive impact to the weight loss. As the reaction time is increased, more weight loss is observed. This is expected because, as time goes by, more water in the sample, which constitutes as the major contribution to the mass, is evaporated leaving behind the solid. This is true since the greater the size is, the longer time is needed to convert to the torrefied material.

From Figure 5, it is observed that, as the heating temperature is increased, the weight loss is also increased. When the biomass is heated, drying process takes place first. Further heating removes new amount of water from chemical reactions through thermo-condensation process, which occurs at temperature above 160°C, as well as the formation of carbon dioxide gas begins. This results to the weight loss of the sample as the heating process takes place. As the heating temperature is increased, the rate of evaporation of water in the material becomes higher, thus the weight loss increases. That is why it is observed that, at temperature 240°C the weight loss is 8.0% while at temperature 280°C, 14.9% weight loss is exhibited which is nearly two times of the previous value.

Referring to Herlina [6] and Farah Dila [7], both concluded that higher temperature promotes higher evaporation and changes the solid to gaseous form. This is because, more cracking occurs at higher temperature resulting in higher gas yield and lower solid yield. From this study, the highest weight loss occured at temperature 280°C and reaction time of 3 hours with the smaller particle size of rubber seed kernel.

As the size increases, weight loss is decreased. This is because, as the size of particles increase, the surface area exposed to the heating process decreases. Therefore, less water can be

evaporated as the process takes place. This is within expectation because as time goes by within 1.5 hours, there are still more water evaporated, leaving behind the solid. The greater the size is, the longer time is needed to convert to torrefied material. This is also proven by the moisture loss analysis which exhibits higher value in smaller sample size compared to the bigger one which will be discussed further in the next part.

Apart from that, with less surface area exposed, less contact area is established for the reaction to take place, either for dehydration or degradation of biomass sample. As a result, less degradation of solid to convert to gas exhibits lesser weight loss for bigger sample size and vice versa.

### 3.3 (c) Effect of Duration, Temperature and Particle Size Composition

Figure 7 shows the comparison of the rubber seed kernel composition before and after heating at different duration of time. The torrefied materials still exhibit carbon and oxygen content as the major composition while others remain as minor ones. However, as the raw material undergoes heating process and the heating duration increases, the carbon content also increases. Thus, the torrefied material contains higher percentage of carbon compared to the raw material. In addition, the increase is more significant at longer time period and higher temperature. In contrast, the oxygen content become lesser as the duration is longer and carbon content is higher.
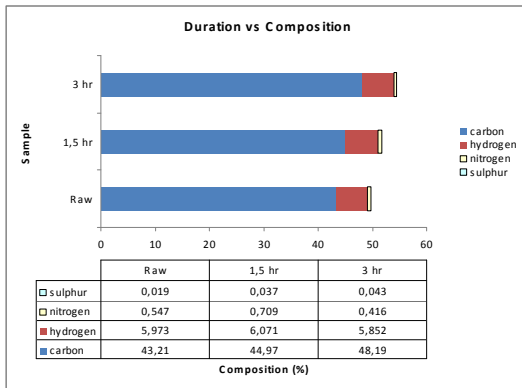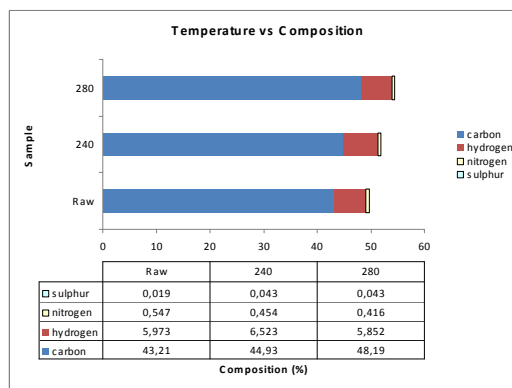


**Figure 7:** Effect of Duration

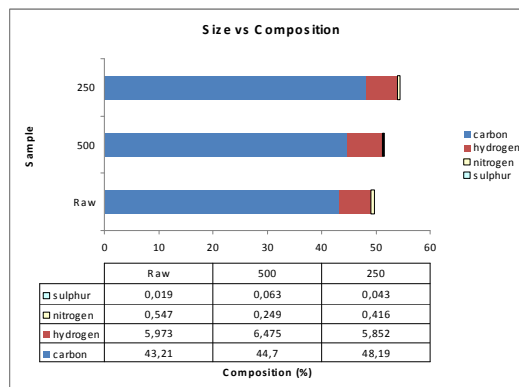**Figure 8:** Effect of Temperature



**Figure 9:** Effect of Size

According to Patrick *et. al* [20], in torrefaction process biomass loses relatively more oxygen and hydrogen compared to carbon. Water from dehydration is the best example, but also all organic reaction products (acetic acid, furans, methanol) and gases (mostly $CO_2$ and CO) contain a considerable amount of oxygen. Therefore, torrefied material has higher carbon content and

lower oxygen content compared to the raw sample. Due to removal of water and $CO_2$, the composition of torrefied material has a lower Oxygen/Carbon and Hydrogen/Carbon ratio.

As longer duration takes place, more water and gases are removed from the biomass sample, therefore lower oxygen content exhibits lower Oxygen/Carbon ratio which is 0.9 and thus the torrefied product becomes a better biofuel. However, the common Oxygen/Carbon ratio according to Prins [8] is 0.69 to 0.72 which is quite low compared to the result obtained. It can be concluded that, the oxygen content in the torrefied product is still high to be accepted as a good biofuel.

Figure 8 shows nitrogen and hydrogen decrease while the carbon content exhibits higher composition at higher temperature. In conjunction with that, the oxygen content decreases as the temperature increases. In this study, the highest percentage of carbon content is at 280°C, which is the maximum temperature of the experiment.

Rapid breakdown of the biomass structure increases tremendously at higher temperature, leaving the decreased amount of torrefied product as discussed in the weight loss section previously. The reason is, at high temperature, the reaction achieves complete conversion to form more stable form of solid. Besides, at higher temperature, greater amount of raw material is oxidised with other component exist in it. With high burn-off rate, most of the original sample has undergone complete reaction with oxygen. Therefore, more water and gas are released from the biomass sample as the temperature increases. That is why hydrogen and nitrogen components decrease while the carbon content increases.

The decrease in Oxygen/Carbon ratio from 1.2 to 0.9 as the heating temperature increases exhibit better biofuel. However, as discussed earlier, the ratio does not meet the torrefied wood ratio which is from 0.69 to 0.72. In addition, the changes in composition is significant only at higher temperature and longer time period as the increase of carbon content is higher compared to at lower temperature and shorter time period.

Figure 9 shows the relationship between the particle size and composition of torrefied material. Theoretically, the lower the particle size, the higher the surface and contact area exposed to the heating process as well as the reaction to take place. High surface area can induce more evaporation of water and other volatile products such as CO and $CO_2$ to leave the sample quickly and thus, resulting in lower volatile matter in the product and higher fixed carbon content. The removal of those water and volatile matter reduces the hydrogen and nitrogen content as well as Oxygen/Carbon ratio which results to better biofuel product. Furthermore, the result is more significant at longer heating time as the change in composition is more compared to at shorter heating time.

From the analysis done to the torrefied products composition with the effect of reaction time, temperature, and sample size, the best biofuel product exhibited is at 280°C for 3 hours reaction time of 250 μm sample which has 48.19% carbon with 0.9 Oxygen/Carbon ratios.

### 3.3 (d) Effect of Duration, Temperature and Particle Size to Moisture Loss

Basically, all the effects studied for moisture content loss are similar to weight loss behaviour. Figure 10 shows the effect of reaction time to the moisture loss of the torrefied material. It is observed that as the reaction time increases, the moisture loss also increases. This is because, as the heating process takes place, water is removed from the biomass sample. Thus, as more time left for the biomass to be heated, more and more water can be removed as time goes by.

Apart from that, the moisture content loss is also affected by temperature where the higher the temperature, the higher the moisture loss is. This is proven by Figure 11. Referring to Zanzi *et. al* [9], at temperatures between 180°C and 270°C an exothermically reaction takes place, as well as the degradation of hemicelluloses goes on. Biomass begins to be brown and gives off moisture, carbon dioxide and large amounts of acetic acid with some phenols. As the temperature

increases, more water can be removed from the biomass sample due to higher heating rate applied to the sample. Therefore, higher moisture content is lost at higher temperature. However, from the graphs, it is observed that time is not really significant as the changes in moisture loss at longer duration are very less compared to other parameters.
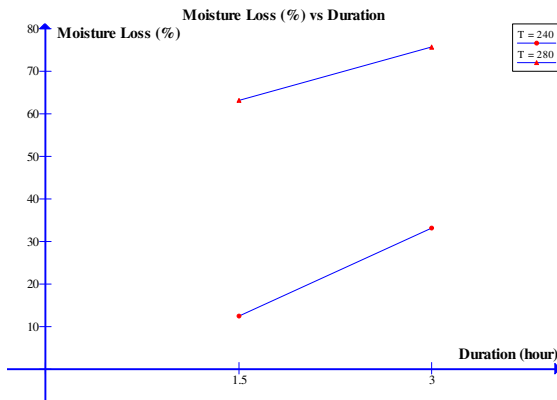

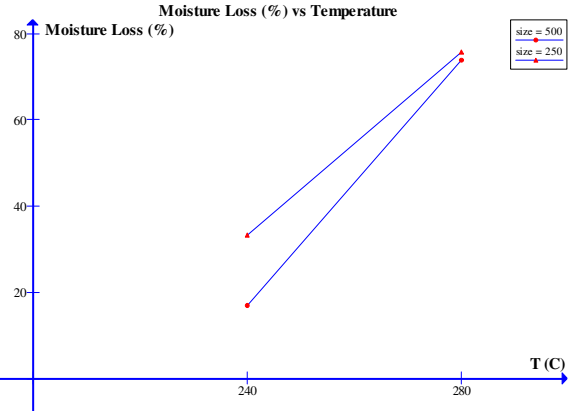
**Figure 10:** Effect of Duration
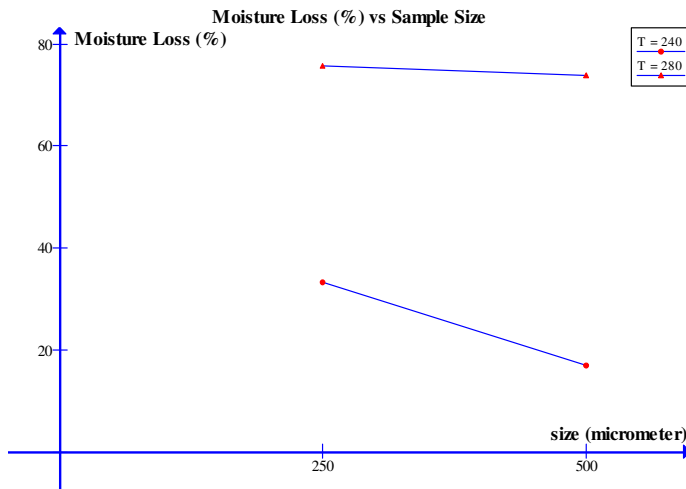


**Figure 11:** Effect of Temperature



**Figure 12:** Effect of Particle Size

The third parameter studied is the effect of sample size to the moisture loss. The smaller sample size exhibits higher moisture content loss. This is due to higher surface area exposed to the hot environment during the heating process. Higher surface area removes more water from the sample thus induces higher moisture content loss.

From the analysis done on the moisture content, it is observed that, the moisture content loss increases with temperature and reaction time. However, for sample size, moisture content loss decreases with the increase of sample size. The maximum moisture content loss is at 280°C for 3 hours long of 250μm sample size which is 75.62%. Thus, the properties of the product can behave like hydrophobic nature that has resistance to absorb water again.

### 3.3 (e) Effects of Duration, Temperature and Particle Size to Calorific Value

For calorific value analysis, the reading was taken by bomb calorimeter before and after torrefaction process. The raw sample calorific value before heating is 17218 J/g.
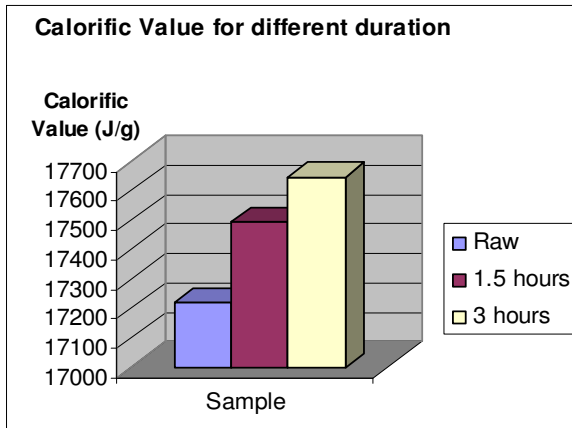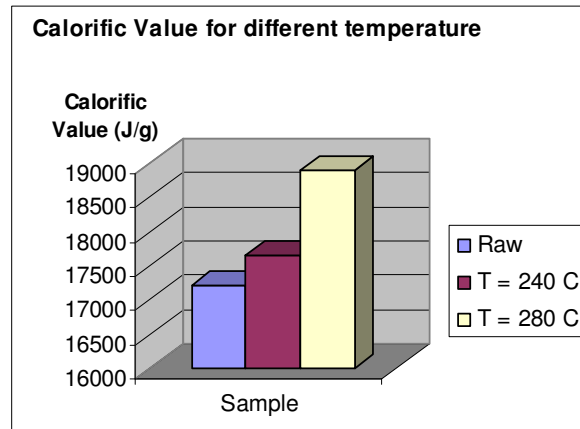
**Figure 13:** Effect of Duration
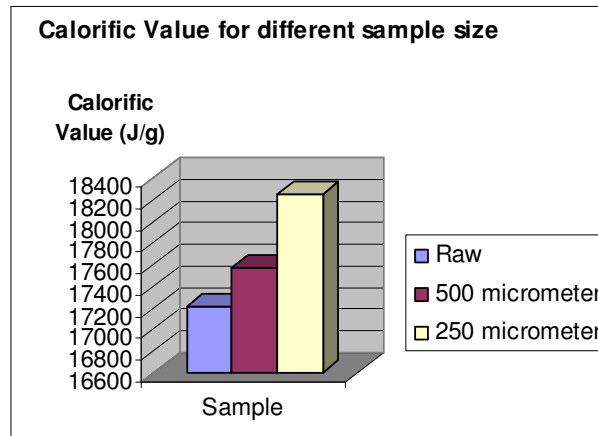


**Figure 14:** Effect of Temperature



**Figure 15:** Effect of Particle Size

Referring to Figure 13, 14 and 15, it is clearly seen that, the torrefied materials can retain the calorific value almost 100% of the initial value. The research done by Itebe *et. al* [23] that torrefaction process can retain up to 90% of the original energy is proven. In fact, the values increase with the increasing heating temperature and reaction time. However, the calorific value decreases with the increasing sample size. The higher the calorific value, the better the torrefied material will be as it provides enough energy to be an alternative fossil fuel.

According to Patrick *et. al* [20], an increase of the calorific is the main result from the increasing carbon content and decreasing O/C ratio with the removal of water and gas during torrefaction. Depending on the torrefaction conditions, the low heating value dry of biomass, specifically wood can be increased from 17-19 MJ/kg to 19 to 23 MJ/kg. Also referring to R. Zanzi *et. Al* [9], at higher temperature, the carbon content in the product increases while the contents of H and O decrease. H/C and O/C atomic ratios decrease with the temperature. As a result, the calorific value (CV) of the solid product increases with the temperature and at longer residence time.

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### 3.3(f)   TGA Analysis

Based on the TGA graph obtained, there are three main regions which are the moisture content represented by the first slope, the volatile matter represented by the second slope, and the fixed carbon represented by the third slope.
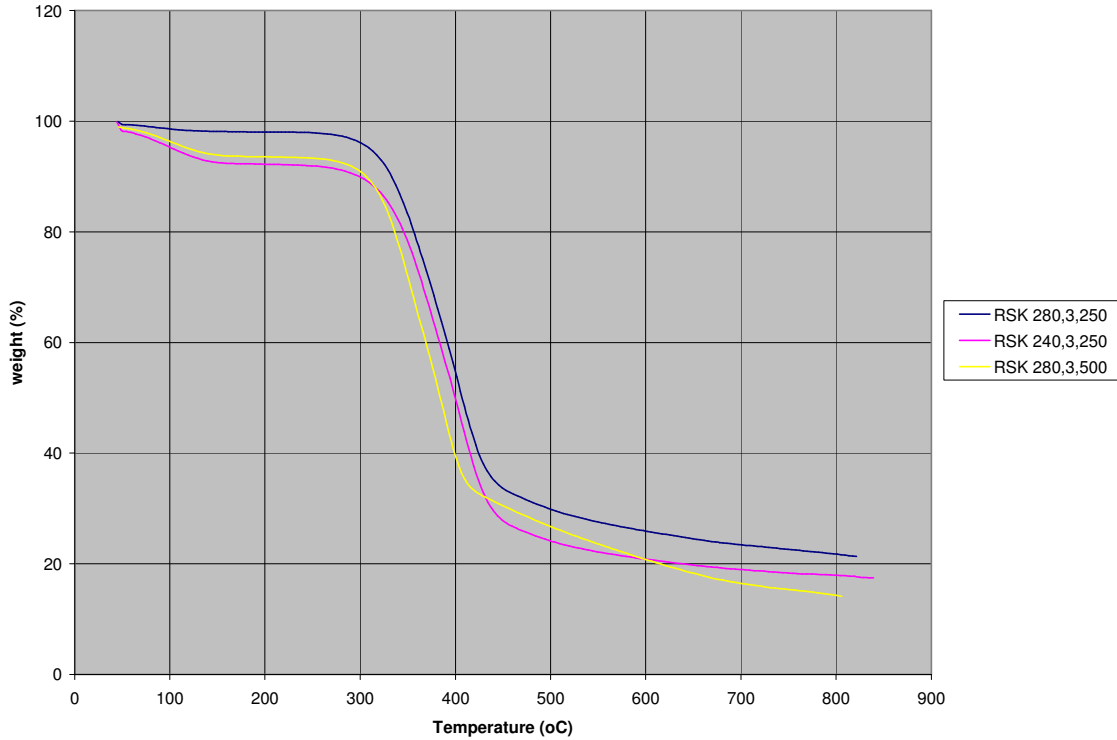


**Figure 16:** TGA graph of Rubber Seed Kernel for each torrefaction condition

From Figure 16, rubber seed kernel of 250 μm that torrefied at 280°C has shown lesser weight reduction than torrefied at 240°C in the first slope, which region referred as moisture content. Water content has been removed approximately 7% difference between the two conditions. However, for rubber seed kernel of 500 μm has shown to remove about 6% more than 250 μm sample condition. At same temperature condition bigger particle size gives off lower moisture content and lower burn off rate due to smaller surface area in contact to reaction.
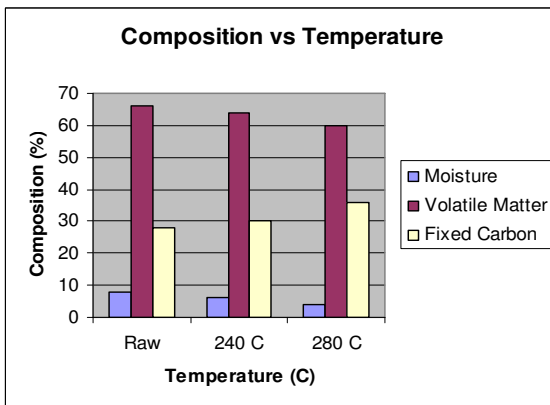


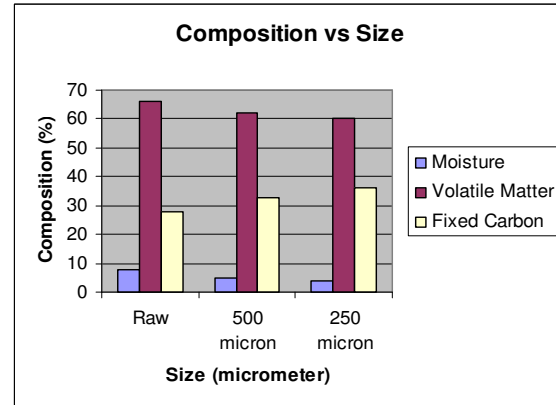**Figure 17:** Effect of Temperature



**Figure 18:** Effect of Size

From Figure 17, it is observed that, the moisture content and volatile matter compositions are reduced slightly as temperature increases. As discussed previously, the reduction is due to the increase in drying rate of the sample at higher temperature. Therefore, more water and volatile matter is removed at 280°C compared to at 240°C. The moisture content is the first element which is decomposed normally at temperature 100 °C to 150 °C where at this temperature the recondensation and depolymerisation occur to remove the moisture. It is important to analyze the behaviour of torrefied material as hydrophobic nature which has the resistance to absorb water. Thus, it is expected that the moisture content within the material has lower value for this purpose. As the temperature increases, more moisture can be removed from the torrefied material.

According to Herlina [6], the volatile matter indicates the by-product of torrefaction which includes non-condensable and condensable gases. High values of volatile matter are a result of high number of functional groups and low number of aromatic structures in organic materials. High volatile charcoal may be easy to ignite but it burns with heavy smoke. In addition, with high volatility, the material commonly will be less friable than ordinary material with low volatile matter. Devolutilisation occurs at temperature of 150 °C to 220 °C. The volatile matter should exhibit low value for it to be more friable. In addition, rate of volatile matter removal increases as temperature increases.

Apart from that, the fixed carbon content increases as heating process takes place and the value also increases at higher temperature. High fixed carbon content illustrates high heating capacity as discussed before. As the temperature increases, more volatile matter is being discharged to the environment which leads to a higher amount of carbon left in the torrefied product. However, the increase is very slight. As referred to Herlina [6], the fixed carbon should illustrate high content for torrefied materials. The fixed carbon content induces high calorific value and hence contributes to become potential fossil fuels for its high energy content. Normally, the carbonization for torrefaction occurs at temperature between 250 °C to 300 °C.

From the composition analysis done using CHNS Analyzer, the percentage of carbon content determined for torrefied material at 280 °C is 48.19%, while the fixed carbon analyzed by TGA Analyzer is 36%. Therefore, we can conclude that about 25% of carbon is burnt as volatile hydrocarbon and 75% of total carbon content remains. On the other hand, the percentage of carbon content of torrefied material at 240 °C, analyzed by CHNS Analyzer is 44.88% while the fixed carbon analyzed by TGA Analyzer is 30%. In total, the remaining carbon content left in the torrefied material is about 67% which is much lower compared to at 280 °C.

Figure 18 shows the relationship between size and the composition of the torrefied products. The results obtained shows that the moisture and volatile matter content decrease as the sample size decreases while the fixed carbon increases. High surface area of smaller sample size causes the evaporation of water and volatile matter to leave the charcoal quickly and thus, resulting in lower volatile matter in the product and higher fixed carbon content. This is due to the decrease in Oxygen/Carbon and Hydrogen/Carbon ratio. However, the changes are not so much that the amounts of those three components are almost equal for different sizes of material.

For the torrefied material with size of 500 μm, the CHNS Analyzer gives carbon content of 44.2% while the TGA Analyzer gives fixed carbon value of 33%. This shows that the remaining carbon left is about 75% while the rest is burnt as volatile hydrocarbon. In comparison, the torrefied material with size of 250 μm also has carbon content left of 75%. This proves that the particle size of the sample does not give much effect to the torrefied material.

## 4. CONCLUSION

It is observed that temperature, particle size, and residence time do affect the physical and chemical characteristics of the torrefied products. Almost 100% of the calorific value in all the samples can be retained or increased by up to 10% from the original waste calorific value. From the Thermo Gravimetric Analysis (TGA), rubber seed kernels exhibited high fixed carbon region

at the respective temperature. At the optimum condition of temperature 280°C and particle size of 0.025 mm, the torrefied material produced is viable to be promoted at a larger scale.

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