Dissertation:
X-Ray Amorphous Pattern Characterization of PETRONAS Petroleum Coke Product as a Potential for Advanced Carbon-Carbon Composite Material Precursors

By

Nadrah Isa (11504)

Dissertation submitted in partial fulfillment of
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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

…..……………………….
(AP Dr Bambang Ariwahjoedi)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this report, 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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NADRAH ISA

ABSTRACT

The interpretation of X-ray Diffraction (XRD) of a crystalline material is facilitated with the abundance of database, and superior software due to the superior quality of the diffraction pattern. However, the analysis of XRD of an amorphous material is difficult as the diffraction pattern is broad and diffused unlike the sharp and well defined x-ray pattern of a crystalline material. An amorphous petroleum coke (pet coke) is obtained from Melaka Refinery Company (MRC). The pet coke is analyzed and characterized in terms of its calorific value, physical properties, morphology, compositional analysis, as well as an XRD pattern. Knowledge of internal structure of Pet coke is useful as it can find application in many engineering and high value applications such as catalyst carrier, adsorbent, and toxic material removal. The activities in Final Year Project 1 (FYP 1) involved a comprehensive literature review of the XRD pattern of an amorphous material. The availability of analytical equipments and apparatus required for the characterization of pet coke has been identified and reserved during FYP 1. In FYP 2, we report the characterization of pet coke from MRC including morphology, calorific value and elemental analysis. A XRD pattern has been obtained and the analysis of the derived pattern is presented in this Final Report.

ACKNOWLEDGMENT

In the name of Allah, the Most Gracious, the Most Merciful. Praise to Him the Almighty for His blessing and guidance in giving me strength, courage, patience and perseverance to endure and complete the Final Year Project (FYP) in Universiti Teknologi PETRONAS.

FYP has provided me with an excellent exposes to the value of engineering, and its importance to the industries. Throughout the duration of the FYP, I have gained a lot of knowledge theoretically and practically to prepare myself for the working environment in the future.

I am in debt with so many people who has made this project an illuminating and enriching venture. My deepest gratitude goes to my supervisor, AP Dr. Bambang Ariwahjoedi, for giving out continuous support and proactive leadership which have been a great inspiration to me. His availability, time and support have been invaluable to me. My sincere appreciation also goes to all lecturers in UTP especially my examiner for the valuable knowledge and beneficial advice.

Heartfelt appreciation is extended to the technologists in UTP, and other external parties that I have dealt with for their assistance, guidance, never-ending supports and for the delightful moment we shared throughout the completion of FYP. Their contribution in providing the expertise, help and cooperation during completing my project is very much appreciated.

My deepest appreciation goes to my parents who have given immense support throughout the duration of the internship being away from home. Without their consent the success today would not be a reality. Last but not least, thousands of appreciations to anyone who has assisted me directly or indirectly in making my Final Year Project a success. May God repay your kindness.

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ABBREVIATIONS

CAL	Centralized Analytical Laboratory
CHNS Analyzer	Carbon, Hydrogen, Nitrogen and Sulfur Analyzer
CE	Chemical Engineering
DNA	Deoxyribonuclelic Acid
EDS	Energy Dispersive X-Ray Spectroscopy
EMR	Electromagnetic Radiation
FESEM	Field-Emission Scanning Electron Microscope
FYP	Final Year Project
HPV	High Production Volume
ICDD	International Centre for Diffraction Data
JCPDS	Joint Committee on Powder Diffraction Standards
ME	Mechanical Engineering
MRC	Melaka Refinery Company
RDF	Radial Distribution Function
UV	Ultraviolet
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The study of the atomic and molecular structure has benefitted from the progress in X-ray diffraction (XRD) techniques. XRD has been successful in unraveling the atomic arrangement of many molecules and substances such as metals, rocks, minerals, DNA, protein and sand and the use of computers has partly contributed to the success (Igunci, 1999). The results of XRD experiment are presented in the form of a diffraction pattern. This information is analyzed, refined and corrected by averaging the atomic arrangement of the specimen and mathematically inverting the data to obtain the detail of the atomic packing arrangement. XRD can produce information on the average spacing between the layers of atoms (called the d-spacing), degree of crystallinity, orientation of the single crystal or grain, size, shape and internal stresses of small crystalline regions (Shimazu, 2000). The information is routinely obtained for single crystals of most materials. A diffraction pattern is therefore a fingerprint of its internal atomic arrangement. A diffraction pattern is produced when that material interacts with a beam of X-ray. This is true whether the material is ordered such as single crystal or amorphous such as a polymer or glass. For example in minerals, many X-ray diffraction data processing softwares can perform automated mineral search and match by comparing a recorded pattern to those stored in the *International Centre for Diffraction Data* (ICDD) database, formerly known as *Joint Committee on Powder Diffraction Standards* (JCPDS) (Hemmer, 2007). A user can set certain criteria such as chemical composition of a sample and names of possible minerals to narrow down the search range.

Normally, the softwares find several possible minerals and ask the user to pick up the best match. If a sample contains many crystalline phases, the search/match is more difficult (Grundy, 1980). The determination of the d-spacing is an important quality control parameter. Oversized guest molecules cannot be accommodated in the intermolecular d – spacing. It will cause excessive strain and becomes disoriented making the petroleum coke ineffective.

1.2 PROBLEM STATEMENT AND PROJECT SIGNIFICANCE

While the use of XRD for crystalline material is highly successful, its use in an amorphous material such as petroleum coke is not widely reported. The inter atomic distance determinations of pet coke may be challenging and obscured by the low degree of crystallinity and method of preparation (size reduction). Accurate information on the characteristics of petroleum coke is desired as a preliminary data for an internal structure of pet coke and characterization. There are no available data on XRD pattern analysis and interpretation of an amorphous pet coke. The analysis and the treatment of the data from XRD pattern of pet coke is attempted by assuming certain portion of the pet coke to behave like a crystalline and ordered material.

1.3 OBJECTIVE AND SCOPE OF STUDY

1.3.1 Objective

The aim of this study is to determine the characteristics of petroleum coke as a candidate for advanced carbon-carbon composite material precursors and to analyze the XRD pattern from Melaka Refinery Company (MRC).

1.3.2 Scope of Study

The characterization of pet coke is accomplished by examining its physical and chemical properties. The pet coke is also subjected to a preliminary XRD and is compared with the hexagonal graphite (coke) pattern.

1.4 RELEVANCY OF PROJECT

The project firstly determines the characteristics of pet coke obtained from MRC. This includes the structural and atomic arrangement of an amorphous. Its abundance in MRC triggers the study of its structural information for other applications such as converting it to carbonaceous materials via liquid crystalline state, like carbon fibers, carbon-carbon composites for advanced aircraft structures. Industrial application for pet coke will be further enhanced in areas such as adsorbent for water decontamination, toxic removal, carrier for catalyst, and many other sectors requiring an accurate configuration of the internal structure of pet coke.

1.5 FEASIBILITY OF PROJECT

Pet coke is obtained from MRC. The characterization investigations of pet coke have been performed in the Mechanical Engineering (ME), Chemical Engineering (CE), and Centralized Analytical Laboratory (CAL) blocks. The XRD determination was performed at Block 17.

The project time line for progress in FYP 1 and FYP 2 is attached as per Table 3.1 and Table 3.2. The equipments for characterization and XRD analysis of pet coke have been identified and the availability has been validated. Preliminary booking and reservation of the equipments have been performed with the relevant technicians.

Over all, the author is confident that the objective and the scope of study are accomplished within the time frame of FYP 1 and FYP 2.

CHAPTER 2

LITERATURE REVIEW

2.1 PETROLEUM COKE

Petroleum coke is a black-colored solid produced by the high pressure thermal decomposition of heavy (high boiling) petroleum process streams and residues (delayed coking in Figure 2.1). There are two forms of pet coke namely green coke and calcined coke. These two substances are grouped together in a category based on their similarity of manufacturing processes which results in similar physical chemical characteristics and chemical composition. The principal difference between the two forms of pet coke is the amount of residual hydrocarbon (also termed volatile matter) in the two products (Youjun Deng, 2009).

Green coke is the initial product from the cracking and carbonization of the feed stocks to produce a substance with a high carbon-to-hydrogen ratio. Green coke undergoes additional thermal processing to produce calcined coke. The additional processing removes volatile matter and increases the percentage of elemental carbon, which results in a lower potential for toxicity of calcined coke (Youjun Deng, 2009).

The hazard potential for the petroleum coke category has been characterized by evaluating existing data, testing green coke to fill data gaps, then ‘reading across’ the green coke will lead us to the other category member i.e. calcined coke. This is justified because, as stated above, green coke contains higher levels of volatile matter, and therefore, it is “worse case” by comparison to calcined coke (Youjun Deng, 2009).

Because petroleum coke (both green coke and calcined coke) is the substance remaining from treating heavy petroleum feed stocks with high temperature and pressure, many of the physical-chemical properties are not meaningful at ambient environmental conditions. At ambient temperature and pressure, petroleum coke exists as a solid, and because it consists predominantly of elemental carbon and a hardened residuum remaining from the feed stocks, the High Production Volume (HPV) Chemical Challenge Program physical-chemical endpoints either cannot be measured using recommended testing procedures or would not provide meaningful information (Youjun Deng, 2009).

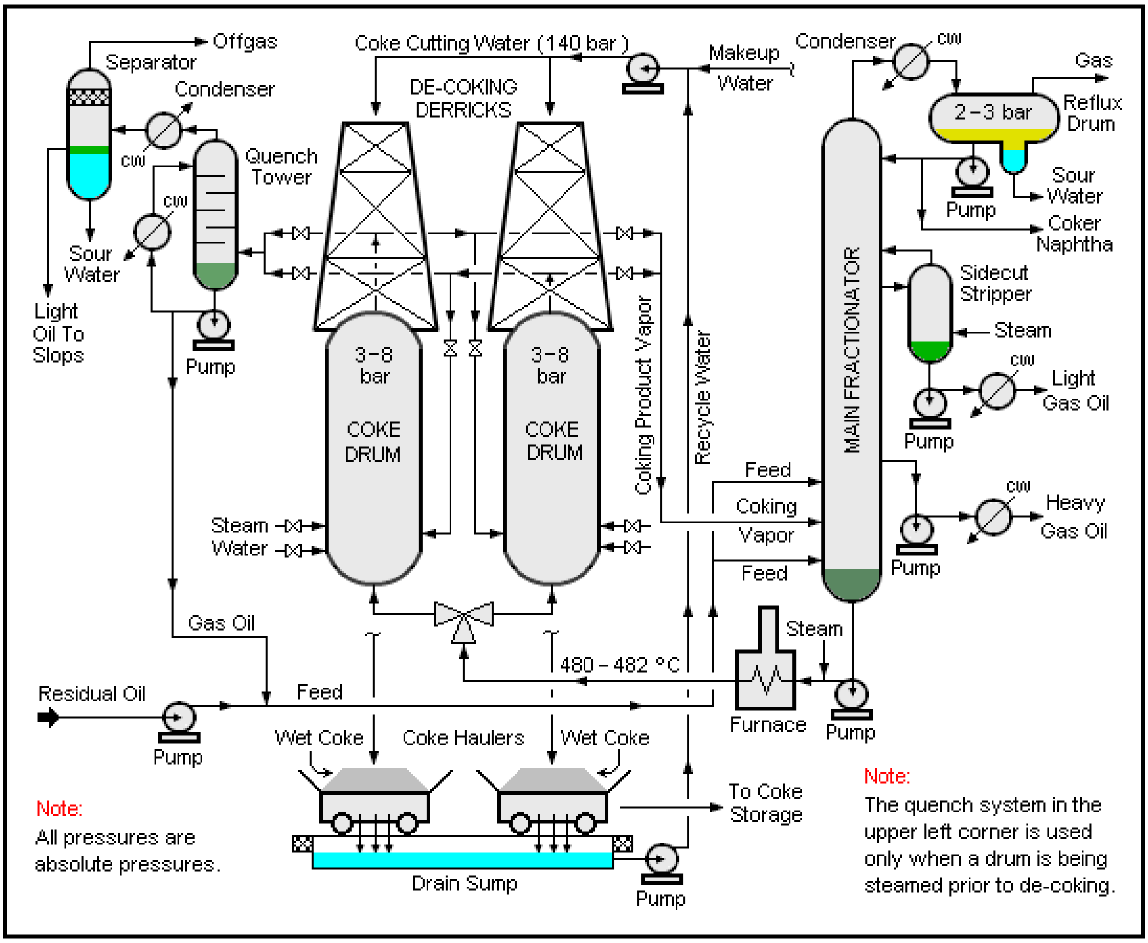


Figure 2.1: Delayed coking process

A delayed coker is a type of coker whose process consists of heating a residual oil feed to its thermal cracking temperature in a furnace with multiple parallel passes (Figure 2.1). This cracks the heavy, long chain hydrocarbon molecules of the residual oil into coker gas oil and petroleum coke (Wikipedia).

2.2 MRC AND THE PRODUCTION OF PET COKE

Pet Coke is produced from MRC and is normally sold to international traders. Pet coke is used as solid fuel for boiler operation, as binder and filler in Portland cement production, and finally as adsorbents. It is useful to determine the internal structure of pet coke by X-ray diffraction method. This way, the purity of pet coke can be determined and more importantly we can add value to pet coke by modifying the internal structure to meet the high performance demands.

The monthly production of pet coke from MRC is 28,000 MT. Pet coke is transported on barges on 3,000 MT per barge or tugboat. MRC serves as the supplier of pet coke while PETRONAS Trading Company (PETCO) and Conoco Phillips act as its buying arm. PETCO sells to its buyers through a bidding process, every 15th day of the month (Nabila, 2012). Buyers will bid its price pegged against Global Coal price from: http://www.globalcoal.com/. Companies with the highest bid will arrange for pet coke transportation from MRC port at Sungai Udang, Melaka. After loading, the barge and tugboat will route to discharge ports such as Surabaya, Koh Shi Chang in Thailand, Batu Pahat, Lumut, and Langkawi. Figure 2.2 shows a typical texture of a pet coke from MRC.

Figure 2.2: Petroleum Coke from MRC

2.3 PRINCIPLES OF X-RAY DIFFRACTION

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incident (theta, θ). The variable *d* is the distance between atomic layers in a crystal, and the variable lambda λ is the wavelength of the incident X-ray beam and *n* is an integer (Clark. C. M., 2004). This observation is an example of X-ray wave interference.

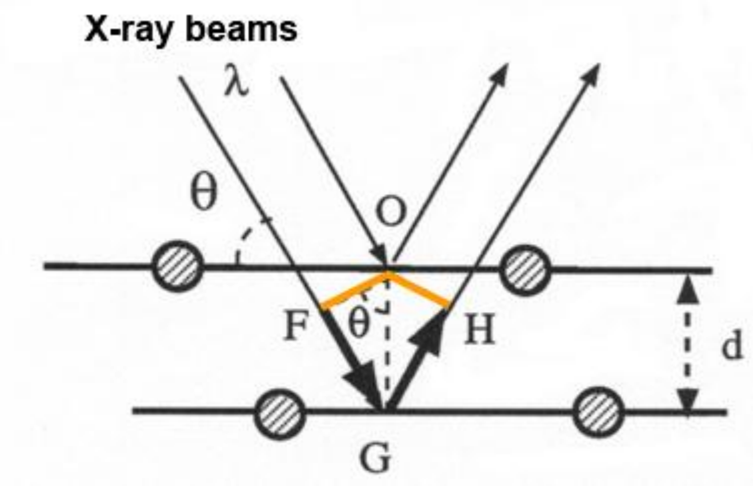


Figure 2.3: Bragg's Law = $n\lambda = 2d \sin\theta$

Figure 2.3 shows X-rays being reflected from a crystal. Each layer of atoms acts like a mirror and reflects X-rays strongly at an angle of reflection that equals the angle of incidence.

X-ray is high energy electromagnetic radiation (EMR). They have energies ranging from 200 eV to 1 MeV i.e. between ϒ and UV radiation in the EMR spectrum. The x ray wavelength of X-ray lies between 10 nm – 1 pm. This is suitable for interatomic investigation in crystals as the interatomic distance in approximately 0.2 nm (2 Å).

The reflected beams will interact constructively and they will generate diffraction patterns as seen in XRD experiments (Clark. C. M., 2004). Figure 2.4 below shows only constructive interference are picked up by the XRD but not the destructive interference waves. It has maximum intensity when $2d\sin\theta = n\lambda$

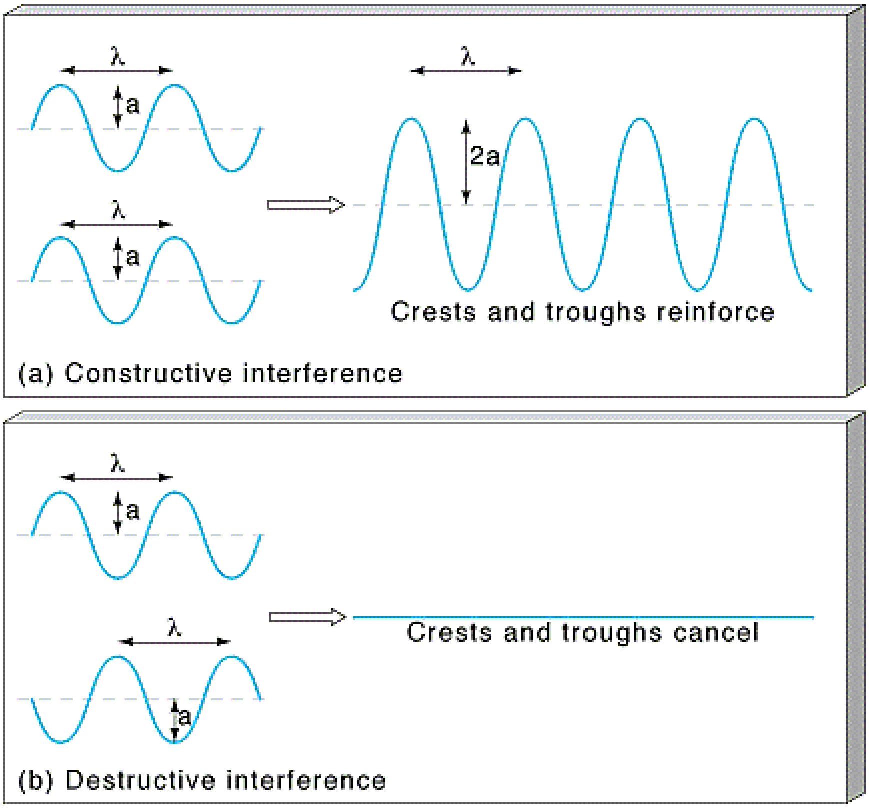


Figure 2.4: Constructive and destructive interferances of X-ray beams.

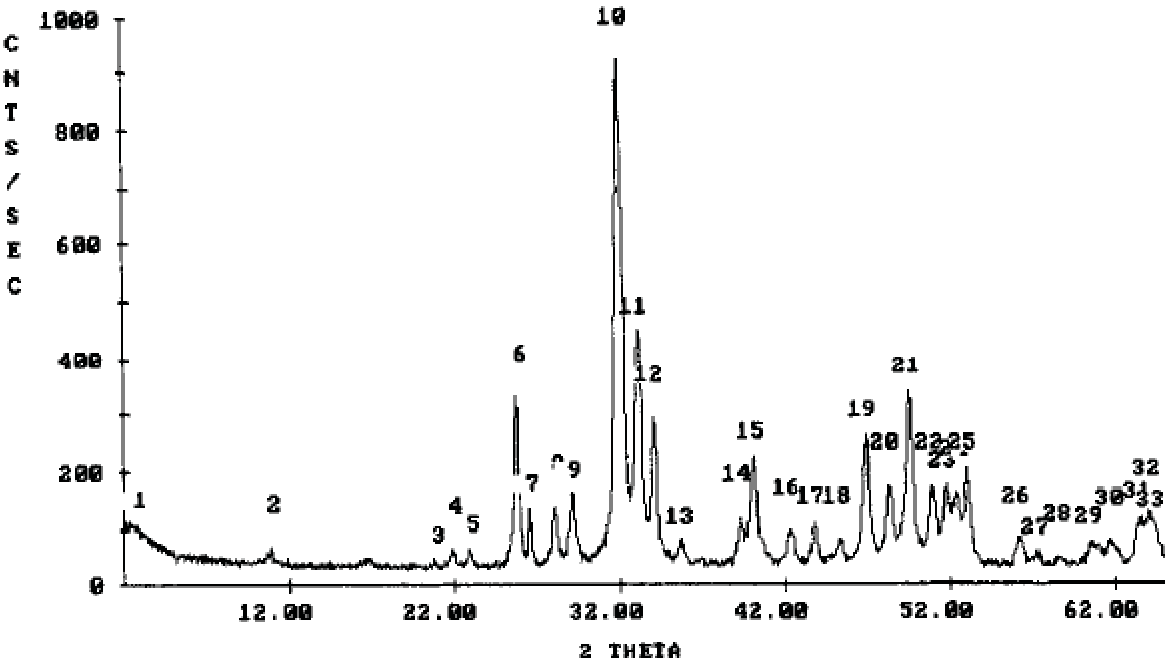
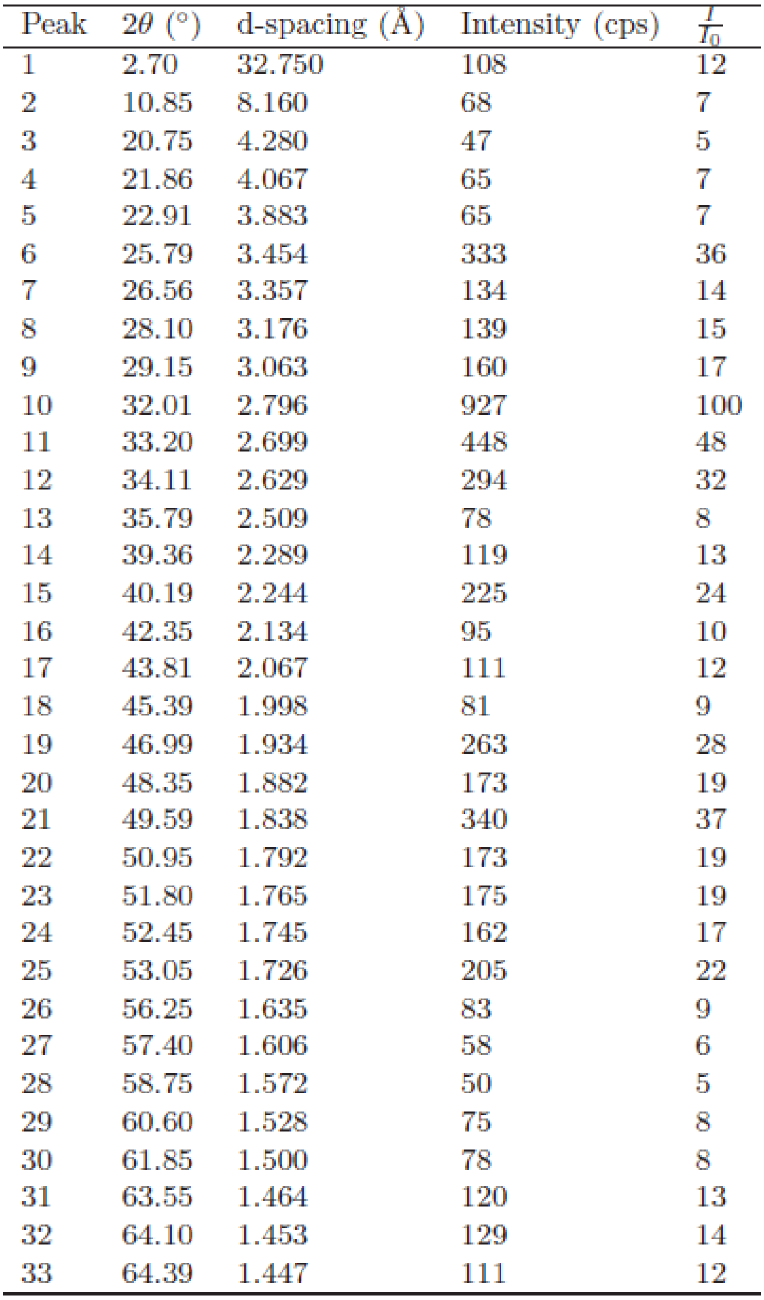


Figure 2.5: Example of X-ray diffraction curve of a crystalline mineral.

Figure 2.5 is an example of an X-ray defraction profile of crystalline mineral showing the count per second (intensity) vs the incident angle 2θ. It has several peaks with the most intense ones at peak number 10. The detail of calculated d – spacing from the values of the incident angle 2θ and intensity is shown in Table 2.1.

Table 2.1: Listing the peak position and 2θ as well as d – spacing from the intensity and intensity ratio.



Peak	2θ (°)	d-spacing (Å)	Intensity (cps)	$\frac{I}{I_0}$
1	2.70	32.750	108	12
2	10.85	8.160	68	7
3	20.75	4.280	47	5
4	21.86	4.067	65	7
5	22.91	3.883	65	7
6	25.79	3.454	333	36
7	26.56	3.357	134	14
8	28.10	3.176	139	15
9	29.15	3.063	160	17
10	32.01	2.796	927	100
11	33.20	2.699	448	48
12	34.11	2.629	294	32
13	35.79	2.509	78	8
14	39.36	2.289	119	13
15	40.19	2.244	225	24
16	42.35	2.134	95	10
17	43.81	2.067	111	12
18	45.39	1.998	81	9
19	46.99	1.934	263	28
20	48.35	1.882	173	19
21	49.59	1.838	340	37
22	50.95	1.792	173	19
23	51.80	1.765	175	19
24	52.45	1.745	162	17
25	53.05	1.726	205	22
26	56.25	1.635	83	9
27	57.40	1.606	58	6
28	58.75	1.572	50	5
29	60.60	1.528	75	8
30	61.85	1.500	78	8
31	63.55	1.464	120	13
32	64.10	1.453	129	14
33	64.39	1.447	111	12

2.4 XRD OF AMORPHOUS MATERIAL

From the previous section, a diffraction pattern is therefore a fingerprint of its internal atomic arrangement. A diffraction pattern is produced when that material interacts with a beam of radiation. This is true whether the material is ordered such as single crystal or amorphous such as a polymer or glass. For example in minerals, many X-ray diffraction data processing softwares can perform automated mineral search and match by comparing a recorded pattern to those stored in the *International Centre for Diffraction Data* (ICDD) database. (Hemmer, 2007). However, the XRD pattern of an amorphous material is quite diffused and the peaks are broader compared to crystalline material. For amorphous material, the distance distribution is in the form of Radial Distribution Function (RDF). It represents the distribution of atomic distribution within that sample. RDF describes the distance distributions of points in 3D space.

2.4.1 Radial Distribution Function (RDF)

Radial Distribution Function (RDF) is used to obtain the internal structure information of pet coke. While the concept of these functions is quite old, its use as descriptors for molecules in the field of spectrum or structure correlation is new. RDF is an excellent descriptor for a wide range of applications (Hemmer, 2007). Almost any physical or chemical property that can be attributed to atoms or molecules may be incorporated to characterize molecules.

Molecules are usually represented in 2D formulae or 3D molecular models. While the three dimensional coordinates of atoms in a molecule are sufficient to describe the spatial arrangement of atoms, they exhibit two major disadvantages: they depend on the size of a molecule and they do not describe additional properties. The first attribute is important for computational analysis of data. Even a simple statistical function, e.g., the correlation, requires the information to be presented in equally sized vectors of a fixed dimension. The solution to this problem is a mathematical transformation of the Cartesian coordinates of a molecule to a vector of fixed length (Hemmer, 2007). The second point can be overcome by including the desired properties in the transformation algorithm (Burian. A., 1998).

2.5 GRAPHITE

The term graphite was introduced by (Werner, 1789). Graphite is a crystalline, polymorphic form of elementary carbon. In isolated carbon atoms, the distribution of electrons is $1s^2$ $2s^2$ $2p^2$. Each carbon atom in the graphite crystal is hybridised trigonally, forming three r and one p bonds. The hybridised orbitals of the sp^2 type give π bonds of a length of 1.42 Ǻ, arranged at 120^o angles with respect to one another, with sheets made up of regular hexagons. The fourth electron of each atom, being in the p orbital, and forms p bonds with all the neighboring atoms. Graphite has a heterodesmic layered structure (Kwiecinska, 2004). The structure of graphite consists of six-membered rings in which each carbon atom has three near neighbours at the apices of an equilateral triangle. Within the large planar layers, there are linkages intermediate between atomic and metallic bonds. The layers in the crystal are held together by van der Waals bonding forces of energy of 0.2 eV/atom. Perfect basal cleavage readily takes place between the layers along the (001) plane. Weak bonding perpendicular to the layers gives rise to easy sliding parallel to the sheets. The model of graphitic structure proposed by (Hull, 1917) and described by (Bernal, 1924) assumes the existence of the basal, hexagonal crystalline lattice.

Disordered nanocrystalline materials are solids that have lost their long-range crystalline order and have become disordered, but are not amorphous. The broad X-ray amorphous halos observed in disordered nanocrystalline materials are related to the crystalline microstructure (crystal size, micro-strain and defects) and are correlated to parent crystalline peaks. (Simon Bates, 2006)

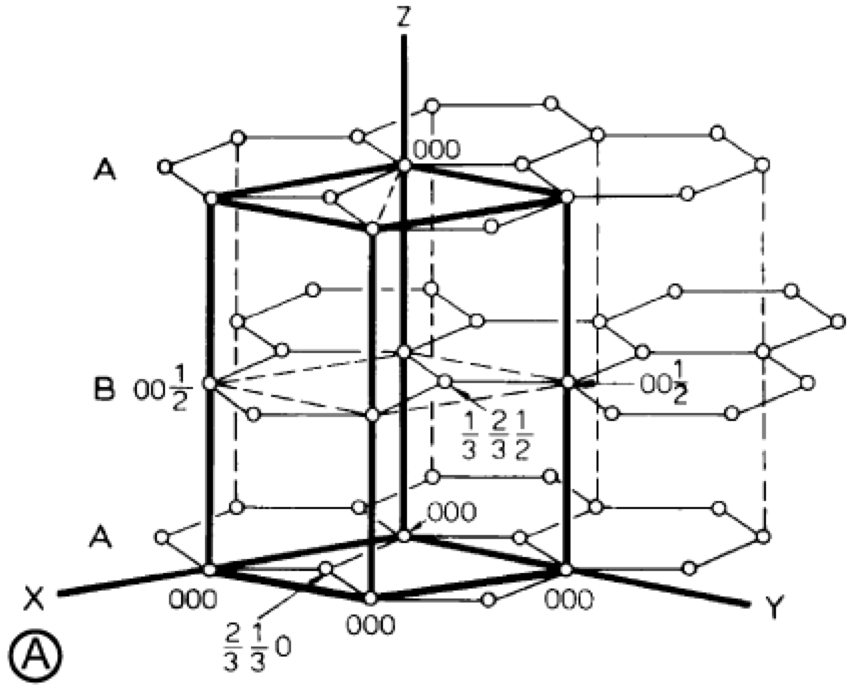


Figure 2.6: (A) Hexagonal lattice of graphite (Reynolds, 1968)

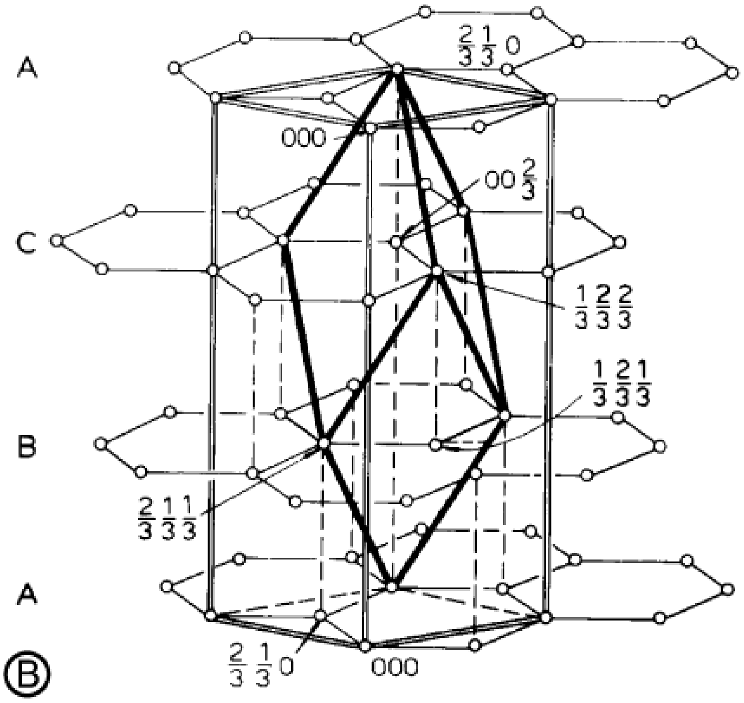


Figure 2.7: (B) Rhombohedral lattice of graphite (Reynolds, 1968)

The described structure of graphite refers to its crystalline forms defined as ideal models. However, in nature graphite usually appears in less perfect forms (real crystals) and in a variety of disordered types. As transitional phases, these forms show varying degrees of graphitization of carbon contained in the carbonaceous substance or organic matter dispersed in sedimentary or metamorphic rocks. They are called semigraphite, meta-anthracite, and anthracite, according to the content of carbon (C) and hydrogen (H) and the degree of ordering of the lattice structure. For establishing transitional phases and pure graphite by the degree of their crystalline perfection, it is necessary to include maximum reflectance measurements (% R_{max}). (Kwiecinska, 2004)

Table 2.2: Graphite and its transitional phases. Graphite occurring in different stress and temperature regimes may have different properties (Kwiecinska, 2004).

Varieties, phases	Symbol	d 002 (Å)	% R_{max}	H/C
Graphite	G	3.354– 3.37	>9.0	0.005–0.10
Semi-graphite	SG	3.37– 3.38	6.5– 9.0	0.10–0.15
Meta-anthracite	MA	3.38– 3.40	< 6.5	0.15–0.20
Anthracite	A	>3.40	< 5.0	≥ 0.20

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY

The pet coke is subjected to X-ray characterization methods by using 6 different equipments that are available in UTP labs. Steps involved can best describe as follows:

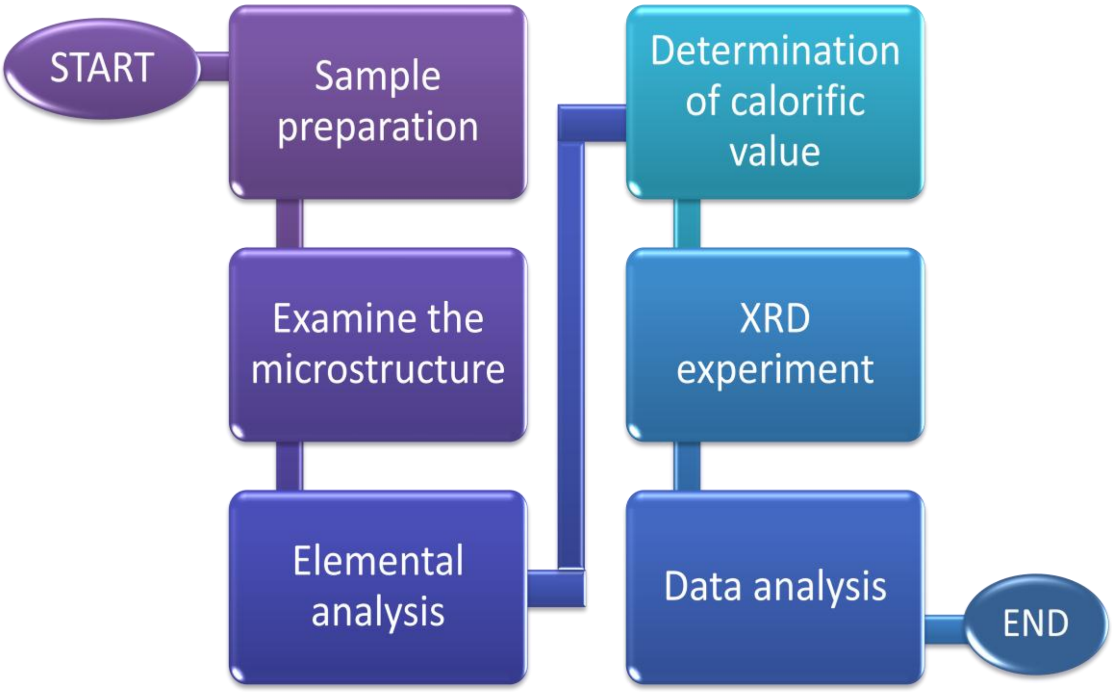


Figure 3.1: Main tasks involved in determination of characteristics of pet coke.

3.1.1 Sample preparation

The pet coke was finely grounded by a ROCKLABS mortar grinder in Block 17. The size of the pet coke was reduced to talc form, with an average diameter of 20 μm. All of the characterization experiments require the pet coke to be in powder form.

3.1.2 Examine the Microstructure

Determination of the microstructure of pet coke was done using Field-Emission Scanning Electron Microscope (FESEM); Model: SUPRA 55VP from Carl Zeiss AG, Germany in Block P. FESEM enables the determination of Nano scale surface structure and morphology of the pet coke sample.

3.1.3 Elemental Analysis

Identification of different elements present in the pet coke sample was determined by using Energy Dispersive X-Ray Spectroscopy (EDS); Model: SUPRA 55VP from Carl Zeiss AG, Germany in Block P. The sample was also tested using the Carbon, Hydrogen, Nitrogen and Sulfur (CHNS) Analyzer (Model: LECO in Block 04-00-06) for comparison.

3.1.4 Determination of Calorific Value

Determination of the calorific value was done by Bomb Calorimeter; Model: IKA C5000 in Block 04-02-06. The mass of powdered pet coke was set to be less than 0.5 g. The author managed to weigh in 0.4734 g of powdered pet coke to be tested. The bomb calorimeter provides the energy content of pet coke when it was combusted.

3.1.5 XRD Experiment

The XRD data collection was performed by a Bruker AXS D8 Advance X-ray powder Diffractometer at Block 17. Powdered samples were scanned from 4-70^{o} in 2θ range with 0.020^{o} step interval and 2s/step counter time. Origin lab-6 software was used for deconvolution of the diffractogram. From here, we obtain a base case spectrum of an amorphous pet coke sample. A simple calculation using the Bragg's Equation was done to compare the result with graphite hexagonal structure.

3.1.6 Data Analysis

All data were gathered and analyzed to come out with a list of characteristics of the pet coke. Conclusions were also made after all of the analysis and calculations have been performed.

Figure 3.2: From top left, counter clockwise - Mortar Grinder, FESEM-EDS, Bomb Calorimeter, CHNS Analyzer, XRD equipment.

3.2 GANTT CHART AND KEY MILESTONE

The timeline showing the schedule of the key activities as well as the key milestones is given in Table 3 below. Table 3.1 shows the project schedule for FYP 1. Table 3.2 shows the project schedule for FYP 2 with actual timeline. The author managed to be ahead of the schedule as the availability of the pet coke and most of the lab bookings were made during FYP 1.

Table 3.1: Project Schedule and Main Activities for FYP 1.

	Activities / Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**M**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Selection of Project Topic	🟧	🟧						**I**							
2	Preliminary Research Work		🟧	🟧	🟧				**D**							
3	Literature Review		🟧	🟧	🟧	🟧	🟧	🟧	**S**	🟧	🟧	🟧	🟧	🟧	🟧	🟧
4	Extended Proposal					🟧	🟧	🟥	**E**							
5	Research Proposal Submission							🟧	**M**							
6	Research Proposal Defense								**B**	🟧	🟥					
7	Methodology and Refinement								**R**	🟧	🟧	🟧	🟧			
8	Equipment Booking								**E**	🟧	🟧	🟧	🟧	🟧		
9	Submission of Interim Draft report								**A**				🟧	🟧	🟥	
10	Submission of Interim report								**K**				🟧	🟧	🟧	🟥

🟧 Timeline
🟥 Milestone

Table 3.2: Project Schedule and Main Activities for FYP 2.

	Activities / Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Literature Review	🟧	🟧	🟧	🟧	🟧	🟧	🟧	**M**	🟧	🟧	🟧	🟧			
2	Sample preparation	🟧	🟧						**I**							
3	Characterization of Pet Coke		🟧	🟧	🟧	🟧			**D**							
4	XRD Experiment				🟧	🟧	🟧	🟧								
5	Analysis of Data					🟧	🟧	🟧	**S**	🟧	🟧	🟧	🟧			
6	Submission of Progress Report						🟧	🟧	**E**	🟥						
7	Validation of Data								**M**	🟧	🟧	🟧	🟧	🟧		
8	Poster Presentation											🟧	🟥			
9	Pre-SEDEX								**B**				🟥			
10	Submission of Draft Report								**R**		🟧	🟧	🟧	🟥		
11	Submission of Technical Paper								**E**				🟧	🟧	🟥	
12	Oral Presentation								**A**				🟧	🟧	🟥	
13	Submission of Final Report								**K**				🟧	🟧	🟥	

🟧 Timeline

🟥 Milestone

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 MORPHOLOGY OF PET COKE USING FESEM

Grounded pet coke has an irregular shape with sharp edges of varying sizes (Figure 4.1). It has a rough surface with many asperities with a typical size of 1 μm X 0.5 μm (Figure 4.2). It would appear that the surfaces touch each other through the asperities contact. This would lead to friction due to the interaction between asperities of different surfaces. Pet coke has no specific orientation but is align equally in all direction. This implies that the material when in use is isotropic as there was no evidence of any specific directional orientation. This agrees well with the growth and formation of pet coke in petroleum precursor is a process which involves the random growth of carbon. It is thought that the pet coke is deposited along the pipes and particularly in dead spaces and where crude oil flows slowly or is at boundary layers. Coke of the graphite type possesses an interlayer lubricity property. Therefore, the information of internal structure is highly important to determine what type of coke is predominant. If the interlayer is not of the graphitic type, it will most likely resist interlayer lubricity making mechanical pigging and removal of this type of coke more frequent compared to the graphitic type. It is obvious that the graphitic type coke will reduce the mechanical downtime maintenance.

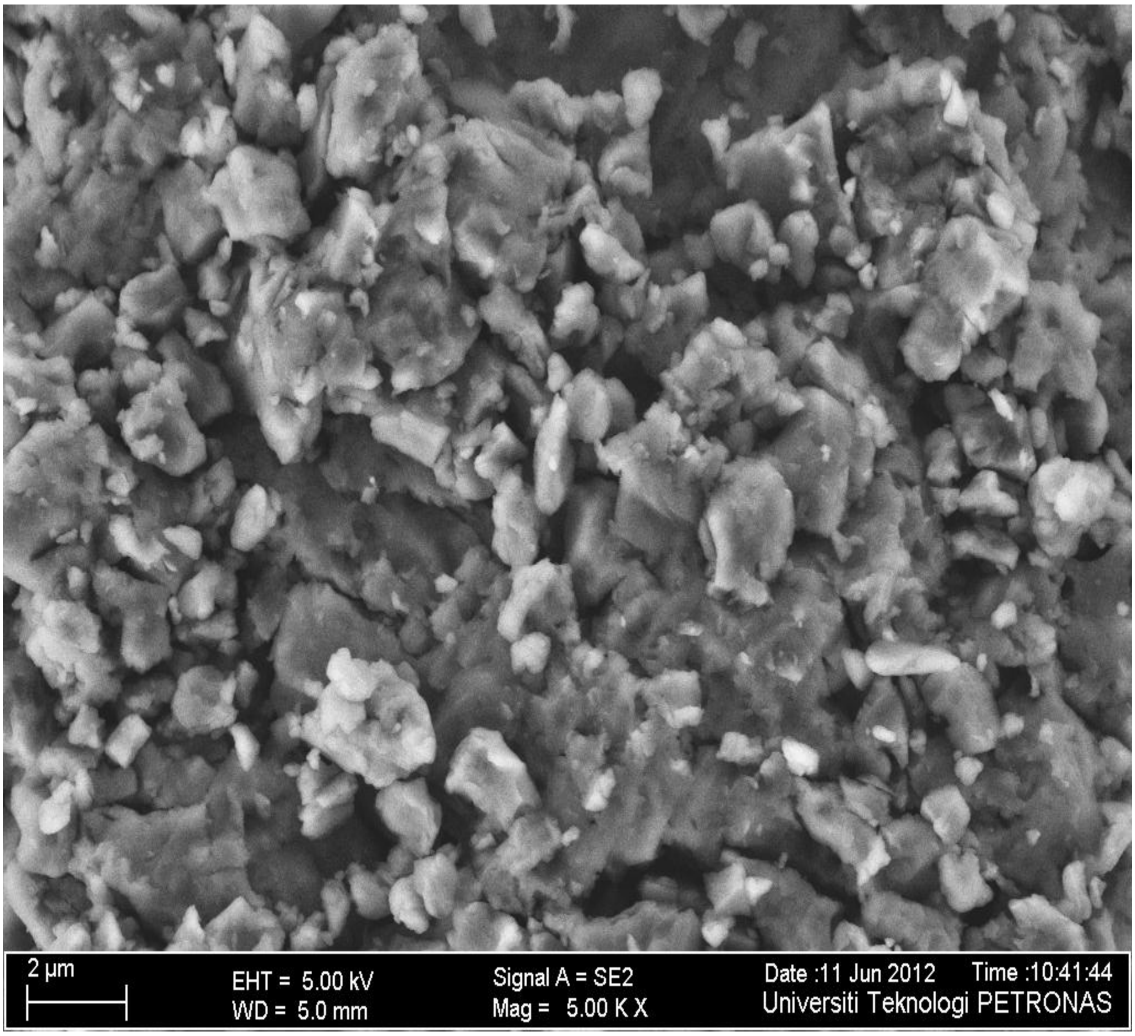


Figure 4.1: Image of pet coke under 5000 magnifications.

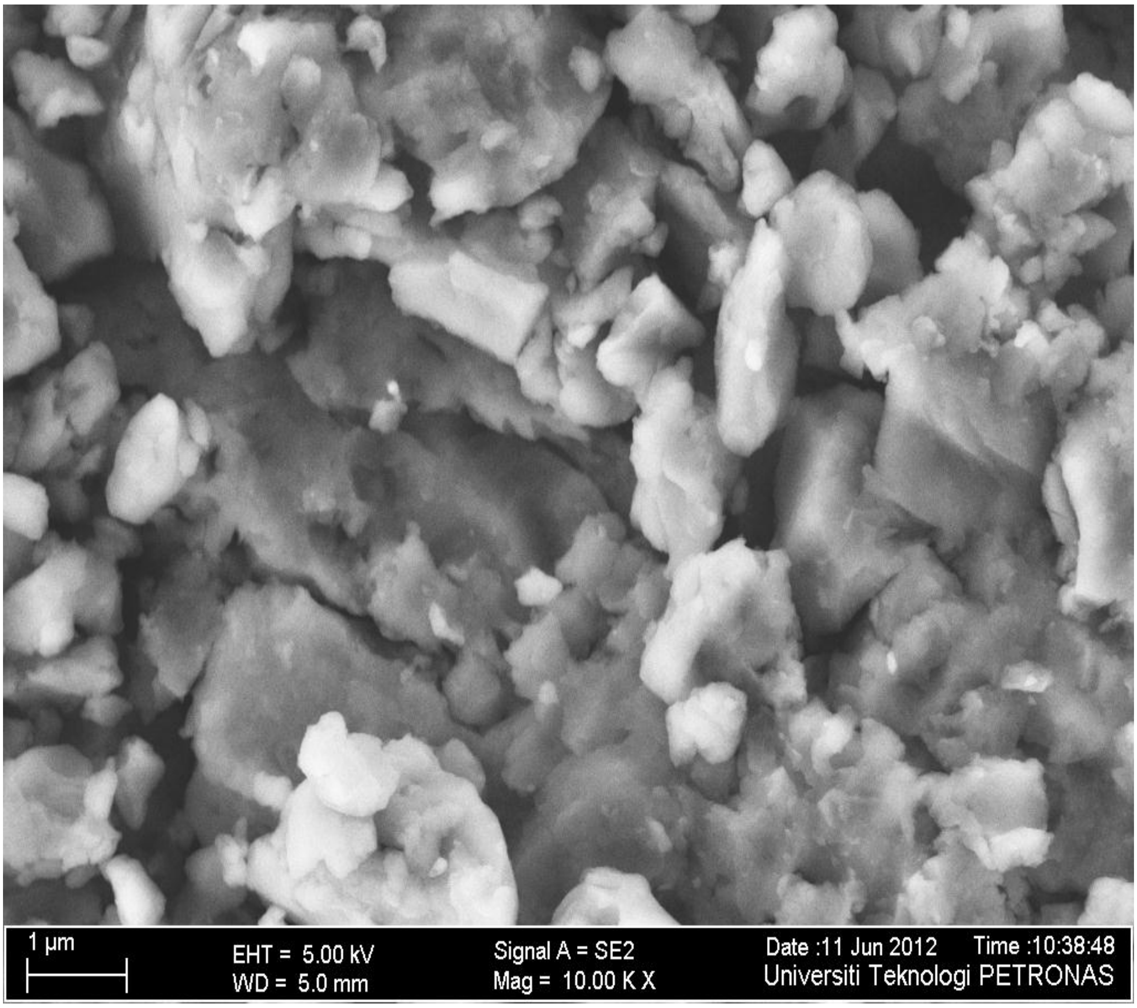


Figure 4.2: Image of pet coke under 10000 magnifications.

4.2 ANALYSIS FROM ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

The identification of different elements present in the pet coke sample is achieved by using EDS. The elemental analysis of the pet coke of Figure 4.2 is shown in Figure 4.3. It has a very prominent carbon peak with minor sulfur and oxygen peaks. The weight percentage and atomic percentage are shown in Table 4.1. The findings support the vast majority of mass fraction of pet coke comprises of carbon with 93.01%. Oxygen on the other hand comprises only 2.07% while sulfur contains approximately double of that, which is 4.92%. A high sulfur content indicates that the crude has a high sour gas (H_2S, thiols, and thio-esters) content which is an evidence that the crude is from Middle Eastern crude. They are the source for corrosion in the refinery. A high oxygen will imply a low resistance against degradation and oxidation.

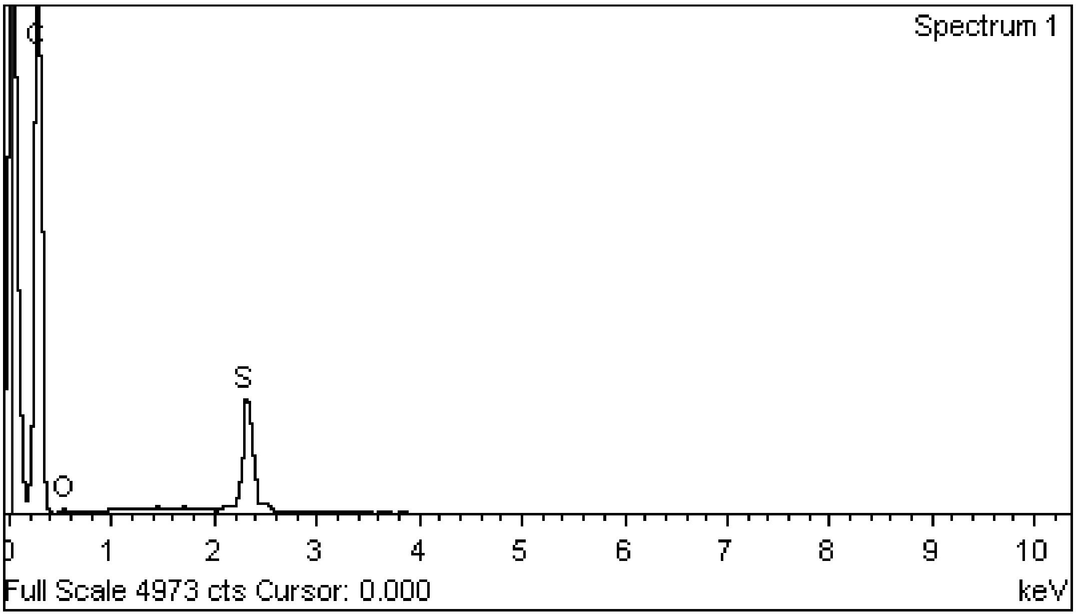


Figure 4.3: Elemental analysis of pet coke.

Table 4.1: The weight and atomic percentage of pet coke.

Element	**Weight (%)**	**Atomic (%)**
Carbon	93.01	96.48
Oxygen	2.07	1.61
Sulfur	4.92	1.91
Total	100.00	100.00

4.3 CALORIFIC VALUE

Calorific value of a substance is related to the strength of the bond. The higher the calorific value, the stronger is the bond. The calorific value of pet coke is 35,506 J/g. The pet coke sample has a higher value from other coke because it is obtained from petroleum refinery as opposed to coke which was obtained from coal. The pet coke from MRC is the better fuel compared to other coke but certainly lesser than methane, petrol, and diesel as shown in Table 4.2. High calorific value tells that the coke originates from Middle Eastern crude. This is evidence of high sulfur and oxygen content formed from crude oil from Middle Eastern origin.

Table 4.2: Calorific value of pet coke in comparison to other fuels

Fuel	**Calorific Value (J/g)**
Pet Coke (MRC)	35,506
Petrol*	48,000
Diesel*	44,800
Methane CH_4 *	39,820
Coke*	28,000 - 31,000
* (Fuels - Higher Calorific Values)	

4.4 MASS FRACTION DETERMINATION FROM CHNS ANALYZER

The mass fraction and atomic weight of pet coke is presented in Table 4.3.

Table 4.3: The mass fraction of elements in pet coke

Element	Mass fraction (%)	Atomic Weight (%)
Carbon	26.38	78.42
Hydrogen	4.212	1.04
Nitrogen	0.714	2.48
Sulfur	2.278	18.06

The largest component is carbon (78.42%), and the smallest component is hydrogen (1.04%). The sulfur content of 18.06% suggests that the pet coke is derived from sour crude oil, probably from the Middle East. A nitrogen content of 2.48% also suggests that it has high alsphaltene content typical of crude oil having a high aromatic component.

4.5 XRD ANALYSIS

Figure 4.4 is the typical pet coke X-Ray Diffraction pattern. It is diffused with no clear sharp peaks and is highly noisy. A software installed with the device is able to smooth the result is shown in Figure 4.5. The 37th peak at angle 2θ equals 25.28° has the highest intensity of 92 counts per second (Appendix A). From here, we can determine the internal structure and inter atomic distance of the pet coke sample. Observations suggest that pet coke is amorphous. However, there are short segments of the carbon chain which can packed regularly contribute to the peaks observed in Figure 4.6.

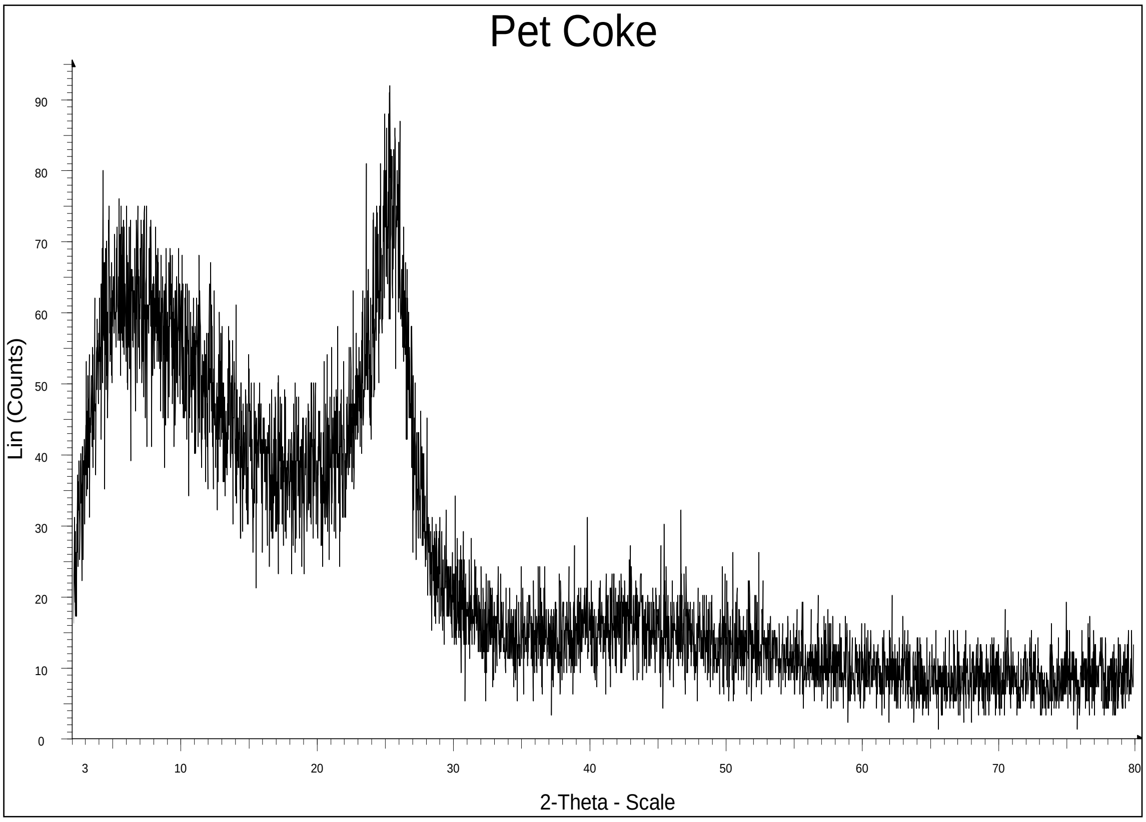


Figure 4.4: XRD pattern of pet coke.

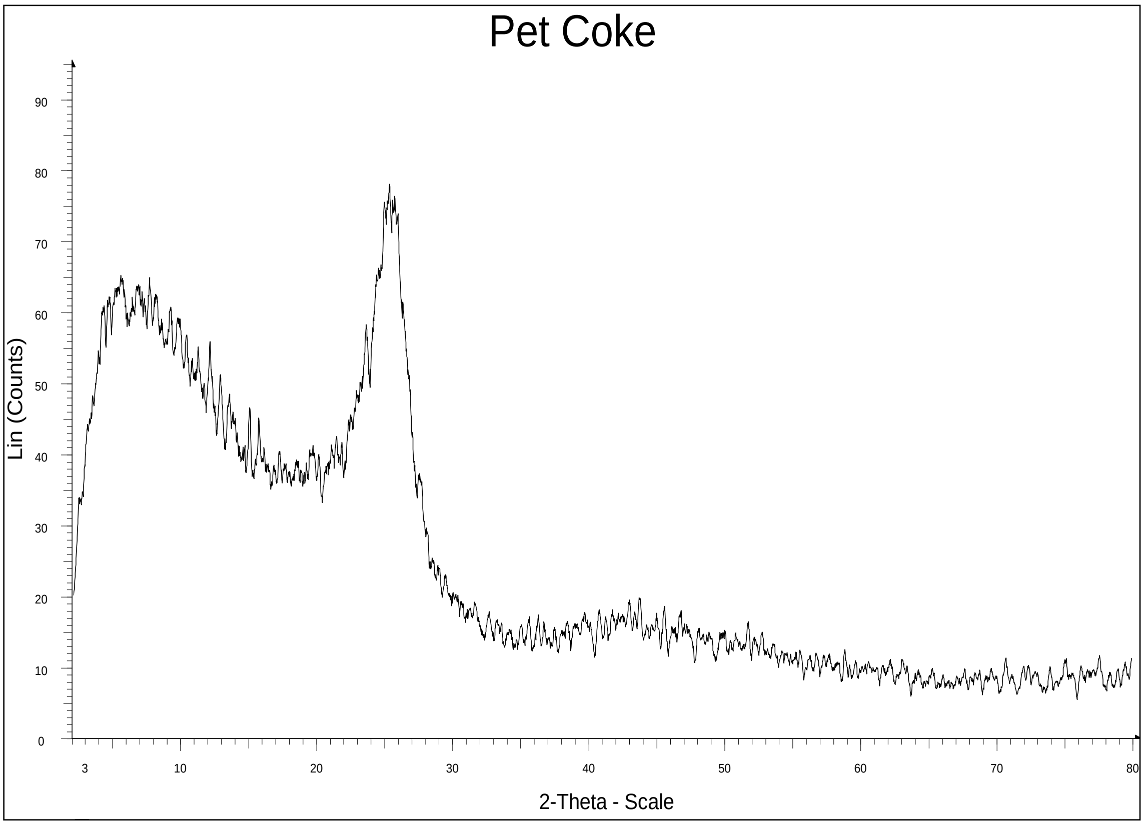


Figure 4.5: XRD pattern of pet coke after applying smoothen parameter.

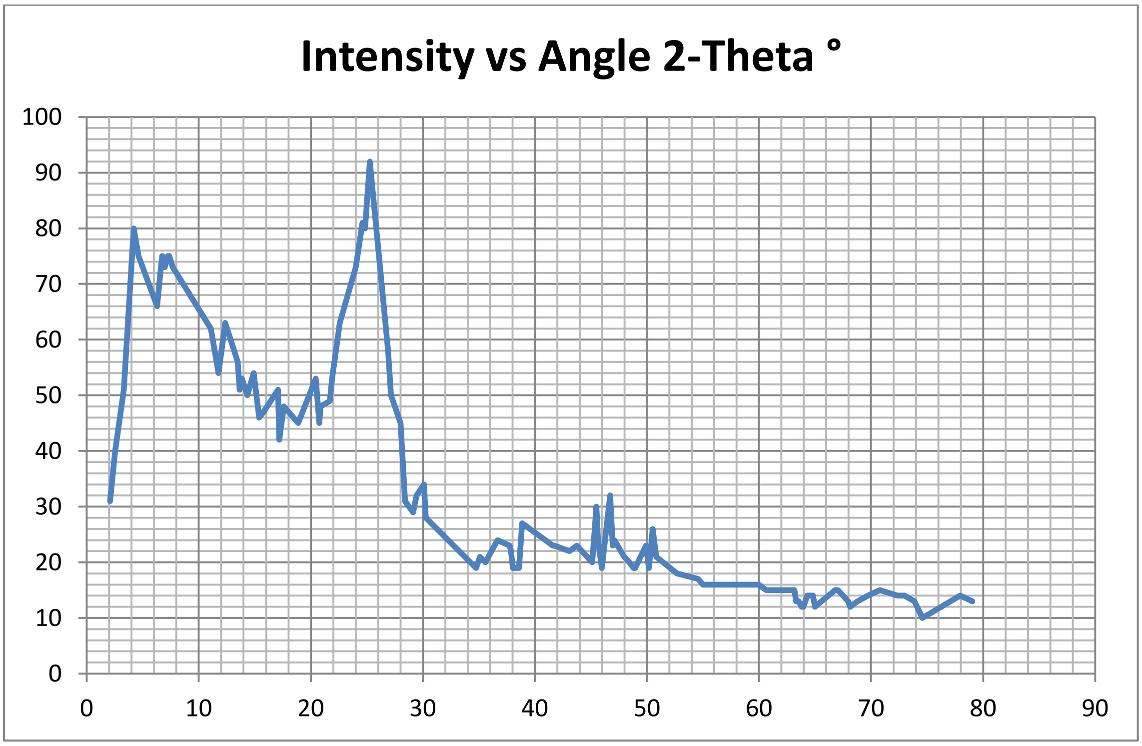


Figure 4.6: XRD pattern of pet coke with regards to 100 points only.

The pet coke sample exhibited high background intensity indicating that the coals contained a proportion of highly disordered materials in the form of amorphous carbon (Klug P. H., 1974). In addition, the coals also contained some graphite-like structures (crystalline carbon) indicated by the presence of a clear band at ~ 25.28^{o}. These observations suggest that, the crystallites in pet coke sample have intermediate structures between graphite and amorphous state called turbostratic structure or random layer lattice structure. (Manoj, 2012). The sharp peak suggests that it is of higher-rank coal.

4.5.1 Calculations

Some calculations are made to calculate the d-spacing of pet coke and compare it to the d-spacing of graphite (hx).

Bragg's Equation
$2d\sin\theta = n\lambda$
θ = angles of incident
d = inter atomic distance
λ = incident wavelength
n = an integer.

$$2d\ sin\theta = n\lambda$$

$$d = \frac{n\lambda}{2\sin\theta}$$

$$= \frac{(1)(0.154 \times 10^{-9}\ m\ )}{(2)\left(sin\frac{25.28}{2}\right)}$$

$$= \mathbf{0.352}\ \boldsymbol{nm}\ or\ \mathbf{3.52}\ \text{Å}$$

By using Bragg’s equation, (first order) the interlayer distance (d) is 0.352nm (3.52 Ǻ), while hexagonal graphite interlayer distance is 0.335nm (3.35 Ǻ). This indicates that the pet coke has larger inter layer distances and probably of Anthracite (Kwiecinska, 2004). The larger inter atomic distance suggest that the interlayer binding is loose. This make it not suitable as an advanced engineering material. However it can accommodate large elements like sulfur and oxygen.

Graphitazional percentage can be calculated by the following equation.

$$\%\, Graphitization = \left[1 - \left(\frac{d_{p-}d_g}{d_g}\right)\right] \times 100\%$$

$$= \left[1 - \left(\frac{(0.352 \times 10^{-9}) - (0.335 \times 10^{-9})}{0.335 \times 10^{-9}}\right)\right] \times 100\%$$

$$= \mathbf{95}\%$$

The result suggests that it is 95% extent of graphitization order. The percentage crystallinity of pet coke sample can be made with comparison from the area of graphite peak which is 200mm^2 to the area f amorphous peak which is 1387 mm^2 can be calculated as:

$$\%\, crystallinity$$

$$= \frac{Area\ of\ graphite\ peak}{Area\ of\ graphite\ peak + Area\ of\ amorphous\ peak} \times 100\%$$

$$= \frac{200}{200 + 1387} \times 100\%$$

$$= \mathbf{12.6}\%$$

This indicates that the pet coke can be converted to crystalline material. Modification can be made to convert the pet coke into its graphite version through control heating and annealing. This can also be done through calcination process that turns green coke into calcined coke.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The objective of the FYP is achieved and the scope of activities is feasible. The pet coke is of hydrocarbon origin. The sulfur is high suggests it is sour crude origin. The calorific value is high which makes it a suitable fuel source for boiler operations. The other benefit it is solid, so the handling of solid is easier for fuel usage. It is also devoid of heavy metal which makes it a valuable catalyst carrier or absorbent, but this benefit is negated by the high capacity of accommodating sulfur and oxygen. For future work the pet coke may be subjected to various treatment and changes to the internal dimensions is determined. This can open up new areas of application of treated pet coke and the drawing property of pet coke into fiber is enhanced.

5.2 RECOMMENDATIONS

For further study, calculation of Fourier Transform is recommended to illustrate the Radial Distribution Function (RDF). The potential of pet coke as an engineering material can also be done by considering pet coke made from crude oil of sweeter origin (lesser sulfur content) as the d-spacing maybe lesser than pet coke derived from sour crude. Future study on conversion of pet coke into liquid crystalline state is also suggested to produce carbon fibers. This may be performed by converting pet coke into its graphite version through control heating and annealing. Graphitic carbon has high interlayer lubricity properties which is useful in fiber production as fiber is required to be drawn many times its original length. Therefore, interlayer lubricity is essential.

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APPENDICES

Appendix A: 100 pints of XRD pattern of pet coke

Peak	**Angle 2-Theta °**	**d-value Angstrom**	**Intensity count**	**% Intensity**
1	2.08	42.43977	31	33.7
2	2.535	34.82839	40	43.5
3	3.305	26.7119	51	55.4
4	4.181	21.11463	80	87
5	4.606	19.17117	75	81.5
6	6.265	14.09727	66	71.7
7	6.627	13.32722	73	79.3
8	6.735	13.11338	75	81.5
9	6.962	12.68734	73	79.3
10	7.239	12.20199	75	81.5
11	7.352	12.01512	75	81.5
12	7.68	11.50208	73	79.3
13	11.076	7.98179	62	67.4
14	11.34	7.79666	59	64.1
15	11.758	7.52064	54	58.7
16	12.347	7.16297	63	68.5
17	13.47	6.56815	56	60.9
18	13.634	6.48968	51	55.4
19	13.841	6.39273	53	57.6
20	14.337	6.17291	50	54.3
21	14.902	5.94023	54	58.7
22	15.377	5.75783	46	50
23	15.79	5.60784	47	51.1
24	17.057	5.19405	51	55.4
25	17.182	5.15662	42	45.7
26	17.59	5.03782	48	52.2
27	18.873	4.69822	45	48.9
28	20.453	4.33873	53	57.6
29	20.762	4.27483	45	48.9
30	20.867	4.25369	48	52.2
31	21.683	4.09525	49	53.3
32	21.91	4.05343	53	57.6
33	22.57	3.93627	63	68.5
34	24.012	3.70306	73	79.3
35	24.62	3.61302	81	88
36	24.826	3.58349	80	87
37	**25.28**	**3.52017**	**92**	**100**
38	26.902	3.3115	58	63
39	27.154	3.28129	50	54.3
40	28.017	3.18224	45	48.9

41	28.418	3.13817	31	33.7
42	29.111	3.06506	29	31.5
43	29.427	3.03286	32	34.8
44	30.097	2.96682	34	37
45	30.253	2.9519	28	30.4
46	34.76	2.57878	19	20.7
47	35.084	2.5557	21	22.8
48	35.581	2.52113	20	21.7
49	36.66	2.44937	24	26.1
50	37.746	2.38133	23	25
51	37.85	2.37504	22	23.9
52	38.022	2.36469	19	20.7
53	38.56	2.33294	19	20.7
54	38.859	2.31566	27	29.3
55	41.603	2.16905	23	25
56	41.754	2.16156	23	25
57	43.08	2.09805	22	23.9
58	43.755	2.06722	23	25
59	45.117	2.00794	20	21.7
60	45.477	1.99288	30	32.6
61	45.62	1.98695	24	26.1
62	45.982	1.97218	19	20.7
63	46.72	1.94271	32	34.8
64	46.941	1.93409	23	25
65	47.076	1.92885	24	26.1
66	47.971	1.89492	21	22.8
67	48.427	1.87814	20	21.7
68	48.787	1.86513	19	20.7
69	48.946	1.85945	19	20.7
70	49.924	1.82529	23	25
71	50.18	1.81657	19	20.7
72	50.518	1.8052	26	28.3
73	50.83	1.79484	21	22.8
74	52.694	1.73566	18	19.6
75	54.57	1.68036	17	18.5
76	54.982	1.66871	16	17.4
77	58.907	1.56655	16	17.4
78	59.98	1.54107	16	17.4
79	60.661	1.52538	15	16.3
80	63.162	1.47086	15	16.3
81	63.301	1.46797	13	14.1
82	63.521	1.46343	13	14.1
83	63.796	1.45778	12	13
84	63.963	1.45436	12	13
85	64.299	1.44757	14	15.2

86	64.806	1.43747	14	15.2
87	64.985	1.43395	12	13
88	66.795	1.39941	15	16.3
89	67.04	1.39489	15	16.3
90	67.968	1.3781	13	14.1
91	68.142	1.37499	12	13
92	68.783	1.36373	13	14.1
93	69.739	1.34737	14	15.2
94	70.8	1.32975	15	16.3
95	72.362	1.30485	14	15.2
96	72.988	1.29518	14	15.2
97	73.86	1.28204	13	14.1
98	74.59	1.27129	10	10.9
99	77.96	1.22455	14	15.2
100	79.053	1.21033	13	14.1