Characterization of Waste Tire Rubber and Standard Malaysian Rubber (SMR 20) as Potential Raw Materials for Pyrolysis

by

Siti Suraiya bt Mohamed Rahmat

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Bandar Seri Iskandar

32610 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr Filipe Manuel Ramos Paradela)

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TRONOH, PERAK

January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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SITI SURAIYA BT MOHAMED RAHMAT

ABSTRACT

Rubber tire is a very useful product that is mainly used in the automotive industry. However, the used rubber tires that are no longer useful for vehicles due to punctures or wear become a problematic waste. One way to reduce the waste rubber tire is by recycling the product. Different methods have been developed over time to find the best way for recycling the waste tires. One of these methods is pyrolysis that allows the conversion of the waste tire rubber into valuable chemical products. This project evaluated the use of the rubber tire as a potential raw material for pyrolysis. The samples of waste tire were pyrolysed at different temperatures, to see the effect of temperature on the product yield. The temperatures used for the pyrolysis were 450^0C, 500^0C, and 550^0C. Each set of temperature will be tested three times to get the average of product yield. From the pyrolysis experiment, it shows that the best result for oil yield is at 500^0C and decreasing after the temperature is increased. Before the pyrolysis of waste tire, elemental analysis was conducted to find the initial composition of waste tire. The elemental analysis was conducted using CHNS for carbon, hydrogen, nitrogen and sulfur content. The analysis showed that the sulfur content in the waste tire is 2.30% and the main component is carbon, with the composition of 83.57%. Thermal decomposition of waste tire was tested using thermo gravimetric analysis (TGA), which showed that the waste tire completely decomposes between 450 to 500^0C and Py-GC-MS was used to obtain the composition of waste tire, mainly showing that the highest component of the waste tire is 1,3-butadiene. The yield of the products of waste tire pyrolysis, the char, oil, and gas, were calculated for the yield for each temperature and the yield vs. temperature graph was plotted. The composition of the product was tested based on the temperature and product yield. The gas yield was analyzed using GC-TCD for the composition of non-condensable gases. The char and oil was tested using CHNS for the composition of carbon, hydrogen, nitrogen and sulfur.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Rubber tires have been used since the production of automobiles began. During that era, the production of waste tires was not a big issue since the production of vehicles was not as significant as today. As time goes by, the uses of rubber have been increasing with applications such as conveyor belts, marine products, windshield wipers, and gloves. In modern day, rubber is widely used in various aspects in human life.

However, the increase in production of rubber tires as a consequence of higher manufacturing of vehicles such as car, buses, trucks and earthmovers, leads to a higher number of used tires that cannot be used due to punctures and wear constituting a problematic source of waste. One way to overcome this problem is by recycling the waste tires. One method that can be used for recycling rubber tires is pyrolysis.

Pyrolysis is a thermochemical process that decomposes the organic material at high temperatures. This process involves the change in physical and chemical compositions of the material. Pyrolysis of used rubber tires can be used to obtain different products such as steel and carbon black from the volatile liquid and gaseous compounds which can be used as fuel.

1.2 Problem Statement

Due to the increasing use of rubber tires in automotive industries, the waste tires from this industry are also increasing rapidly. This may be due to the punctured or worn tires that can no longer be used on the road. This causes a problematic waste due to the large volume produced, with tires containing components that are ecologically problematic. Several factors based on the material such as the quality of the tire, and the percentage of natural and synthetic rubber. The composition of material in different types of tires may cause the result to vary with others tires.

Therefore, during this project, the tire used throughout the project remains the same to keep it constant for the result and the analyzed data will be compared to the unused natural rubber.

1.3 Objectives of Study

In order to obtain data for the composition of the waste tire, elementary analysis was conducted. This research was carried out based on two objectives;

i. *To find and compare the characteristics of SMR 20 with the waste tire*
ii. *To find out if the waste tire has potential to be used as a raw material in the pyrolysis process.*

1.4 Scope of Study

In this study, the main subjects under investigation are;

i. *The composition of the product fractions derived from pyrolysis*
ii. *The analyze data from the experiment*

CHAPTER 2

LITERATURE REVIEW

2.1 Waste Tire Rubber

The disposal of waste tires has been one problematic issue as they contributed to ecological problems and their amount has been increasing for many years. According to R. Helleur et al. [1] Europe, USA and Japan generate more than $5x10^6$ tonnes of waste tires per year. They also added that the USA and Canada dispose waste tires on a ratio of one tire per person per year. There is also a rapid expansion of automotive industries in the South East Asia which leads to an increase in the disposal of waste tires. This rapid increase in the accumulation of tires all over the world has led to disposal becoming a potential hazardous situation.

There are several ways to reduce this negative effect on the environment, the use of available technologies for non-biodegradable waste [1]. A way to recycle the waste tires is by using conventional methods for energy recovery by simple combustion in cement kilns or by co-combustion with coal. Another way of handling the waste tires is by using the tire powder for low-value rubber goods. Unfortunately, this method does not solve the problem of increasing waste tires and is not highly profitable.

An appropriate way of handling the disposal or the recycling of waste tires should be to replace the problematic method of stockpiling waste tires in landfills that leads to breeding of mosquitoes and also to ecological problems since the rubber tires present a high potential hazard to environment. G. Mazloom et al. [3] also said that the disposal of the waste tires had become an environmental threat. Alternative processes for tire recycling have been considered, focusing on the valorization of the waste tires. A study by A. Quek and R. Balasubramaniam [2], mentions that only 13% of the waste tire is actually recycled into other products whereas the rest is disposed to the landfill or is dumped illegally.

This has also been acknowledge by W. Kaminsky et al. [4] in their research the authors stating that the disposal of waste tires become a major environmental problem in most countries. This is because the tires are designed to be extremely resistant to physical, chemical and biological degradation and they are also not readily decomposed under atmospheric condition. The most relevant way to reduce the stockpile of waste tires is by incineration and recycling. As the waste tire can produce valuable secondary raw material, recycling will be the best alternative and the best ecological approach.

Waste tires are an inhomogeneous form of waste and the composition of the tires varies depending on the grade, age and also manufacturer. Other than that, tires commonly contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cords. Carbon black that is contained in the tires is significant to strengthen the rubber and also protect the rubber from wear. Fillers are also present and work to make the rubber softer and more workable [5].

They also added that the waste tires dumped at the landfills can pose a potential fire hazard [4]. The presence of tires makes the fires very hard to extinguish and produce high contamination on the environment, atmosphere, soils, and also the groundwater. The combustion will produce toxic gases that release dangerous chemicals such as mutagenic and carcinogenic. For the authorities to perform incineration of waste tire, a proper and expensive air emission system is required.

According to O. Senneca et al. [6] the possibility of reusing the polymeric base of tires as a source of chemical stock and also liquid fuel had been explored and unsuccessful. Apart from that, the indirect material recycling had been proven to yield low quality product.

I. de Marco Rodriguez et al. [7] mention that waste tires are hard to recycle because of the complex nature of tires. The main component of tires rubber is a chemically cross-linked polymer and this made the tire neither fusible nor soluble and causes the tires to not be able to be remolded into other shapes without serious degradation. This was agreed by A. Quek and R. Balasubramaniam [2] where they stated that waste tire is difficult to recycle due to the properties which are resistant to natural degradation. The long chain polymer that exist in the tire, which is polyisoprene, polybutadiene, and styrene-butadiene copolymers that bond with sulfur makes the process of degradation complex.

They also added that tires are a complex mixture of very different materials which include rubbers, carbon blacks, steel cord and also other organic and inorganic minor components [7]. V. K. Gupta et al. [8] also mention that the rubber tires are composed of a mixture of polymers of styrene butadiene rubber, natural rubber and butadiene rubber and other additives such as carbon black and zinc oxide.

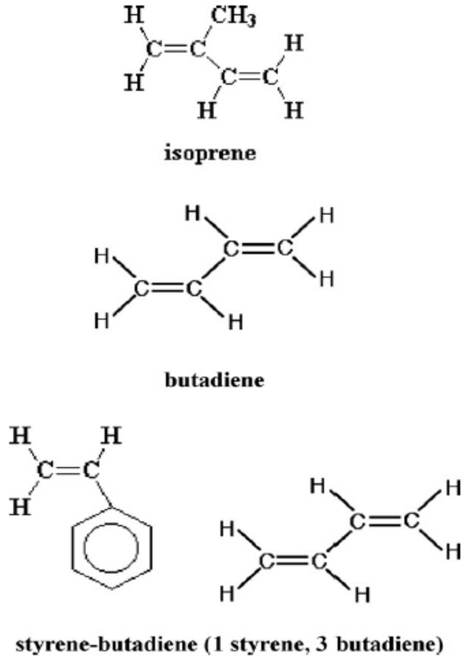


Figure 1: Rubber monomer in tires

From the research conduct by M. Miranda et al [9], they claimed that the waste tires have heating values higher than coal. If a proper technology is applied to the material, it can be a good source for energy and organic content recovery. They also added that the thermochemical process has the advantage of having high flexibility with respect to feedstock characteristics and allows converting different polymeric-base wastes.

Many alternatives had been tried along the years such as retreading, reclaiming, incineration and grinding. However, all this methods have their own limitations and drawbacks.

2.2 Pyrolysis

In the study by R. Helleur et al. [1] pyrolysis is an established process method but for rubber tires, pyrolysis is only used on a laboratory scale and in industrial trials as it is relatively new for this industry. It has the potential to transform the used tires into a useful recyclable product. Pyrolysis involves the decomposition of organic wastes at relatively high temperature in an inert atmosphere or under vacuum condition. They also added that this pyrolysis process can result in useful recovery apart from being environmentally friendly. The typical pyrolysis can recover up to 33-38 wt% pyrolytic char, 38-55 wt% oil and another 10-30 wt% gas fraction [1].

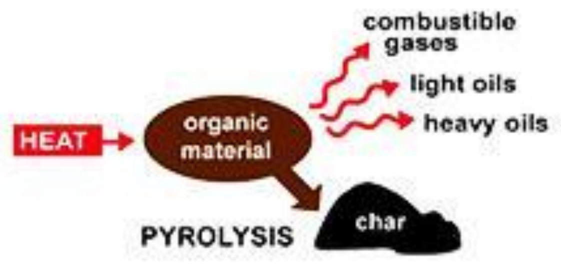


Figure 2: Pyrolysis of organic material

There are various waste tires pyrolysis systems such as fluidized bed, shaft furnace, extruder and rotary kiln. They also mention that to avoid increased cohesion force between the carbon particles in the char, and also poor dispersion ability in rubber production, they suggest a maximum temperature of 600^{0}C [1].

Pyrolysis is one of the most promising techniques for reclaiming fuel and other valuable products because it can yield solid, liquid and gas product altogether. The solid product of this process is usually called char and can be restored to carbon black, which can constitute a high-value market [2]. The thermogravimetric analysis (TGA) was often used in the pyrolysis process. It has the benefits of;

i. Minimizing the experimental uncertainties,
ii. Continuously assessing the kinetic over an entire temperature range

Tire pyrolysis is mainly dependant on the composition of the tire and the bonding between the polymers which makes the tire resistant to change. Therefore, this factor will influence the thermal degradation and operating condition of the pyrolysis process.

There are several parameters that affect the rate and products of pyrolysis. A. Alsaleh et al [5] have outlined parameters such as temperature, which plays an important role in pyrolysis as it affects the distribution of gas, liquid and solid phase. Other important parameters include heating rate, feedstock composition and particle size. Heating rate affect mainly on the degradation rate as well as the maximum volatilization of the material. The particle size affects the end products of the pyrolysis to ensure a uniform heating throughout the particles and achieve a complete converted desirable products.

S. M. Guilermo et al. [4] mention that the amount and specific characteristics of the fractions may vary depending on the process temperature and reaction time. The components such as pyrolytic oils (a mixture of paraffin, olefins, and aromatic compounds) can be used directly as a fuel or can be added to a petroleum refinery feedstock.

They also added that pyrolytic gas contains high concentration of methane, butadiene and other hydrocarbon gases which have high calorific values sufficient to heat the pyrolysis reactor. The carbonized residue which is pyrolytic char can be used as the precursor for activated carbon manufacture [4]. In a study by G.C. Choi et al. [10] they said that pyrolytic oil from the waste tires was a potential source of chemical feedstock for industrial processes such as benzene, toluene, xylene and limonene.

Due to variation in the tire rubber type and additives, the chemical compositions of pyrolysis oil produced during pyrolysis were complex. The main component of pyrolysis oil is aromatic compounds with percentage of 65-79 wt. % as high temperature favors the formation of aromatic compounds [10]. It is also stated by G.C. Choi that pyrolysis oil produced from the process has high calorific value and possess the same property as commercial heating oil which make pyrolysis oil one alternative to conventional fuel.

In the study by P.T. Williams and S. Besler [5], they discuss about the thermogravimetric analysis (TGA) which has been used to study the pyrolysis process of different type of waste material. TGA measures the loss in weight of a sample as the temperature is raised at uniform rate. It has been used to determine the devolatilization characteristics of a raw material. TGA is an appropriate analytical tool to use in pyrolysis of waste tires as the physical and mechanical properties of mixed rubber exist in the tires are sensitive to small deviations in the amount of single type of polymer content in the tires [6]. Thus, it is necessary to apply proper analytical tools to monitor the blend of rubber composition.

It is also used to provide the net weight loss and the calculation of kinetic parameters although based on simplified assumptions which do not correspond to the complex chemical reaction in the thermal degradation of the sample. Besides, the data provided useful assessment of reaction parameters such as temperature and heating rate [5].

In a paper by I. de Marco Rodriguez et al [7] they stated that pyrolysis can be considered as a non-conventional method for recycling waste tires and appropriate for complex material as the tires cannot be remolded. In the process of pyrolysis, the organic volatile matter of the tires will decompose to low molecular weight products, liquids, or gases which are useful as fuels or chemical sources. Meanwhile the inorganic component and the nonvolatile carbon black remain as the solid residue and can be recycled in other applications [7].

CHAPTER 3

METHODOLOGY

3.1 Research Methodology and Project Activities

The methodology for conducting this research is by conducting experiments and analyzing the data obtained. As the objective of this project is to get the composition of the tire using analytical equipment and to establish if it is a suitable raw material for pyrolysis, the result obtained from this experiment can be used to compare with other literature results derived from a similar research. The results collected can hence further enhance the research and development on the waste tires management.

The rubber tire was bought form the local automotive shop located in Seri Iskandar, Perak and cut according to the length needed. The elementary analysis of the waste tire will be conducted using CHNS elementary analysis which is essential to analyze the elemental composition of tires, thermogravimetric analysis (TGA) for thermal analysis and bomb calorimeter to measure the heat of combustion. Other elemental testing that was conducted is moisture content and ash content of the tire. The rubber tire was cut into strips of about 1-2 mm and also crushed into powder for the sample testing. The same methodology was applied to the Standard Malaysian Rubber (SMR 20) for sample testing. The samples will underwent several tests to compare the results and to analyze the data obtained.

The pyrolysis reaction was then conducted using a drop-type pyrolyzer. A further analysis will be done to analyze the composition of the pyrolysis products. The char and oil yield will be analyzed with CHNS for the char and oil elemental composition. Whereas the gas yield was analyzed using GC-TCD to obtain the composition of gas.

3.2 Experimental Procedures/Approach

The figure below shows the general experimental procedures that were implemented in this research project.

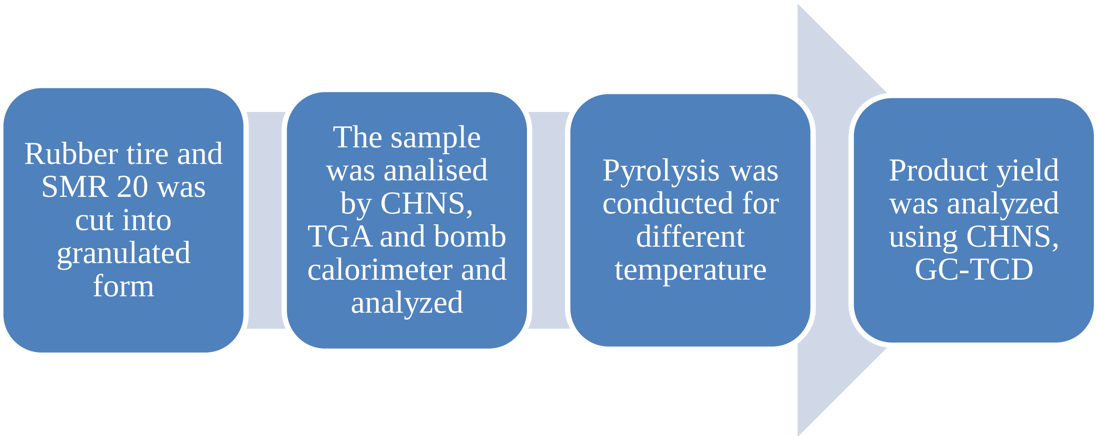


Figure 3: Project Flowchart

3.2.1 Experiments and Equipment Needed

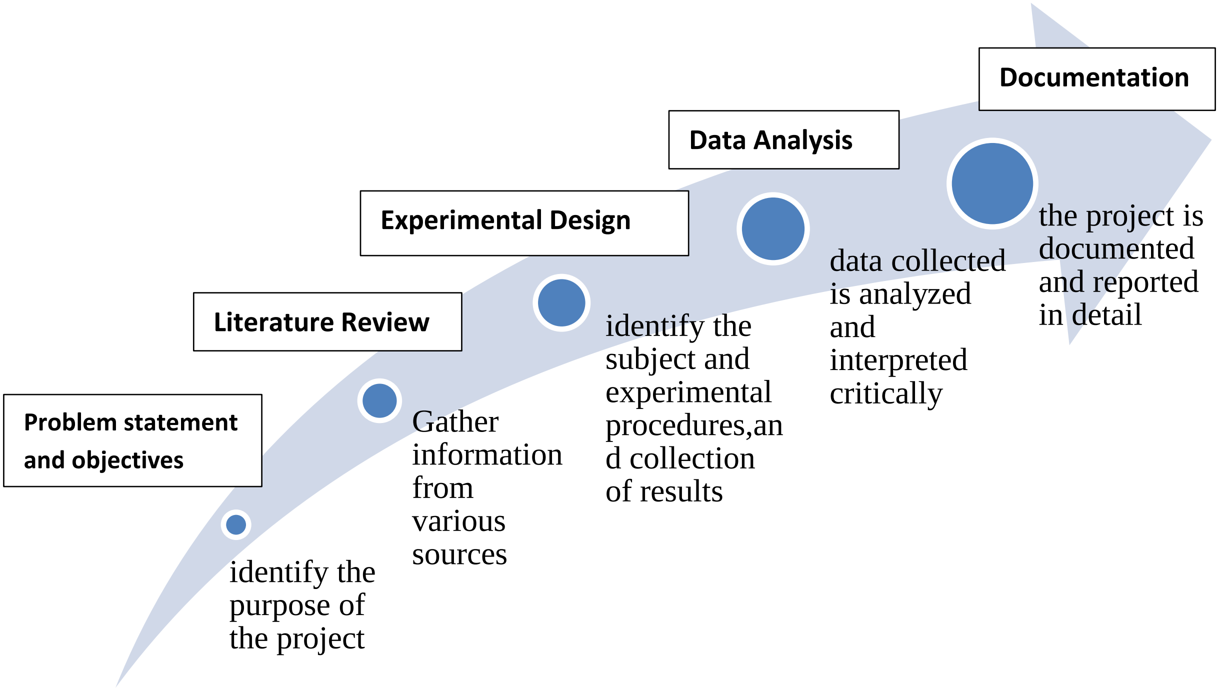
Table shows the experiments and equipment needed during this study.

Experiment	Equipment
Thermal analysis of waste tire	• Thermogravimetric analysis (TGA)
Elemental composition of waste tire and products	• CHNS
Heat of combustion analysis	• Bomb calorimeter
Pyrolysis	• Drop-type pyrolyzer
Primary pyrolysis	• Pyrolysis-GC-MS
Composition of non-condensable gas	• Gas Chromatography-Thermal Conductivity Detector (GC-TCD)

Table 1: Equipment and Experiment for Project

3.3 Key Milestones

Several key milestones for this research must be achieved in order to meet the objectives of the project.



3.4 Gantt Chart

Table 2 and 3 below shows the gantt chart that need to be followed during this study for FYP I and FYP II respectively.

NO	DETAIL / WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Title														
2	Preliminary Research Work and Literature Review														
3	Submission of Extended Proposal Defence							●							
4	Oral Proposal Defence Presentation														
5	Buy waste tire sample														
6	Processing tire into granulated form														
7	Heat of combustion experiment														
8	Interim report writing														
9	Submission of Interim Final Report														●

Table 1: Gantt chart for FYP I

NO	DETAIL / WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Sample preparation															
2	Elemental analysis for moisture and ash content															
3	Elemental analysis for CHNS															
4	Pyrolysis experiment															
5	Analysis for pyrolysis product															
6	Submission of Progress Report								•							
7	Pre-EDX											•				
8	Submission of Draft Report												•			
9	Submission of Dissertation													•		
10	Submission of Technical Paper													•		
11	Oral presentation														•	
12	Submission of Project Dissertation															•

Table 2 : Gantt chart for FYP II

3.5 Preparation of samples

Figure 4: Waste rubber tire

Figure 5: Natural rubber (SMR 20)

The sample was prepared using waste car tire and SMR 20. The tire was cut into several parts and the metal wire section was removed. For this project, only rubber with fabric portion was used as it easier to cut and handle. To conduct the experiment, the material needs to be in small particle to ensure that all material is reacting in the process. The rubber was then granulated in a Tool Cutter and Granulator (KEF Motor A/S).

After the rubber has been granulated, it is noted that the rubber contained fiber that needed to be removed before conducting the experiment, else the result will show some deficiency. The fiber was then removed after granulate, because it is easier to remove as it disentangled from the rubber.

Tire was cut and steel removed

Rubber was cut to small pieces

Granulated rubber

Figure 6: Tire cutting flow

For SMR 20 sample, the sample was cut into small pieces as it easier to cut. As the SMR 20 is natural rubber, the pieces tend to stick when place together.

Figure 7: Small particle of SMR 20

3.6 Heat of combustion experiment procedure

For this experiment, sample from both waste tire and SMR 20 were used. This experiment was conducted using IKA –WERKE C2000 mainly to see the differences between the heat of combustion of waste tire and SMR 20.

i. The sample for waste tire was prepared for weight range from 0.5 to 0.7 mg.
ii. The samples were put in the bomb cup with ignition wool.
iii. The cup was put inside the bomb and placed in the calorimeter.
iv. The sample weight was key in on the panel and the experiment was run for 15 minutes.
v. After 15 minutes, wait until the reading was stable and the data was collected.
vi. The same procedure was repeated for SMR 20 sample.

Figure 8: bomb calorimeter

3.7 Elemental Analysis (CHNS)

This experiment was conducted to find the composition for carbon, hydrogen, nitrogen and sulfur in the sample. For this project, this experiment was conducted before and after the pyrolysis to see the different in composition of raw material and the product composition using Perkin Elmer Elemental CHNS/O 2400.

i. Weight the sample and put in aluminum foil.
ii. Place the sample accordingly in the provided container
iii. Start the instrument and calibrate
iv. Insert the sample container in the instrument and insert the input data and gas.
v. Record the result by using the software in the computer.

3.8 Pyrolysis experiment procedure

For pyrolysis, a drop-type pyrolyzer was used for fast pyrolysis of the sample. The assembly of the equipment is shown in Figure 9 [12]. The pyrolysis was conducted for both sample of waste tire and SMR 20. The temperature is manipulated for both samples at 450^0C, 500^0C, and 550^0C.

i. Prepare the sample with a desired particle size and quantity.
ii. Assemble the reactor.
iii. Prepare the condenser and fix a plastic bag to the condenser outlet to collect the non-condensable gases.
iv. Place the thermocouple into the reactor to measure the temperature inside the reactor. Make sure nitrogen supply tank is sufficient.
v. Switch on the equipment.
vi. Open the two valves and the valve to the gas bag to create inert condition.
vii. Utilize the vacuum pump which uses the water esperator and the nitrogen gas supply to create inert condition in the bag first and then immediately close the valve to the gas bag. Continue to do the inertizing for the reactor

and close the ball valve just above the reactor. Then place the sample and do the inertization and close the second ball valve.

viii. Calibrate the reactor temperature by adjusting the temperature of the heater through the temperature controller on the side.

ix. Drop the biomass into the reactor by opening the ball valve just above the reactor.

x. Consistently record the time until no more continuous smoke is detected and also record the final time when there is no gas pulse detected.

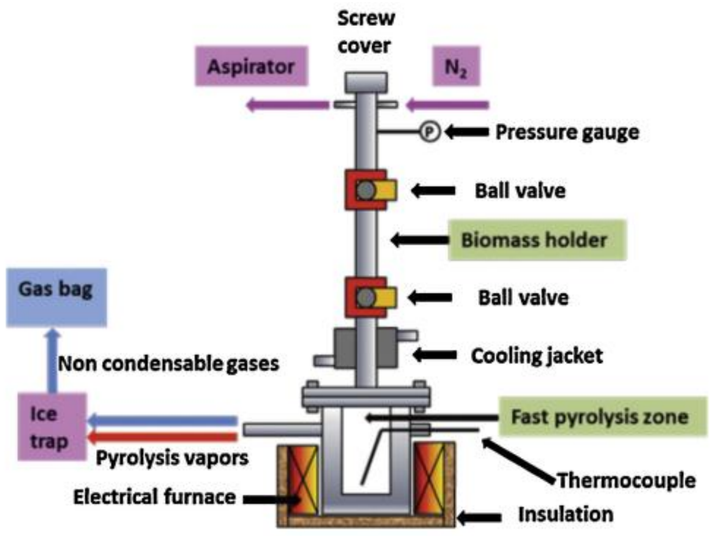


Figure 9: Schematic diagram of the drop-type fixed-bed pyrolyzer

3.9 GC-TCD Procedure

A Shimadzu GC-8A GC-TCD was used in the project to find the composition of the non-condensable gas yield after pyrolysis experiment. Calibrate the equipment before used. A Davidson Grade 12 Silica Gel was used for packed column for carbon dioxide detection and Molecular Sieve 5A packed column to detect CO, CH_4, O_2, and H_2.

i. The gas collected from the pyrolysis is connected to the piping of GC-MS
ii. Insert the data and parameter in the control panel of the computer before running the sample.
iii. Run the equipment for each set of temperature to get the retention times of the peaks.
iv. Save the experiment and collect the data for each temperature.
v. The result is then analyzed and the unknown gases are identify using the calibration curve for different gasses.
vi. The experiment is repeated if necessary.

3.10 Primary pyrolysis of waste tire

GC-MS with pyrolysis (Py-GC-MS) was used to find the composition of waste tire for primary pyrolysis. The Py-GC-MS is used to see the composition of the waste tire with pyrolysis take place using the equipment. The sample is send to the Centralized Analytical Laboratory to run the sample and the result is collected.

3.11 Thermogravimetric Analysis Procedure

TGA is conducted for the waste tire to find the thermal decomposition of waste tire. This is essential as the temperature for the degradation of waste tire affects the result of the pyrolysis.

i. Ensure that the nitrogen gas is connected to the instrument before starting the experiment.
ii. In the control panel, insert the necessary data for the sample.
iii. Using the tweezers, insert the sample in the empty crucible and weight the sample before starting the experiment.
iv. Installed the crucible in the TGA and start the experiment.
v. The heat rate is 30^0C/min. Wait until the desired temperature is reached. After reaching the temperature, wait another 30 minutes to let the TGA to cool down to room temperature.
vi. Save the data from the control panel.
vii. Repeat the experiment with another sample.
viii. The data is collected and the graph is tabulated.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Analysis of waste tire

4.1.1 Composition for waste tire and SMR 20 before experiment

Component	Waste tyre	SMR 20
Moisture (Mass %)	1.48	3.80
Ash (Mass %)	2.30	0.86
Fixed carbon	38.59	35.27
Calorific value (MJ/kg)	38.71	44.38
C (Mass %)	83.57	85.38
H (Mass %)	9.89	12.29
N (Mass %)	0.61	0.56
S (Mass %)	2.30	1.27

Table 4: Composition of waste tire and SMR 20 before experiment

Table 4 shows the elementary analysis for both samples. The proximate analysis was conducted to find the moisture content and ash content for the sample. Waste tire shows higher ash content than SMR 20 but lower moisture content than SMR 20. The ultimate analysis shows that both waste tire and SMR contain high carbon composition. Both of samples contain sulfur, but waste tire has higher sulfur content than SMR 20. The heat of combustion for both samples shows a higher value than the heat of combustion of fuel [11] which 34.08 MJ/kg for carbon and 29.6 MJ/kg for coal.

4.1.2 TGA experiment

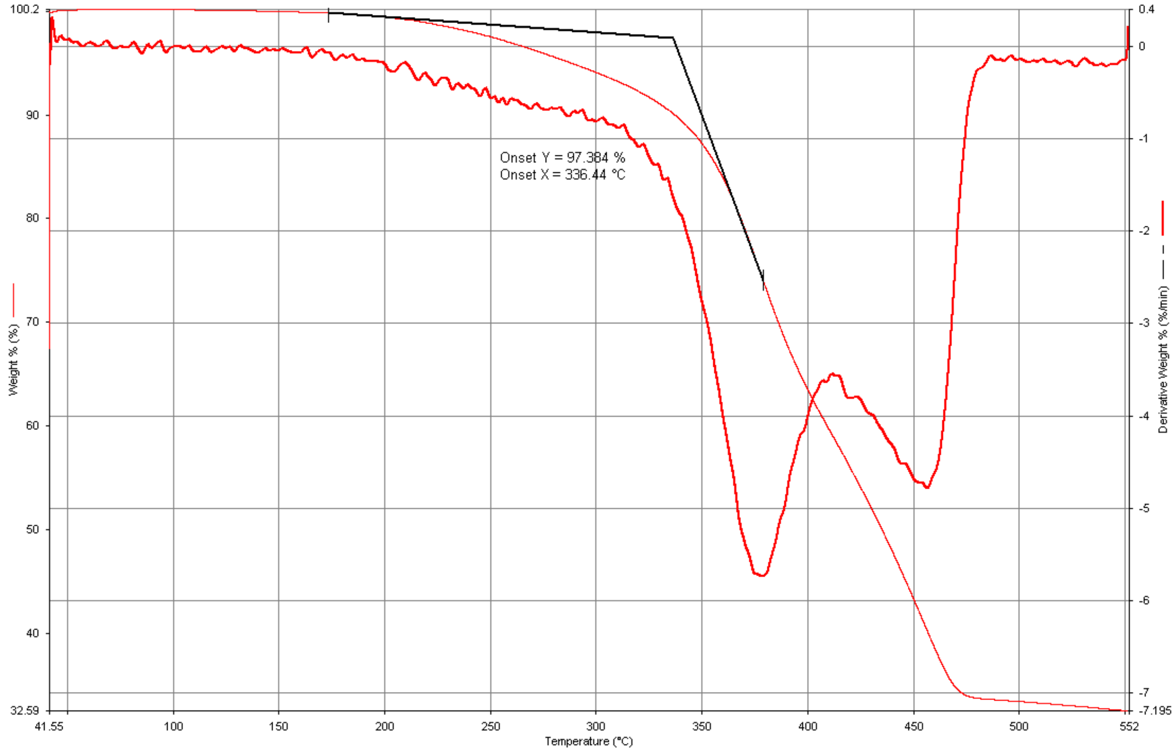


Figure 10: TGA result for waste tire

As can be seen in the figure above, the TGA was conducted from 30^{0}C to 600^{0}C at heating rate of 30^{0}C/min. The result curves shows that the degradation of waste tire took place at a range from 200^{0}C to 500^{0}C. The degradation of waste tire start at 336.44^{0}C and continue to degrade until 450^{0}C. This is attibuted to the degradation or volatilization of additives contained in the tires such as oils and stearic acid at the temperature between 200^{0}C to 300^{0}C and degradation of the styrene-butadiene and natural rubber at 300^{0}C to 460^{0}C [10]. The degradation continue until 500^{0}C with the decomposition of butadiene rubber [10]. The trend is similar with other literature which shows that the waste tire is completely decomposed at 500^{0}C. The pyrolysis temperature can be set at 500^{0}C since the waste tire seems to be completely decomposed at this temperature.

4.1.3 Py-GC-MS for waste tire

	RT	Compound
1	1.350	Propene
2	1.475	1,3-Butadiene
3	2.847	Toluene
4	5.039	Benzene
5	23.187	Oleic Acid
6	47.683	17-Pentatriacontene
7	17.113	2-Octenal,
8	1.811	1,3-Cyclohexadiene
9	12.336	D-Limonene
10	1.671	2-Pentene, 4-methyl-, (Z)-
11	1.832	1,3-Cyclopentadiene, 5-methyl-
12	47.683	Pentatriacontene

Figure 11: Py- GC-MS for waste tire result

This experiment was conducted to find the primary pyrolysis of waste tire. From the Py-GC-MS result, the highest peak is 1.475 which is 1,3-butadiene, a monomer used in the production of synthetic rubber such as tire. The second highest peak 1.350, classified as propene which is double bond polymer used in wide range of petrochemical product. The third highest peak goes to pentatriacontene which is a linear alkene with molecular formula of $C_{35}H_{72}$. This polymer bond makes the tire resistant to natural degradation and hard to be remolded into other form of material without a serious degradation.

Other compounds derived from the Py-GC-MS of tire are benzene, limonene, toluene, and xylene in relatively low percentage. Most of the percentage of cyclic alkene was derived from d-limonene degradation. Further elaboration of the compound pyrolysis will be discussed in the discussion section.

4.2 Waste tire pyrolysis

In each experiment, the time with temperature was note down to see the fluctuation in temperature during the experiment as the temperature need to be keep constant. After each experiment, the products from pyrolysis name char, oil and gas were collected. The experiment was conducted until no further release of gas was observed because the gas coming out from the reactor indicates that the reaction is take place [12].

The product yield were calculated based on the mass percentage. The mass balance calculation was used to calculate the product yield. The yields of the char and oil were determined by the change in weight of the reactor and condenser after the experiment. The following relation was used to estimate the product yield. The yield of solid and liquid are given <± 2 experimental error as it is acceptable range of error in pyrolysis [12].

$$\text{Char (wt. \%)} + \text{Oil (wt. \%)} + \text{Gas (wt. \%)} = 100$$

The experiment was conducted with different temperature to see the impact of temperature on product yield. Different temperature may result in different amount of product yield. It is well known that the important parameter for pyrolysis is the temperature [12]. The result of the pyrolysis is shown in the following section.

4.2.1 Pyrolysis at 450^{0}C

Figure 12: Char of waste tire at 450^{0}C

Figure 13: Oil of waste tire at 450^{0}C

First trial

To reach desired temperature		During experiment	
Time (min)	Temp (^{0}C)	Time (min)	Temp (^{0}C)
0	27	0	450
2	41	2	422
4	56	4	448
6	89	6	453
8	120	8	465
10	142		
12	175		
14	210		
16	248		
18	323		
20	403		
24	429		
26	449		

Table 5: Data of the first trial at 450^{0}C

Pressure before experiment – 0.4 bar

Pressure after experiment – 0.5 bar

Composition	Yield (mass %)
Solid	48.37
Liquid	29.16
Gas	20.25

Table 6: Product yield at 450^{0}C first trial

Second trial

To reach desired temperature		During experiment	
Time (min)	Temp (^0C)	Time (min)	Temp (^0C)
0	26	0	450
2	40	2	432
4	65	4	425
6	85	6	438
8	127	8	451
10	189	10	457
12	212	11	454
14	269		
16	310		
18	337		
20	395		
24	424		
26	450		

Table 7: Data of the second trial at 450^0C

Pressure before experiment- 0.3 bar

Pressure after experiment- 0.5 bar

Composition	Yield (mass %)
Solid	49.55
Liquid	33.40
Gas	17.05

Table 8: Product yield at 450^0C second trial

For both trial of waste tire at 450^0C, the result shows a similar trend of high production of char than oil.

4.2.2 Pyrolysis at 500^{0}C

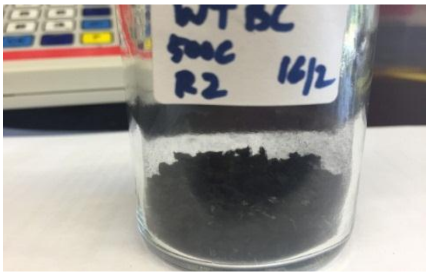


Figure 14: Char of waste tire at 500^{0}C

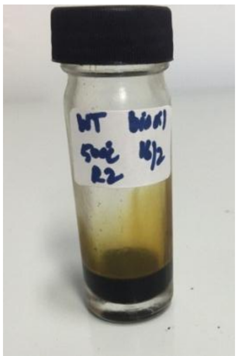


Figure 15: Oil of waste tire at 500^{0}C

First trial

For reach desired temperature		During experiment	
Time (min)	Temp (^{0}C)	Time (min)	Temp (^{0}C)
0	27	0	500
2	39	2	504
4	45	4	503
6	78	6	512
8	121	8	533
10	168	10	541
12	274		
14	290		
16	381		
18	438		
20	473		
24	500		

Table 9: Data first trial during experiment at 500^{0}C

Pressure during experiment- 0.4 bar

Composition	Yield (mass %)
Solid	46.23
Liquid	37.72
Gas	17.54

Table 10: Product yield at 500^{0}C first trial

Second trial

For reach desired temperature		During experiment	
Time (min)	Temp (^{0}C)	Time (min)	Temp (^{0}C)
0	23	0	500
2	28	2	501
4	40	4	503
6	69	6	518
8	116	8	539
10	153	10	548
12	214		
14	282		
16	355		
18	407		
20	457		
24	500		

Table 11: Data for the second at 500^{0}C

Pressure before experiment – 0.4 bar

Pressure after experiment – 0.6 bar

Composition	Yield (%)
Solid	45.08
Liquid	35.66
Gas	20.26

Table 12: Product yield at 500^{0}C second trial

For both trials, the consistency can be seen as only slight different in percentage of mass. For the temperature 500^{0}C, result shows that oil yield productionis higher than during 450^{0}C.

4.2.3 Pyrolysis at 550^0C

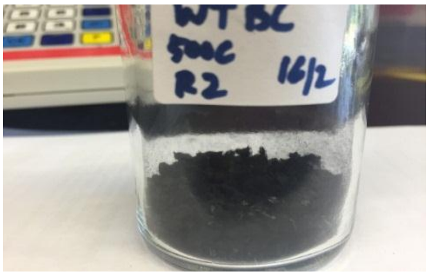


Figure 16: Char of waste tire at 550^0C

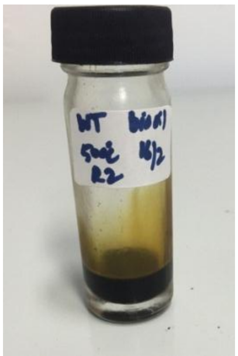


Figure 17: Oil of waste tire at 550^0C

First trial

For reach desired temperature		During experiment	
Time (min)	Temp (^{0}C)	Time (min)	Temp (^{0}C)
0	25	0	550
2	37	2	546
4	51	4	563
6	92	6	568
8	132	8	577
10	171	10	571
12	215		
14	319		
16	368		
18	399		
20	439		
24	496		

Table 13: Data for the first at 550^0C

Pressure during experiment- 0.4 bar

Composition	Yield (mass %)
Solid	43.51
Liquid	28.94
Gas	25.55

Table 14: Product yield at 550^0C first trial

Second trial

For reach desired temperature		During experiment	
Time (min)	Temp (^{0}C)	Time (min)	Temp (^{0}C)
0	23	0	550
2	32	2	542
4	47	4	553
6	79	6	572
8	127	8	575
10	174	10	572
12	248		
14	297		
16	351		
18	482		
20	535		
24	550		

Table 15: Data for the second trial at 550^{0}C

Pressure before experiment – 0.4 bar

Pressure after experiment – 0.6 bar

Composition	Yield (%)
Solid	45.35
Liquid	27.49
Gas	26.38

Table 16: Product yield at 550^{0}C second trial

The result for pyrolysis at 550^{0}C shows the increasing yield of gas more than oil yield. The pyrolysis analysis was discussed in the discussion section.

4.3 Analysis of pyrolysis product

4.3.1 Analysis for char and oil yield

After conducting the pyrolysis, the elemental composition of the char and oil yield was obtained by CHNS. The proximate analysis for the moisture, ash and fixed carbon content was also conducted.

Temperature (^{0}C)	Moisture	Ash	Fixed Carbon
450^{0}C	1.41	6.56	73.78
500^{0}C	1.29	7.67	76.05
550^{0}C	0.48	9.36	81.12

Table 17 : Proximate analysis of char

Temperature (^{0}C)	Carbon	Hydrogen	Nitrogen	Sulfur
450^{0}C	84.30	1.95	0.18	2.80
500^{0}C	86.99	0.47	0.23	2.87
550^{0}C	87.91	0.62	0.16	2.93

Table 18 : Char CHNS composition

	450^{0}C	500^{0}C	550^{0}C
Moisture	1.41	1.29	0.48
Ash	1.29	7.67	9.36
Fixed carbon	73.78	76.05	81.12
C	84.30	86.99	87.91
H	1.95	0.47	0.62
N	0.18	0.23	2.87
S	2.80	2.87	2.93

From the result obtained, it can be seen that the carbon composition of the char is increasing with the temperature. While the hydrogen and nitrogen are decreasing with higher temperature. The sulfur composition increased with the temperature. The moisture content of char is low than the raw material moisture content while the ash content is higher than the raw material ash content.

However, the moisture content is decreasing at higher temperature and ash content is increasing at higher temperature. The fixed carbon of char is higher than the feedstock fixed carbon content and increasing with increasing temperature.

Temperature (^{0}C)	Carbon	Hydrogen	Nitrogen	Sulfur
450^{0}C	83.06	9.88	0.53	1.28
500^{0}C	83.27	9.93	0.51	1.30
550^{0}C	86.07	10.09	0.54	1.39

Table 19 : Oil CHNS composition

From the result for oil experiment, it shows that the carbon composition is high and similar trend with the char composition. However, the hydrogen content in oil is relatively high compared to char. The sulfur content in the oil is lower than in the char but shows the same increasing trend.

Component	Calorific value (MJ/kg)
Waste tire	38.71
Char	30.7
Oil	41

Table 20: Determination of heating value

From the above table, the calorific value for oil is 41 MJ/kg shows a high value than the conventional liquid fuels which indicate that the potential of the oil to be used as alternatives to fossil fuels [15]. However, the oil need to be treated properly and suitable treatment for oil such as decanting, desulphurization and hydro treatment should be considered before using the oil.

The reuslt also shows that the calorific value for char also high which can be a potential solid fuel if further analysis for the char was conducted.

4.3.2 GC-TCD Analysis for gas yield

Non- condensable gas from fast pyrolysis is often assume as the by-product from the pyrolysis reaction. It is usually overlooked by many literatures.To find the unknown composition of the non-condensable gas, GC-TCD was used to find the weight composition of the gases. From the standard calibration curve of gases, the unkown gas was identify and the composition is calculated.

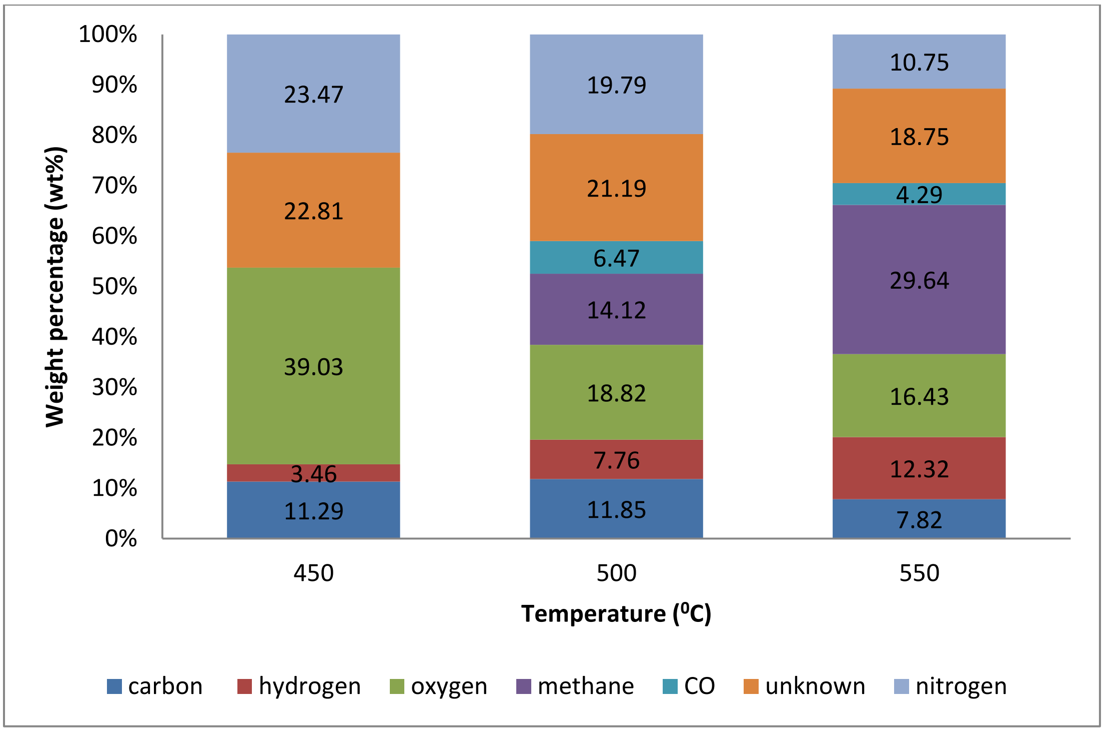


Figure 18: Gas composition for non-condensable gas

From the figure, the volume for each composition can be find using the standard calibration curve (MS-5A) in Appendix A for given type of gases. From the volume, the percentage composition can be calculated. the result show that highest composition in the gas for 450^{0}C is oxygen and no composition of methane and carbon monoxide detected at this temperature.

At 500^{0}C, the oxgygen composition was decreased and composition of methane and carbon monoxide is detected. The unknown is the highest at this temperature, but for overall trend, the unknown composition is decreasing at higher temperature. The unknown composition was a mixture of air other than the stated gas in the graph. The composition of methane is highest at 550^{0}C The lowest composition in the experiment is carbon monoxide for all temperature.

4.3 Discussions

From the waste tire elemental analysis, it can be seen that the percentage of sulfur is 2.30% which is relatively high and attention should be given to the product yield as the sulfur content might be high in the oil produced. To reuse the oil for commercial usage, the sulfur needs to be removed from the oil. Further analysis need to be done on the oil produced from the pyrolysis to find the amount of sulfur contained in the pyrolysis product.

From the Py-GC-MS experiment, it proves that at high temperature, the selectivity of alkene compound is high. As mentioned in the result, the highest yield is 1,3-butadiene considered as the main compound from the primary pyrolysis of the waste tire. Other aromatic hydrocarbons such as toluene, xylene and styrene show a present of relatively low percentage. The gaseous compound such as hydrogen, carbon monoxide, carbon dioxide cannot be detected by the equipment as the molecular weight of the gas is low [13].

D-limonene was one of the main products from the pyrolysis. Chain alkenes and cyclic alkenes was mainly form from the degradation of D-limonene or natural rubber, or through Diels- Alder reaction [13]. D-limonene itself was generated from natural rubber and then transform into chain alkenes, cyclohexenes and aromatics compound [13]. Below table shows the pyrolysis product from the degradation of D-limonene found in the Py-GC-MS.

	RT	Compound
1	1.350	Propene
2	1.477	1,3-Butadiene, 2-methyl-
3	2.847	Toluene
4	5.039	Benzene, 1,3-dimethyl
5	9.275	Benzene, 1-ethyl-3- methyl
6	1.965	1,3-Cyclohexadiene, 1- methyl
7	2.587	1,4-Cyclohexadiene, 1- methyl-
8	1.711	2-Pentene, 3-methyl-

Table 21: Pyrolysis product from limonene

The transformation of D-limonene can be seen when the temperature of pyrolysis is at 500^{0}C to 600^{0}C. During this temperature, the species of alkene increased. The yield of alkene will be ascending mildly if the temperature is higher than 600^{0}C [13] and the D-limonene mostly convert to aromatics.

The Py-GC-MS is used to help finding and understand the primary pyrolysis mechanism of the raw material. From the experiment, it can be concluded that the primary pyrolysis products from waste tire at 500^{0}C are mostly alkenes rather than alkanes or aromatics [13].

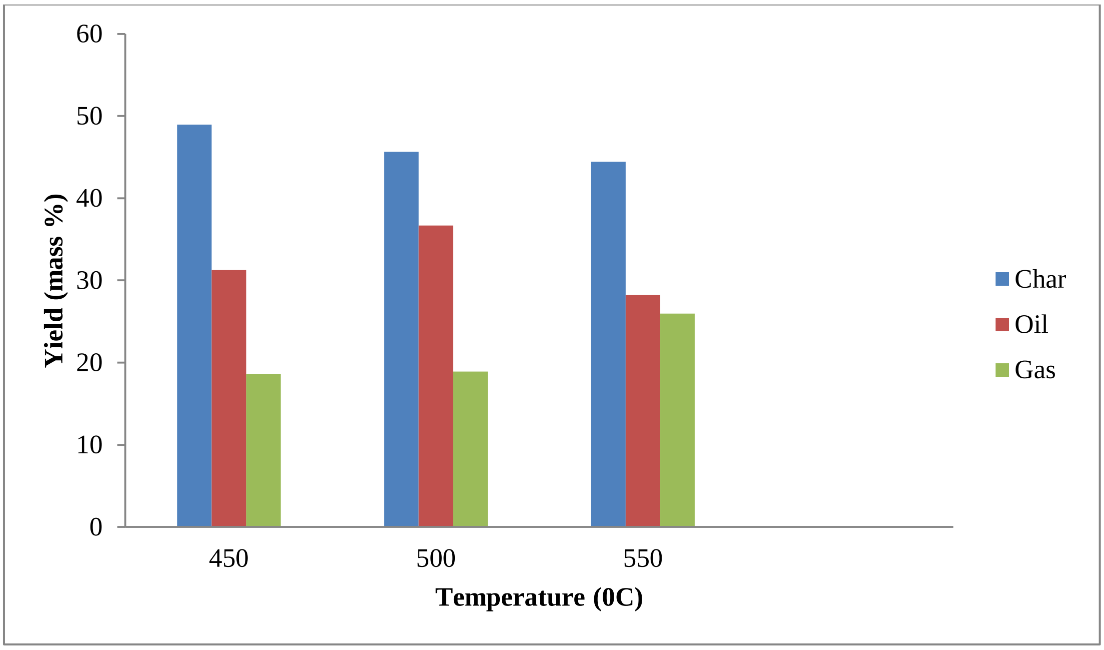


Figure 18: Influence of temperature on product yield

From Figure 18, the impact of temperature on product yield can be seen with 50^0C temperature interval from 450^0C to 550^0C. Two trials of experiment were done for each temperature. The average was taken from both trials to get the average yield of the product. The results show that, the char yield is decreasing from 450^0C to 550^0C. The char yield decrease with the increase of temperature is possible due to the pyrolyzed vapor and decomposition of solid [12].

Oil in the other hand is increasing from 450^0C to 500^0C but decreased at 550^0C. The highest oil yield is 36.69% at 500^0C. This shows that temperature was an important factor in obtaining desired product yield [12]. Pyrolysis for temperature higher than 550^0C was not conducted assuming that the decreasing trend continues. This trend during pyrolysis can be explained by two successive reactions:

$$Char \rightarrow Oil \rightarrow Gas \text{ [16]}$$

At lower temperature, the first reaction is predominant. When the temperature was increased, the second reaction is more favorable and leads to more production of gas. Consequently, the oil yield become lower as the reaction rate of second reaction is higher. This trend for pyrolysis was observed by many researchers [5, 7, 10, 12].

Pyrolysis trend also can be justified by heating rate factor. The increase of heating rate will affect the degradation rate of waste tire and also affecting the temperature for the maximum volatilization to happen and stop. Higher heating rate will lead to higher temperature which cause secondary reactions as mention before and leads to increase in the production of gas [5]. The secondary reaction nature can gives impact to the gas and oil composition.

When the temperature is higher, the gas residence time will be longer in the reactor and this can lead to volatilization of oil to gas [5]. Hence, the optimal temperature was find the have maximum yield of oil. This is usually the goal from pyrolysis as the oil is most valuable product from the reaction.

The proximate analysis of the feedstock and product shows decreased in moisture content after the pyrolysis. This may due to the dehydration reaction from the heating process. The dehydration rate is increased as the temperature increased and the moisture content become lower. It can be observed that the ash content become higher after the pyrolysis process. However, when the ash percentage is multiplied with the yield of char, the actual ash content of the char remained constant.

For the CHNS analysis of char and oil, it can be noted that the higher the temperature, the highest the carbon composition. This is due to the reduction of volatile residue content in the char which cause the increase in fixed carbon content. As the temperature increases, the degree of conversion of the volatilization reaction also increases. The char yield from pyrolysis also shows that the amount of solid content decreased, and has a higher graphitization (fixed carbon content) which also agreed with the elemental analysis results which shows the incremental value of carbon content in the char [14].

The elemental analysis also, shows that the hydrogen composition decreases with the temperature shows the larger aromatization degree of char, as the aliphatic fraction decreased with growing temperature and aromatic fraction is more favorable in Diels-Alder reaction [10]. This aromatic compound gives a significant carbon-like structure to the char which cause the char have high fix carbon content compared to the initial feedstock [14].

The char also shows a high sulfur content and ash content which makes it hard to re-use. This might because of the contain of sulfides in metals in the char [10]. Advance treatment need to be done to remove the sulfur content from the ash before using it commercially such as in the rubber industry.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

Pyrolysis was used for thermal degradation of organic material. The pyrolysis process will change the chemical and physical of the material. The introduction of pyrolysis for recycling was tire shows a positive result on the experiment conducted. In this project, drop-type pyrolyzer was use and fast pyrolysis is applied.

The pyrolysis of waste tire leads to a production of char, oil, and gas fraction. From the pyrolysis conducted, the highest oil yield was at 500^0C with 36.69%. The trend for pyrolysis is showing that as the temperature increases after achieving the optimum yield, the oil yield will decreases as it leads to more cracking of char which produces more gas rather than oil. From the analysis of pyrolysis product, the char and oil have a high percentage of carbon content. The sulfur content for oil is lower than the char but has the same increasing trend. From Py-GC-MS pyrolysis oil consist most of aliphatic and aromatic compound such as limonene and xylene.

From the study, it shows that the temperature is important parameter in pyrolysis and effect in the product yield. To improve the result, the temperature needs to be control to ensure that the changes in temperature are relatively low to get a better result for pyrolysis. More research on waste tire pyrolysis should be performed specially on the pyrolysis product so that it can be used commercially.

5.2 Recommendation

Some improvements can be made in terms of the preparation of the sample. To have an easy and productive way for handling the sample, some initiative should be planned first such as search for a shredded tire rather than using a whole tire. This is because handling a whole tire is difficult and consumes much time for removing other material such as steel and fabric.

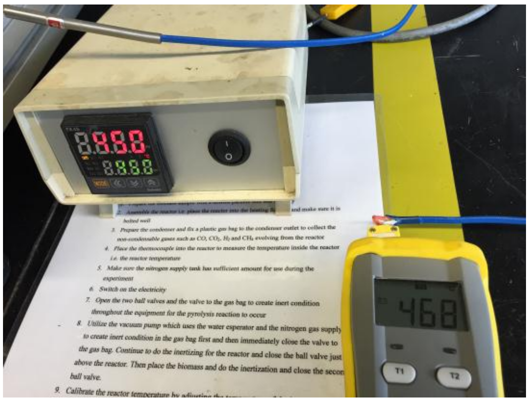


Figure 20: Reading from thermocouple higher than actual

The thermocouple gives a higher reading than the desired temperature. This may due the thermocouple touch the wall of reactor or not sensitive to temperature. Temperature control system can be applied to ensure the temperature is according to the specification. The thermocouple should be more sensitive to temperature so that it shows the correct temperature inside the reactor.

The Py-GC-MS experiment for waste tire can be conducted at different temperature such as 400^{0}C, 500^{0}C, 600^{0}C, and 700^{0}C to obtain better result and can see clearly the selectivity and change in the alkene bond as the temperature increase in the primary pyrolysis and the degradation of the alkene compounds.

Due to time constrain the SMR 20 pyrolysis was not carried out for this project. For further enhancement of the results, the pyrolysis of natural rubber may be considered in the future.

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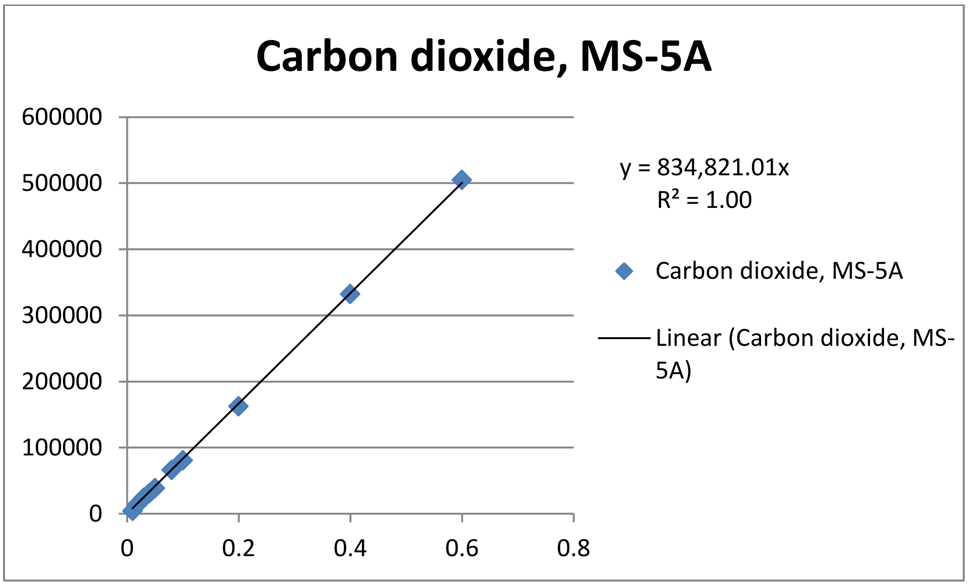
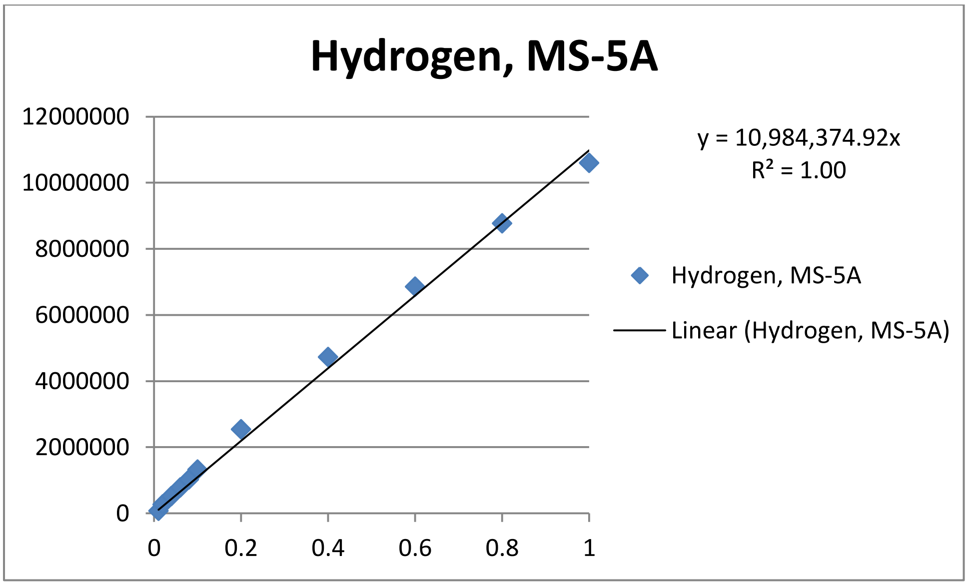
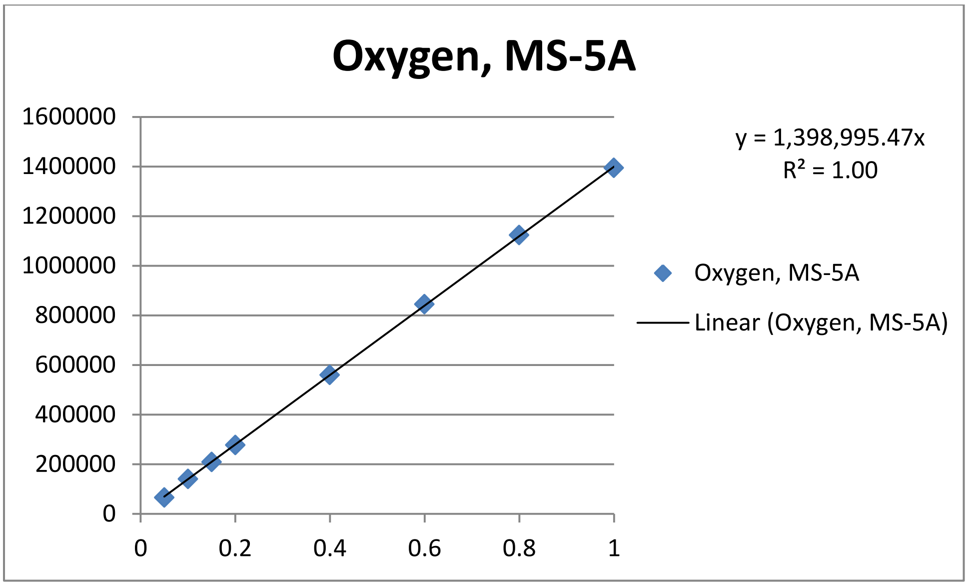
APPENDICES

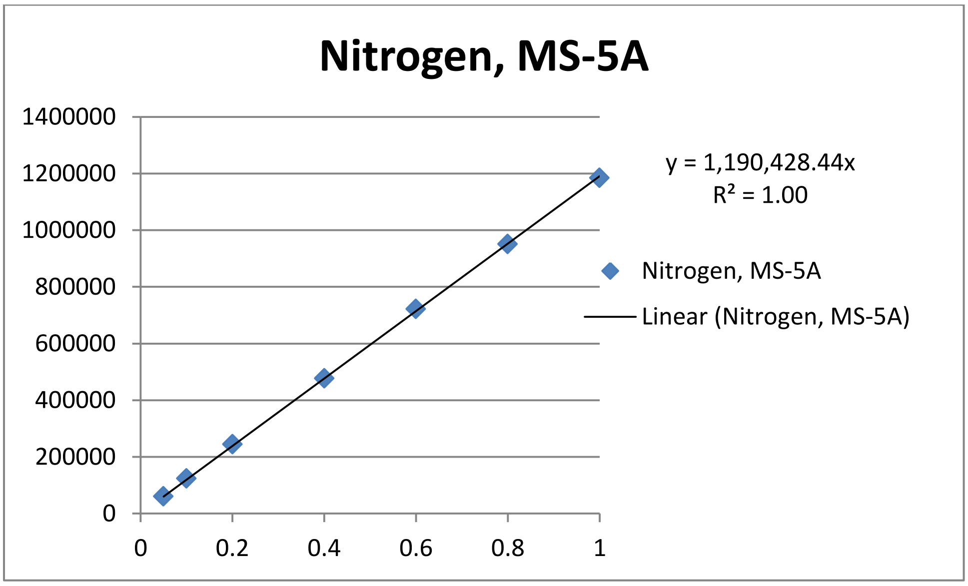
Appendix I

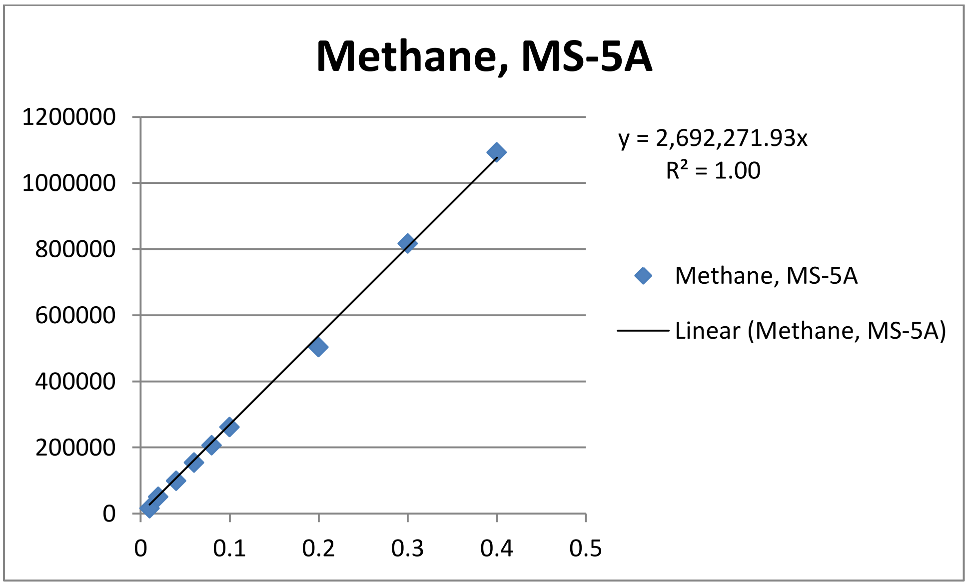
Standard Calibration Curve for Gas

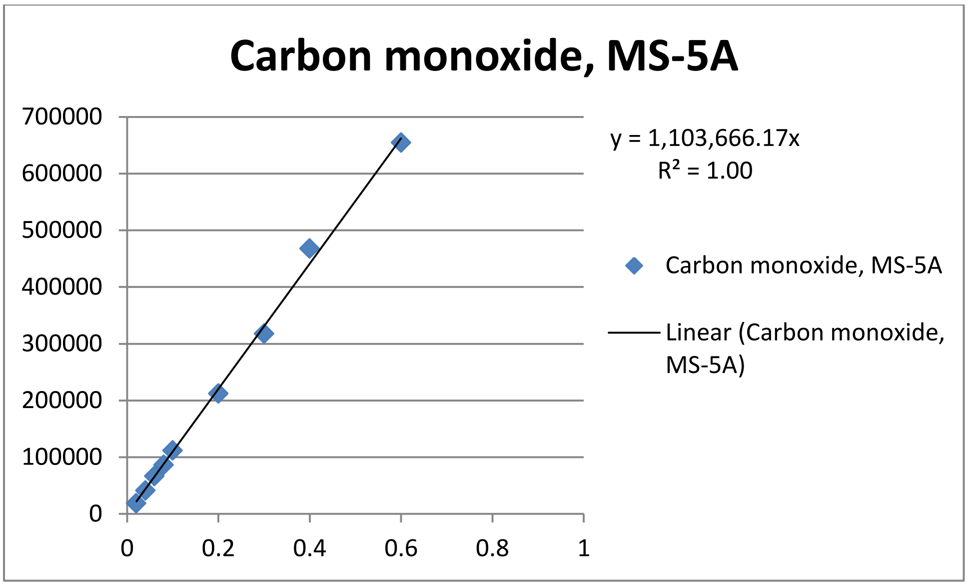





Oxygen, MS-5A
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
0
0.2
0.4
0.6
0.8
1
y = 1,398,995.47x
R² = 1.00
Oxygen, MS-5A
Linear (Oxygen, MS-5A)


Nitrogen, MS-5A
1400000
1200000
1000000
800000
600000
400000
200000
0
0
0.2
0.4
0.6
0.8
1
y = 1,190,428.44x
R² = 1.00
Nitrogen, MS-5A
Linear (Nitrogen, MS-5A)


Methane, MS-5A
1200000
1000000
800000
600000
400000
200000
0
0
0.1
0.2
0.3
0.4
0.5
y = 2,692,271.93x
R² = 1.00
Methane, MS-5A
Linear (Methane, MS-5A)


Carbon monoxide, MS-5A
700000
600000
500000
400000
300000
200000
100000
0
0
0.2
0.4
0.6
0.8
1
y = 1,103,666.17x
R² = 1.00
Carbon monoxide, MS-5A
Linear (Carbon monoxide, MS-5A)