Dispersibility Study of Nitrated PETRONAS Cokes

by

Mohd Farhan Bin Mat Hassan

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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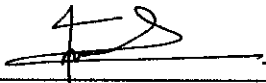
Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2010

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.

(MOHD FARHAN BIN MAT HASSAN)

ABSTRACT

Petroleum coke is a non-polar material which means it is not dispersible. Coke is insoluble and thus limits the development of petroleum coke based product. The dispersibility study of nitrated coke is an important prerequisite in order to understand the pattern of dispersibility over the time. To understand the nature and constitution of nitrated coke, or to separate the organic matter of coke for its conversion to useful products, detailed systematic studies on the solubilization characteristic of cokes in organic solvents is a must. This study will compare the stability of the suspension (colloid) among three samples of nitrated cokes (difference in nitration temperature) versus time. The reasons behind the solubility and the dispersibility characteristic of nitrated coke are also discussed. The experiment conducted will involve the usage of UV-vis spectrophotometer. The earlier findings are showing that the nitrated cokes dispersed in acids and neutral solution. A part of that, treated cokes dissolved in high pH solution. A recommendation is suggested whether a 'new water dispersible solid coke' should be further developed or vice versa. The complete substitution is, if ever achievable, a long term goal. Possible problem encountered also will be also being discussed throughout this report.

ACKNOWLEDGEMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Background Study

Petroleum coke is a byproduct of the oil refining industry. It has high heating value and low price. Owing to the increasing demand for heavy oil processing, the production of petroleum coke is increasing. The high availability and low price of petroleum coke make its combustion for power generation increasingly attractive (Wang, 2004). Hence the utilization of coal and residue cokes can meet the demand of today's and future energy.

Calcined petroleum coke (CPC) is the product from calcining petroleum coke. This coke is the product of the coker unit in a crude oil refinery. The calcined petroleum coke is used to make anodes for the aluminium, steel and titanium smelting industry. The petroleum cokes are produced in refineries using three different types of coking process: delayed; fluid and flexicoking (Jun Lee, *et. al.*, 1997).

The solid residue remaining from refinement of petroleum by the "cracking" process is also a form of coke. Petroleum coke has many uses besides being a fuel, such as the manufacture of dry cells and electrodes. Gas works manufacturing syngas also produce coke as an end product, called gas house coke.

1.2 Problem Statement

1.2.1 Problems Identification

Petroleum coke is used extensively as a fuel, particularly in the cement industry. Its cost has fallen to virtually zero, but at the same time, the quality has declined. In particular, sulphur contents have risen to the order of 5–7% and the mineral matter content has also increased. These changes have led to modifications of the combustion systems of plants using the fuels (Salvador, 2003). Petroleum coke is a non-polar material which means it is not dispersible. In other words, coke **is insoluble and thus limits the development of petroleum coke based** product. However, after undergo nitration treatment, water dispersible solid fuel can be produced.

The dispersibility study of nitrated coke is an important requirement in order to understand the pattern of dispersibility over the time. The effects of dispersibility characteristic in certain temperatures as well as various pH should also be fully understand. In that way, the application of treated coke can be further developed.

1.2.2 Significant Of The Project

In current situation, petroleum coke is undesired byproduct and has very less significant economic value. Hence, the coke is being wasted. The characteristic of solid cokes itself causing the limit of its development. Solid cokes can't be transported through pipelines and hard to be sprayed that restricted the solid coke from being applied easily for energy source.

To understand **the nature and constitution of nitrated coke**, or to **separate the organic matter of coke for its conversion to useful products**, detailed systematic studies on the solubilization of coke in organic solvents is a must. Therefore, the maximum possible enhancement in the solubility of coke in a solvent has become an art and a challenging job for the coke scientists. Among the various available methods, oxidative degradation of coal has been observed to be less cumbersome.

2

This research is aimed to turn up this wasted petroleum coke into something innovative that can benefits human as well as giving profits to the company especially PETRONAS. This is done by making the coke soluble in the water so it will have all the benefits of liquid fuel rather than solid fuel. This is not impossible if the research and development of this side product from oil refinery process is conducted thoroughly.

1.3 Objectives & Scopes Of Study

The objectives of this study are:

1) To compare the **stability of the suspension (colloid) among three samples of nitrated cokes (difference in nitration temperature) versus time using UV-vis spectrophotometer.**

2) To determine the **factors based on chemical and scientific reasoning for the dispersibility pattern of nitrated cokes**.

3) To recommend the **possibility for the treated (nitrated) coke to be further developed as water dispersible solid fuel for future usages**.

The research will also include the experiment using acidic and bes solution. This research is a continuous research from previous Final Year Project which already achieved its objective to prove that nitrated solid coke can be water dispersible.

The scope of study, as outlined by the objectives above includes focusing on the **dispersion characteristic of 3 different types of nitrated cokes versus time**. This will consider the study of turbidity and the settling rate of the colloid. Other elements such as chemical component involves will also be discussed. It is proposed that the characteristic of the cokes should be obtained by using a UV-vis spectrophotometer.

At the end of the project, the conclusion of this experimental based project will be concluded whether the project should be continued or revised.

1.4 The Relevancy of the Project

Today's energy sector is facing the most important challenge of meeting this rising demand for energy. This increasing demand, combined with the predicted decline in conventional oil production in 10-20 years, can be met by increased utilization of coke; the oil refinery residue. A higher potential in meeting the mentioned challenges altogether is attributed to the substitution of fossil fuels by clean renewable fuels on one side and the enhancement of material and energy efficiency on the other. Hence, this project is relevant in order to maximize the usage of nonrenewable energy which in this case is petroleum. The 'new created dispersible coke' should be the other alternative of fuel which will give high economic value and has the potential to be further developed and put into commercial.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Petroleum Cokes

Petroleum coke or petcoke, a refinery byproduct, has generally been considered as an unusable byproduct because of its high sulfur content. However energy industries now view petcoke as a potential feedstock for power generation because it has higher carbon content than other hydrocarbons like coal, biomass and sewage residue. This gives petcoke a great edge over other feed stocks to generate power, (Ramkumar, 2008). Petroleum coke is a byproduct of the coker refinery process which upgrades fuel oil by heating it and cracking it to higher valued gasoline, jet and diesel components.

2.1.1   Origin of Petroleum Cokes

Cokes originated from crude oil. **Crude oil** is the term for "unprocessed" oil, the stuff that comes out of the ground. It is also known as **petroleum**. Crude oil is a fossil fuel, meaning that it was made naturally from decaying plants and animals living in ancient seas millions of years ago. Because crude oil is made up of a mixture of hydrocarbons, this first and basic refining process is aimed at separating the crude oil into its "fractions," the broad categories of its component hydrocarbons.

Crude oil is heated and put into a still-a distillation column- and different products boil off and can be recovered at different temperatures. The lighter products; liquid petroleum gases (LPG), naphtha, and so-called "straight run" gasoline are recovered at the lowest temperatures. Middle distillates; jet fuel, kerosene, distillates (such as home heating oil and diesel fuel) come next. Finally, the heaviest products

5

(residuum or residual fuel oil) are recovered, sometimes at temperatures over 1000 degrees F. This is where the cokes come from. The simplest refineries stop at this point.
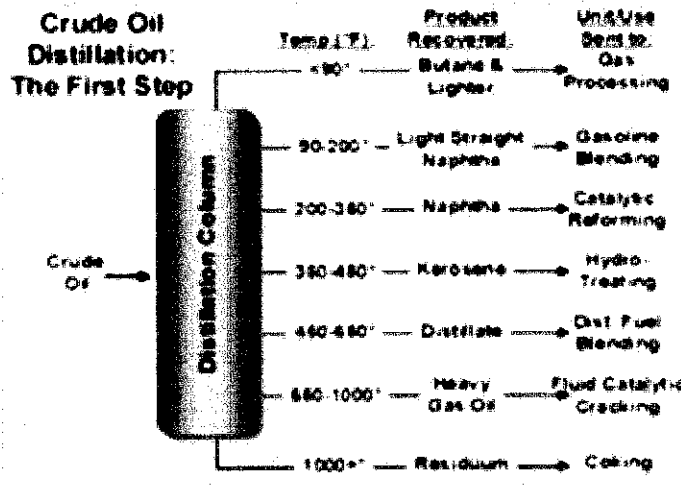
Figure 1: The oil refining process starts with a fractional distillation column.

2.1.2 Types of cokes and It's applications

The various types of coke are generally used for specific applications. **Green coke** can be prepared by different processes and as a consequence may be described as delayed process coke, fluid process coke or flexicoke. The green coke must have sufficiently low metals content in order to be used as anode material. Green coke with this low metals content is referred to as anode grade coke.

Green coke is the primary solid carbonization product from high boiling hydrocarbon fractions obtained at temperatures below 900 K. It contains a fraction of matter that can be released as volatiles during subsequent heat treatment at temperatures up to approximately 1600 K. This mass fraction, the so-called volatile matter, is in the case of green coke between 4 and 15 weight percent, but it depends also on the heating rate. Green Coke may contain up to 15% residual hydrocarbon. The green coke with too high metals content will not be calcined and is used for burning. This green coke is called fuel grade coke (Wikipedia.com).

6

Calcined petroleum coke (CPC) is the product from calcining petroleum coke. Calcined coke is produced by heating green coke to temperatures up to 1200°C. .The calcined petroleum coke is used to make **anodes** for the aluminium, steel and titanium smelting industry. Generally there is lower ash (<0.5%), lower moisture (8-10%) and lower Volatiles (8-10%) than steam coal, resulting in a much higher heating value, on the order of 14,000 Btu/lb. There is generally higher sulfur, ranging from about 4 % to 7 %, while the HGI varies from 35 to 75. **Needle coke** for instance is calcined and then used in the production of **electrodes** due to its lower electrical resistivity and coefficient of thermal expansion.

Petroleum coke is increasingly being used as full or partial placement for coal in electrical power generation. The blending of coke with coal, in appropriate proportions, allows for environmental emission compliance and improves ignition and flame stability. Fluidized bed combustion is commonly used to burn petroleum coke. Gasification is increasingly used with this feedstock (often using gasifiers placed in the refineries themselves).

Most coke produced is fuel grade, meaning it competes with coal. Some coke is very low in Iron, Nickel and Vanadium, thereby achieving a higher value in the aluminum anode industry. V and Ni (chemically bonded) and Na (dissolve as sodium chloride in water which is entrained with a crude oil) catalyzed anode oxidation accelerating anode consumption and are ingot impurities (Jun Lee, *et. al.*, 1997).

Production costs associated with petcoke are minimal because it is a byproduct of the refining process, and prices are generally determined by the competitive steam coal price. Pricing is also generally discounted to compensate for sulfur, HGI and the extra difficulties of the end user managing both coal and coke inputs.

Presently, there is about 60 million tons/year of coke produced worldwide, most of it located at coastal refineries in North and South America. In a few years it will be close to 70 million tons/year as new refineries with cokers are being built in the US, Mexico and Venezuela. Since the Americas are generally coal exporters, most of this

coke is also exported to the same areas that consume imported steam coal: primarily Japan and Europe.

Cement plants and power plants are the 2 greatest consumers of pet coke. There is some limited use as space heating and in commercial brick kilns in Europe, and a small but emerging market for met coal blending component for the steel industry. While the higher sulfur may limit the coke in a coal or petroleum coke blend in a plant designed for coal, more recently designed Circulating Fluidized Bed (CFB) boilers can burn 100% high sulfur coke (Ramkumar, 2008).

2.2 Effects of Nitration On Hydrocarbons

Nitration is one of the oldest and the most extensively studied reactions. Moreover, this process has been the most acceptable and favoured route for the manufacture of explosives, precursors for dyes and intermediates, and industrial solvents. The nitro group was introduced in the organic matrix of hydrocarbon via **oxidative nitration**, using dilute nitric acid. An effect of nitration towards petroleum coke is de-ashing. There are indications that are of the possibility of removing ash from carbonaceous material by treating them with nitric acid. Oxidization causes coal organic matter solubilization. The total amount of hydrogen diminishes through the removal of aromatic hydrogen in nitration.

An example of nitration is shown below using benzene as the hydrocarbon. Nitration happens when one (or more) of the hydrogen atoms on the benzene ring is replaced by a nitro group, NO_2. The experimental results reveal that introduction of the nitro group substantially enhanced the solubilization of hydrocarbon in aqueous organic solvents. The study reveals that the nitro groups present in oxynitrated hydrocarbons had an important role in solubilizing it in aqueous organic solvents (Debapriya, 2007).

The nitrated mesophase lost its original hydrophobicity and can be readily dispersed in distilled water and dissolve at high pH. The electrolytic and colloidal natures are due to the presence of hydrophilic ionizable groups introduced as a result of nitration (B Ariwahjoedi and B. Rand, 1989).

8

Benzene is treated with a mixture of concentrated nitric acid (I) (II) and concentrated sulphuric acid at a temperature not exceeding 50°C. The mixture is held at this temperature for about half an hour. Yellow oily nitrobenzene is formed. The concentrated sulphuric acid is acting as a catalyst. The nitro group introduced to the compound enhanced the solubility of the hydrocarbon.

$$\text{Benzene} + HNO_3 \longrightarrow \text{Nitrobenzene} + H_2O \qquad \cdots\cdots\cdots\cdots\cdots (I)$$

$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O \qquad \cdots\cdots\cdots\cdots\cdots (II)$$
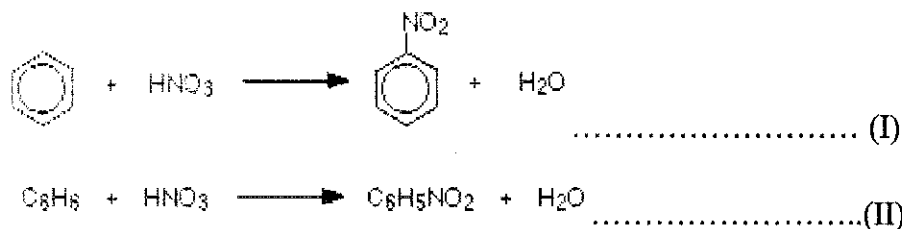
The role of the NO_2 group is of utmost importance, with respect to hydrocarbon solubilization in aqueous organic solvents. Previous research has proved that calcined coke can be water dispersible after treating with nitration. The properties of the calcined coked also did improve after nitration (Hidayah, 2009).

The earlier studies on the oxidation of coke using air, permanganate, nitric acid, trifluoroacetic acid–hydrogen peroxide, and performic acid have been performed. These studies have suggested specific mechanisms of oxidative degradation, with respect to each type of oxidant. In the past, the oxidation of coal preceded using 16 N nitric acid, with intent to produce aromatic polycarboxylic acid. Because the reaction is vigorous and nonspecific, much degradation occurred; this degradation was due to the severity of the reactions, and, therefore, solubility studies on coke/treated coal became difficult (Debapriya, 2007).

The use of nitric acids alone resulted in the formation of a large amount of complex oxidation products which on electrolysis remained in the center compartment, even in the presence of excess alkali (B. Juetter, 1937).

2.3 Spectrophotometry

In physics, spectrophotometry is the quantifiable study of electromagnetic spectra. It is more specific than the general term electromagnetic spectroscopy in that spectrophotometry deals with visible light, near-ultraviolet, and near-infrared. Also, the term does not cover time-resolved spectroscopic techniques.

Spectrophotometry involves the use of a spectrophotometer. A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the color (or more specifically the wavelength) of light. Important features of spectrophotometers are spectral bandwidth and linear range of absorption measurement (Zhu, 2004).

Perhaps the most common application of spectrophotometers is the measurement of light absorption, but they can be designed to measure diffuse or specular reflectance. Since electrons can occupy only discrete energy states, the way radiation interacts with matter can indicate its chemical identity.

Chemists commonly use absorbance spectroscopy, or how a substance absorbs photons of light, to obtain both qualitative (identity) and quantitative (amount) information. The quantitative measurement is achieved because each photon of light absorbed corresponds to the excitation of a single electron.

All spectrophotometer instruments designed to measure the absorption of radiant energy have the basic components as follows:

1. A stable source of radiant energy (Light);

2. A wavelength selector to isolate a desired wavelength from the source (filter or monochromator)

3. Transparent container (cuvette) for the sample and the blank;

4. A radiation detector (phototube) to convert the radiant energy received to a measurable signal; and a readout device that displays the signal from the detector.
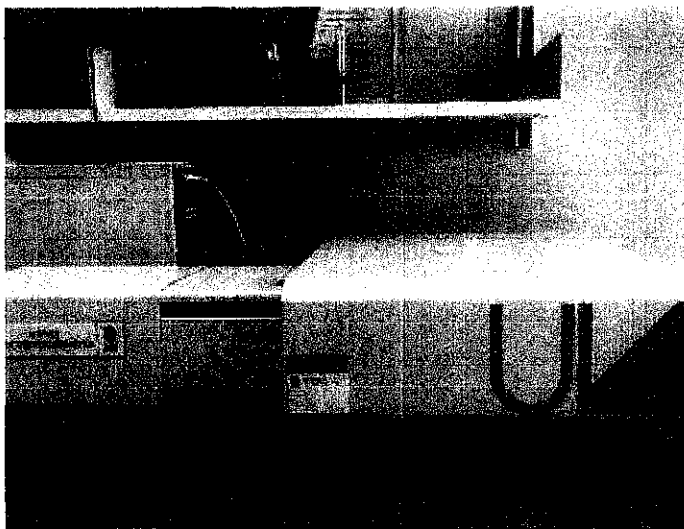
Figure 2: Spectrophotometer used in Chemical Laboratory

The energy source is to provide a stable source of light radiation, whereas the wavelength selector permits separation of radiation of the desired wavelength from other radiation. Light radiation passes through a glass container with sample. The detector measures the energy after it has passed through the sample.

The readout device calculates the amount of light absorbed by the sample displays the signal from the detector as absorbance or transmission. The spectrophotometers which are used for such measurements may vary from simple and relatively inexpensive colorimeters to highly sophisticated and expensive instruments that automatically scan the ability of a solution to absorb radiation over a wide range of wavelengths and record the results of these measurements. (*http://www.rrcap.unep.org*)

In this project, the stability of the dispersion of the colloid will be determined as time increase using spectrophotometer. A spectrophotometer is a machine which operates on the principle of Beer-Lambert's Law; that is: the absorbed light is directly

proportional to the concentration of the solution while the transmitted light is inversely proportional; the darker the solution, the more concentrated it is.

2.4 Beer's Law Plot

Beer's law plots are commonly straight-line graphs in which absorbance is plotted versus concentration (Judith, 1999). Scientists use many methods to determine the identity and quantity of a substance in samples. Spectroscopy is a simple and powerful method for performing both qualitative and quantitative analyses.

Beer-Lambert Law, more commonly known as *Beer's law*, states that the optical absorbance of a chromophore in a transparent solvent varies linearly with both the sample cell path length and the chromophore concentration. *Beer's law* is the simple solution to the more general description of Maxwell's far-field equations describing the interaction of light with matter. In practice, Beer's Law is accurate enough for a range of chromophores, solvents and concentrations, and is a widely used relationship in quantitative spectroscopy.

Each chemical species has a unique spectral fingerprint based on where electrons are located with respect to the nucleus. For example, a solution of sodium ions sprayed into a flame will change the flame's color to a bright yellow, while a solution of lithium ions will cause the flame to burn a deep red color. Data from a spectrophotometer can be collected and graphed in what is called an absorption spectrum.

Before using *Beer's law* as an analytical tool, it is necessary to select a suitable wavelength and determine whether Beer's law is valid (linear) at the wavelength selected. If possible, select the wavelength at maximum absorbance (called λmax). The maximum will always be at the same wavelength (even if the calibration on the instrument dial is in error) and can be found by any experimenter under any conditions. This allows detection of lower concentrations of sample.

Absorbing radiation of molecule changes with the interaction species. Two empirical laws have been formulated about the absorption intensity. Lambert's law states that the fraction of the incident light absorbed is independent of the intensity of the

12

source. Beer's Law states that the absorption is proportional to the concentration of the absorbing species. From this law, Eq. (1) is determined (William, 1989; and Brands,2002).

$$\log \frac{I_0}{I} = A = \varepsilon c l.$$

Io and *I* are the intensities if the incident and transmitted light, respectively, *l* is the path length of the absorbing solution, and *c* is the concentration. Log_{10} (I_0/I) is the absorbance or capcity density; ε is known as the molar extinction (Sandhu, 2002).

Absorbance is measured in a spectrophotometer by passing a collimated beam of light at wavelength λ through a plane parallel slab of material that is normal to the beam. For liquids, the sample is held in an optically flat, transparent container called a cuvette. Absorbance (A_λ) is calculated from the ratio of light energy passing through the sample (I_0) to the energy that is incident on the sample (I):

$$A_\lambda = -\log (I/I_0)$$

Beer's law follows:

$$A_\lambda = \varepsilon_\lambda bc$$

ε_λ = molar absorptivity or extinction coefficient of the chromophore at wavelength λ (the optical density of a 1-cm thick sample of a 1 M solution). ε_λ is a property of the material and the solvent.

b = sample pathlength in centimeters

c = concentration of the compound in the sample, in molarity $(\text{mol } L^{-1})$

In an absorbance experiment, light is attenuated not only by the chromophore, but also by reflections from the interface between air and the sample, the sample and the cuvette, and absorbance by the solvent. These factors can be quantified separately, but are often removed by defining I_0 as the light passing through a sample "blank" or

13

"baseline" or reference sample (for example, a cuvette filled with solvent but zero concentration of the chromophore is used as the blank).

Many factors can affect the validity of *Beer's law*. It is usual to check for the linearity of Beer's Law for a chromophore by measuring the absorbance of a series of standards. This "calibration" can also remove errors in the experiment, the equipment, and the batch of reagents (such as cuvettes of unknown path length).

Beer's law states that the absorbance is directly proportional to the concentration of a solution. If you plot absorbance versus concentration, the resulting graph yields a straight line. The equation for the straight line (termed regression line) can be used to determine the concentration of an unknown solution once the %T has measured.

2.4.1   The Importance of Concentration

The proportion of the light absorbed will depend on how many molecules it interacts with. Suppose we have got a strongly coloured organic dye. If it is in a reasonably concentrated solution, it will have a very high absorbance because there are lots of molecules to interact with the light. However, in an incredibly dilute solution, it may be very difficult to see that it is coloured at all. The absorbance is going to be very low.

2.5 Solubility Factors

2.5.1   Mellitic Acids

Mellitic acid, $(C_6(COOH)_6)$ the benzene hexacarboxylic acid (III), is known as an oxidation product of various carbonaceous materials. It is very resistant to further oxidation, and is of definite structural significant (B. Juettner, 1937). The acid may be prepared by the oxidation of pure carbon, or of hexamethyl benzene, in the cold, by alkaline potassium permanganate (F. Schulze, 1871).

14

It crystallizes in fine silky needles and is soluble in water and alcohol. It is a very stable compound, chlorine, concentrated nitric acid and hydriodic acid having no action upon it. It is decomposed, on dry distillation, into carbon dioxide and pyromellitic acid when distilled with lime it gives carbon dioxide and benzene (S.F Darlow 1960).

(III)
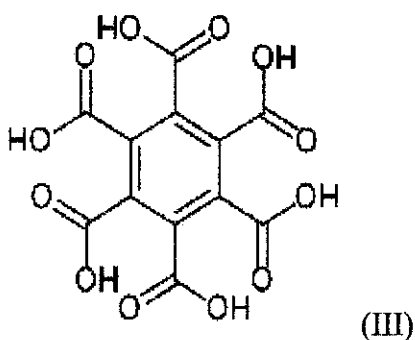
The presence of mellitic acids play important role in this research because of the –COOH groups available on it that will affect the solubility of the hydrocarbon. The presence of hydrophilic, ionizable groups (nitro, amino, carboxyl/ other oxidize groups and sulphonic groups) is responsible for the electrolytic nature of mesophase aqua-sol, (B. Ariwahjoedi & B. Rand, 1989).

2.5.2   Humic Acids

Humic acid is a principal component of humic substances which are the major organic constituents of soil, (humus), peat, coal, many upland streams, dystrophic lakes and ocean water. It is produced by biodegradation of dead organic matter. The effects of humic substances on the solubility and mobility of organic contaminants has been the subject of numerous studies. Humic acids, found in soil and groundwater, have a surface activity similar to that of surfactants.

Humic acids is also a factor that determining the solubility of the hydrocarbons. In the first phase of the study, it was found that humic acids concentrations as low as 0.1g/L could enhance the solubilization of aromatics from diesel fuel. While pH and

ionic strength did affect the solubility, the concentration of humic acid was the most important factor governing solubility (S. Lesage *et. al*, 1995).

A typical humic substance is a mixture of many molecules, some of which are based on a motif of aromatic nuclei with phenolic and carboxylic substituents, linked together; the illustration shows a typical structure. The functional groups which contribute most to surface charge and reactivity of humic substances are phenolic and carboxylic groups.

Concentration of humic acids in solution will affect the colour of the solution. In general the more percent of humic acids, the darker the solution it will be.

2.6 Colloidal Phase

The word "Colloid" was derived from the Greek, "kolla" for glue, as some of the original organic colloidal solutions were glues. This term was first coined in 1862 to distinguish colloids from crystalloids such as sugar and salt.

Colloids have been studied by scientists since the early 1800's. The early part of the 20th century saw a number of major developments in both chemistry and physics, some of which had direct influences on the study of colloids. A number of methods for studying colloidal particles were developed, including diffusion, electrophoresis, and scattering of visible light and X-rays. A colloid is a type of mixture in which one substance is dispersed evenly throughout another.

The colloid state of residue can cause several problems during processing stages. For instance it determines the rheological behavior of product, decides about formation of cokes in conversion process and cause for fouling during transport (Laux, 1997).

Each type of mixture has special properties by which it can be identified. For example, a suspension always settles out after a certain period of time. That is, the particles that make up the suspension separate from the medium in which they are suspended and fall to the bottom of a container. In contrast, colloidal particles typically

16

do not settle out. Like the particles in a solution, they remain in suspension within the medium that contains them.

Table 1: Example of dispersing phase and dispersed phase of colloid

		Dispersed Phase		
		Gas	Liquid	Solid
Dispersing Phase	Gas	None: all gases are soluble	Liquid aerosol, Examples: fog, mist	Solid aerosol, Examples: Smoke, dust
	Liquid	Foam, Examples: Whipped cream	Emulsion, Examples: Milk, mayonnaise, hand cream, blood	Sol, Examples: Paint, pigmented ink
	Solid	Solid foam , Examples: Styrofoam, Pumice	Gel, Examples: Gelatin, jelly, cheese, Opal	Solid sol , Examples: Ruby glass

Colloids also exhibit Brownian movement. Brownian movement is the random zigzag motion of particles that can be seen under a microscope. The motion is caused by the collision of molecules with colloid particles in the dispersing medium. In addition, colloids display the Tyndall effect. When a strong light is shone through a colloidal dispersion, the light beam becomes visible, like a column of light. A common example of this effect can be seen when a spotlight is turned on during a foggy night. The spotlight beam can be seen because of the fuzzy trace it makes in the fog (a colloid).

Therefore detail knowledge about the forming mechanism of the colloid disperse phase and about the factor responsible for stabilizing respect precipitating the disperse phase is very important and significant for this study.

17

CHAPTER 3

METHODOLOGY

1. WORK PROCESS

3.1 Procedures

The experiment will be conducted as below. First we need to find the maximum absorbance at specific wavelength for nitrated coke dispersed in distilled water by varying the concentration. UV-Vis spectrophotometer will be used. From the data, graph of Lambert-Beer Law is plotted.

The defined maximum absorption wavelength will be used again for the experiment on intensity of absorption versus time. The graph of absorbance versus time is plotted in term of nitrated temperature and pH of the buffer solution. Dispersibility graph for each solution is plotted and the trend is being analyses and discussed. The reasons behind the solubility and dispersibility are analyzed.

The final step is to conduct a simple testing to determine the settlement time of nitrated coke in neutral and acidic solution using a test tube. The height layer of dispersed part is measured per time.

Note that distilled water is used in the earlier part as the control specimen. The methodology for each part is summarized as below:

3.1.1 Initial preparation

1) **Weight 0.01 gm of sample nitrated** coke prepared at $75^{o}C$.

2) **Measure 100 ml of distilled water** and add into the beaker containing weighted coke

18

3) Stir or shake the mixture for 5 min until it disperse equally in the distilled water.

3.1.2 Determination of maximum absorption wavelength

1) Set the spectrophotometer wavelength control to the desired wavelength.

2) Using solution **prepared in part 1** to measure the absorbance between **200 and 600 nm**. Be certain to recalibrate using the blank solution at each wavelength. To save time, initially make measurements at increments of 25 nm.

3) Record these values in the first. Once the region from 200 to 600 nm has been measured, notice the portion(s) of the curve with the λmax. Choose four wavelengths below and above your highest absorbance wavelength.

4) The wavelength with the highest absorbance is λmax and should be used in next part for the Beer's law plot. **Record your Absorbance vs. wavelength data**

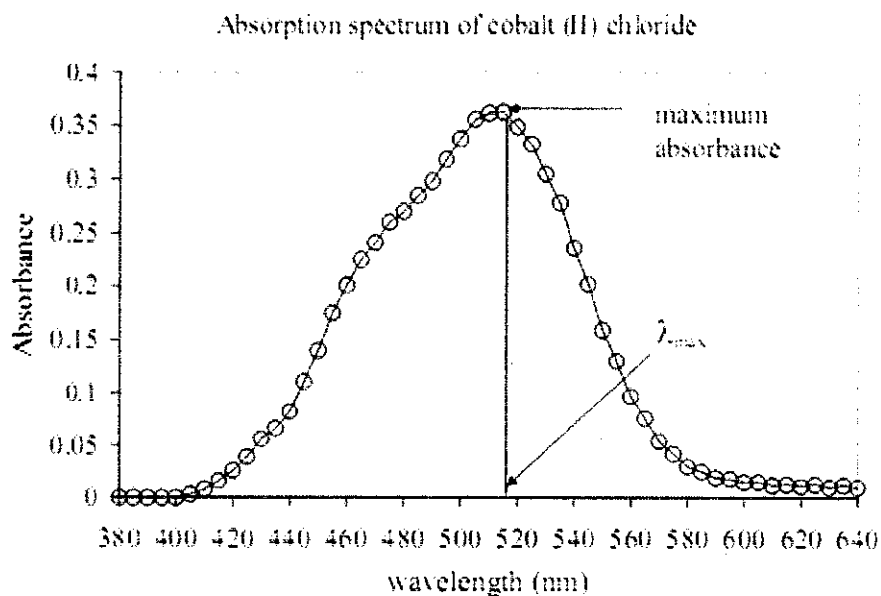5) Data from a spectrophotometer can be collected and graphed in what is called an absorption spectrum.

Figure 3: Example of data collected from spectrophotometer

3.1.3 Preparing of a Beer's Law Plot & Define Optimum concentration

1) The next step is to determine if Beer's law is valid at λmax. Set the spectrometer to the selected λ max, and determine the absorbance of samples at **0.05g Mass%, 0.1g Mass%, 0.2g Mass% of petcoke nitrated at 50°C** solution. Beer's law plot will be a straight line. Remember the point where absorbance and concentration both have a value of 0.00 is a data point.

2) Now obtain samples of the prepared nitrated coke **at step no 1**. At the selected wavelength, determine the absorbance for each solution and record these on your data sheets.

3) **Repeat** step 1 & 2 for nitrated petcoke **at 75°C and 95°C.**

4) Measure the absorbance of each of the solutions of known concentration at the analytical wavelength.

5) Plot the data for all known concentrations on the graph. **Draw the best straight line** through the five known points on the **Absorbance vs. Concentration** graph.
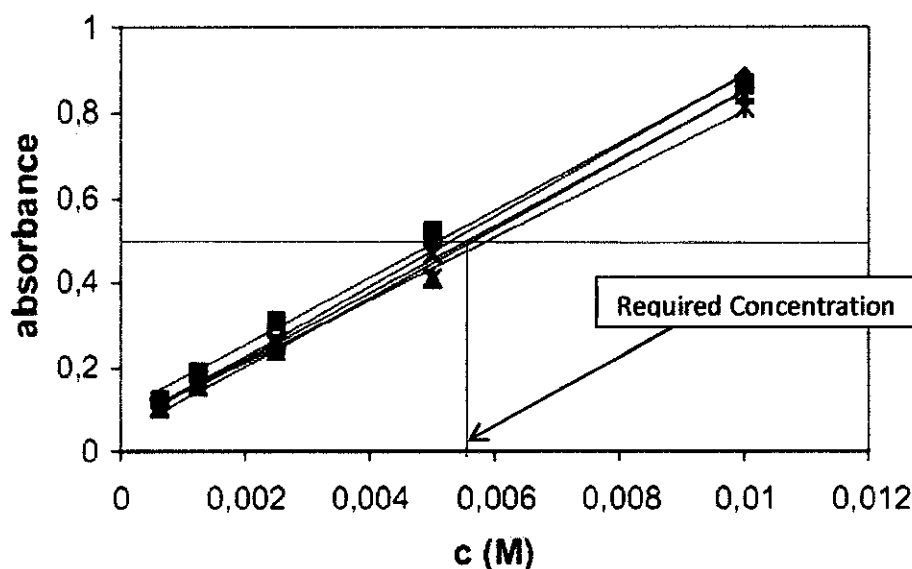

Figure 4: Example graph of Absorbance vs. concentration. (Nalan, 2005)

6) **Define concentration** for each coke at various temperatures at **absorbance of 1** (example).

7) Using the **concentration at defined absorbance data**, measure and plot the data of **Absorbance versus time for 30 minutes (at 5 min increment) for each** prepared nitrated coke at various temperature, **50°C, 75°C and 95°C** solutions using the same λ **max.**
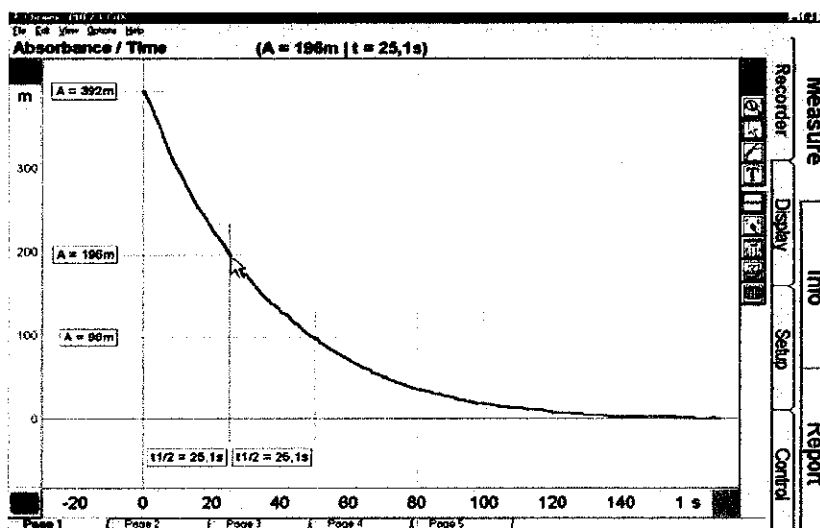
Figure 5: Example graph of Absorbance vs. Time graph

3.1.4   Absorbance Versus Time (Revised)

Since the concentration at absorbance value of 1 using Beer's Law cannot be obtained, the experiment is proceeding by using direct mass% concentration. The procedure taken is listed below:

1) Weight 0.01 gm of petcoke and mixed with 100 ml of buffer solution at 3 differences **pH each which are at pH 4, 7 and 10.**

2) Set the UV-Vis wavelength as per define earlier (maximum wavelength).

3) Obtain graph of absorbance versus time.

4) Plot the data of **Absorbance versus time for 30 minutes (at 5 min increment) for each** prepared nitrated coke at various temperature, **50°C, 75°C and 95°C**

5) Discuss about the dispersibility pattern of petcoke for each graph.

3.1.5 Testing and Verifying Methods (Additional)

Since the nitrated only dissolve in pH 10 (high pH) but disperse in neutral and acid pH, another testing should be done to determine the settlement of dispersed cokes to settle down at the bottom of the medium. The methods are shown below:

1. Measure and add 0.2g of petcoke at 50°C into 100ml of pH 4 buffer solutions (or 0.02g/10ml solution) in a test tube.

2. Shake the mixture until it equally dispersed. Then stop shaking.

3. Measure the level (differentiate the level by a layer) between clear solution and dark solution (enriched with petcoke) using a ruler.

4. Take the measurement every 2 minutes until all the dispersed nitrated cokes settle down.

5. Repeat procedure by using 75°C and 90°C nitrated petcoke.

6. Repeat again from 1 to 7 by change pH4 of buffer solution with pH7.

7. Plot graph level (height) versus time.

8. Record all observation, changes and data required for analysis.

9. Discuss the data obtained.

3.2 Tools, Hardware and Chemicals

The equipments needed in conducting the experiment are listed below:

1. UV-VIS Spectophotometer
2. Stirrer/ Glass Rod
3. Beaker
4. Test Tube
5. Fume cupboard
6. **Concentrated Nitric acid**
7. **Concentrated Sulphuric Acid**
8. **Buffer solution at pH of 4, pH 7 and pH 10.**
9. **Calcined Petroleum coke (from PETRONAS Penapisan Melaka)**

3.3 Safety Precautions

Standard laboratory procedure must be followed. Safety glasses must be worn during this experiment.

3.4 Brief Experimental Works Procedures

Three types of nitrated cokes was prepared earlier at 3 difference temperatures which are at 50°C, 75°C and 95°C is used is examined in this experimental work. In previous research, the original calcined cokes were refluxed with concentrated sulfuric acid and concentrated nitric acid and dried at 3 different temperatures. The sulfuric acid was acting as a catalyst. It also absorbed water. The **resulted nitrated cokes** then were used to find the maximum absorption wavelength. The Beer's Law plot was applied in order to get the maximum absorption.

After the maximum absorption wavelength was defined using the UV-Vis spectrophotometer, those 3 types of nitrated cokes at different temperature were weighted each 0.002gram before mixed with 20 ml of buffer solution at pH of 4,7 and 10. Then, using the spectrophotometer again the absorbance is recorded versus time. The measurement is taken a very 5 minutes until the final reading is constant. All the characteristic of the dissolve or dispersed coke in buffer solution is observed and analyzed. The pattern of the graph obtained was then further discussed.

In order to differentiate and verify the setting rate of the petcokes to settle down in buffer solution of pH 4 and pH 7, the 3 nitrated cokes were analyzed again. The settlement time is recorded by letting it 'free falling' in a test tube for a certain time and the time was measured. In this case, the test is not done for pH 10 since the nitrated petcokes fully dissolved in alkaline solution. The data obtain was analyzed and discussed.

CHAPTER 4

RESULT & DISCUSSIONS

4.0 RESULTS & DISCUSSIONS

4.1 Results

The nitrated cokes react differently and has unique characteristic when difference types of pH (buffer solution) are used as a solvent. For each type of cokes, which are nitrated at 50°C, 75°C and 95°C has shown different pattern of result that will be discussed below.

4.1.1 Determining of Maximum absorption wavelength

In order to determine the light adsorption for the dispersed coke in solution, UV-vis Spectrophotometer is used. The interface of the *UVProbe software* is shown below:
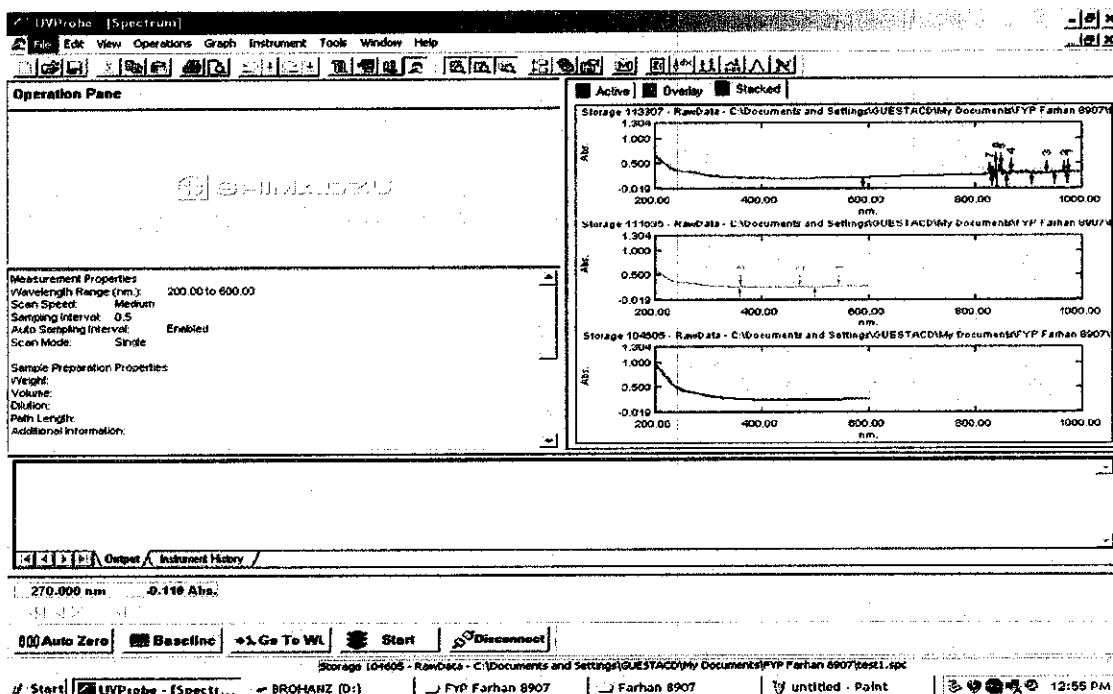

Figure 6: The interface of UVProbe software- UV-vis spectrophotometer.

Several data are taken in order to determine the maximum wavelength. The graph of absorbance versus wavelength is plotted below:
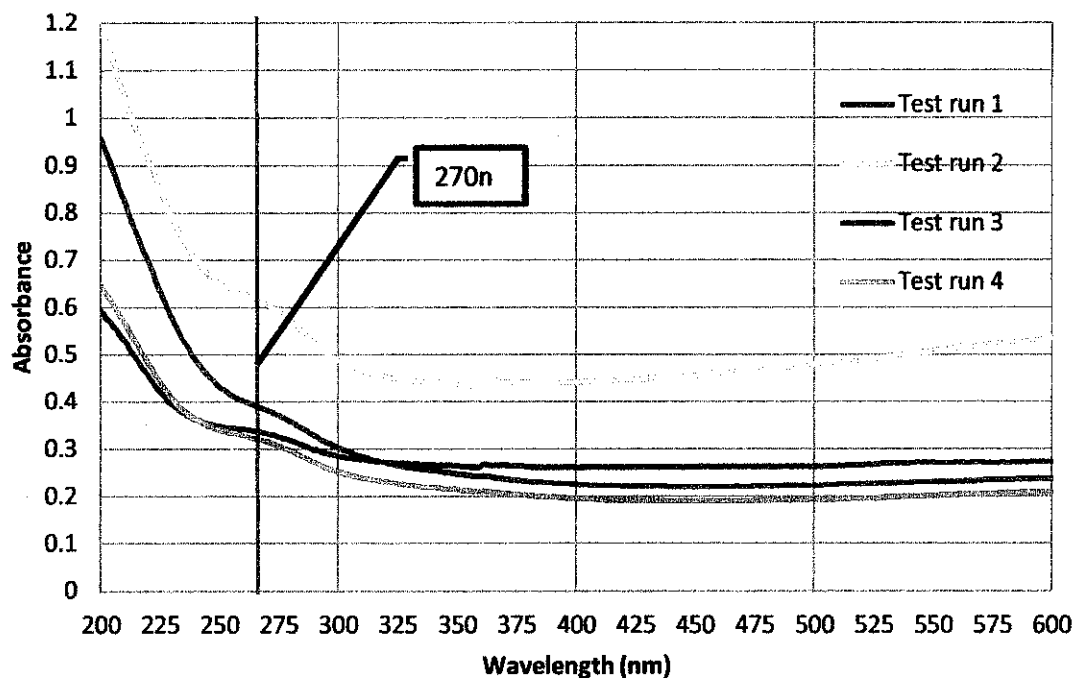
Figure 7: Absorbance versus wavelength (standard)

From the plotted absorbance versus wavelength graph, the maximum absorption wavelength is found to be approximately **270nm.**

4.1.2   Beer's Law Plot

Using the defined maximum absorption wavelength **(270 nm)** earlier, experiment is repeated using different concentration of dispersed petcokes to prepare the data for Beer's Law plot. The table is showing the result of absorbance for each concentration for respective samples.

Table 2: Concentration of 3 samples nitrated cokes and respective absorbance.

Sample of Petroleum cokes	Concentration Mass (%)	Absorbance
50°C	0.05	0.27
	0.075	1.39
	0.1	3.10
	1.5	3.05
	0.2	1.53
75°C	0.05	2.62
	0.075	2.00
	0.1	1.17
	1.5	1.22
	0.2	1.47
95°C	0.05	1.72
	0.075	2.24
	0.1	2.70
	1.5	2.60
	0.2	2.41

The data from the table is then plotted in the graph below to obtain the beer's Law plot.
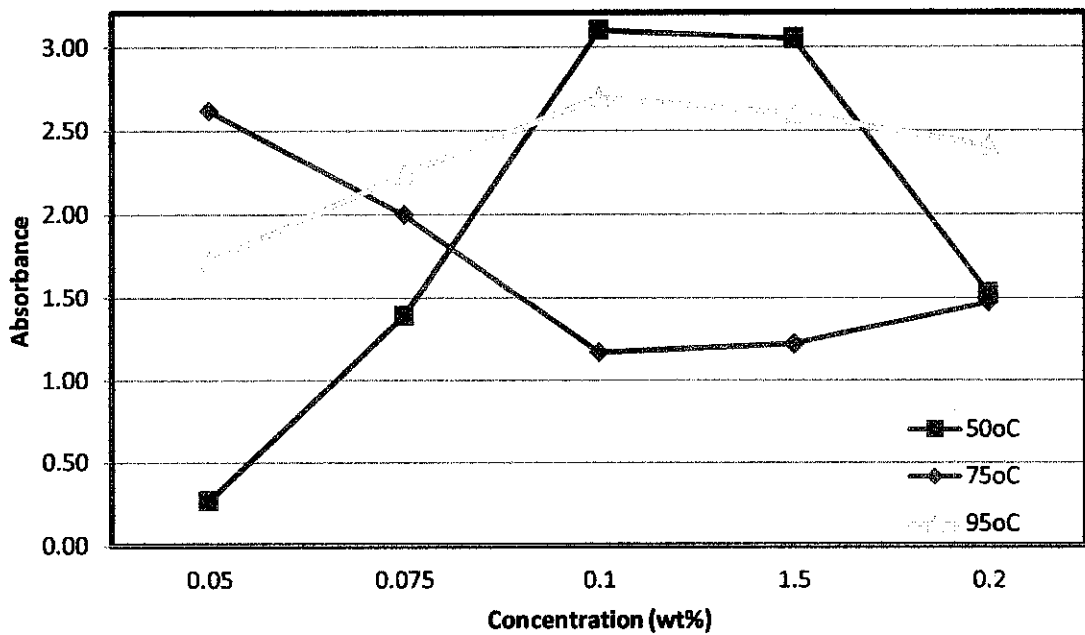

Figure 8: Beer's Law plot.

26

From the graph above, a linear graph of Beers Law is cannot be obtained. The possible cause for the reading is because of the limitation of the UV-Vis to read **partially dissolved sample or undissolved.** Note that UV-Vis only read best fully dissolved sample. Since the nitrated petcoke does not dissolve in distilled water, the system begins to show anomalous behavior and absorbance concentration at value of 1 was unable to be determined as proposed in the methodology. Hence, **this result is only being used for additional knowledge and lesson learned only.**

4.1.3 Absorbance Versus Time

Note: Standard 0.01 gm of petcokes was mixed with 100ml of each different buffer solution (0.002gm in 20 ml buffer solution). The mass % of petcokes cannot exceed 0.01gm per 100ml of solution because of the limitation of UV-Vis spectrophotometer.

I.   Graph absorbance versus time (Based on dried temperature)

Absorbance vs Time @ 50C

$y = 0.0009x + 2.4813$

$y = -0.0026x + 1.5299$

$y = 0.001x + 0.0412$

Figure 9: Graph for Absorbance versus time using nitrated coke at 50°C

27

Absorbance vs Time @ 75C

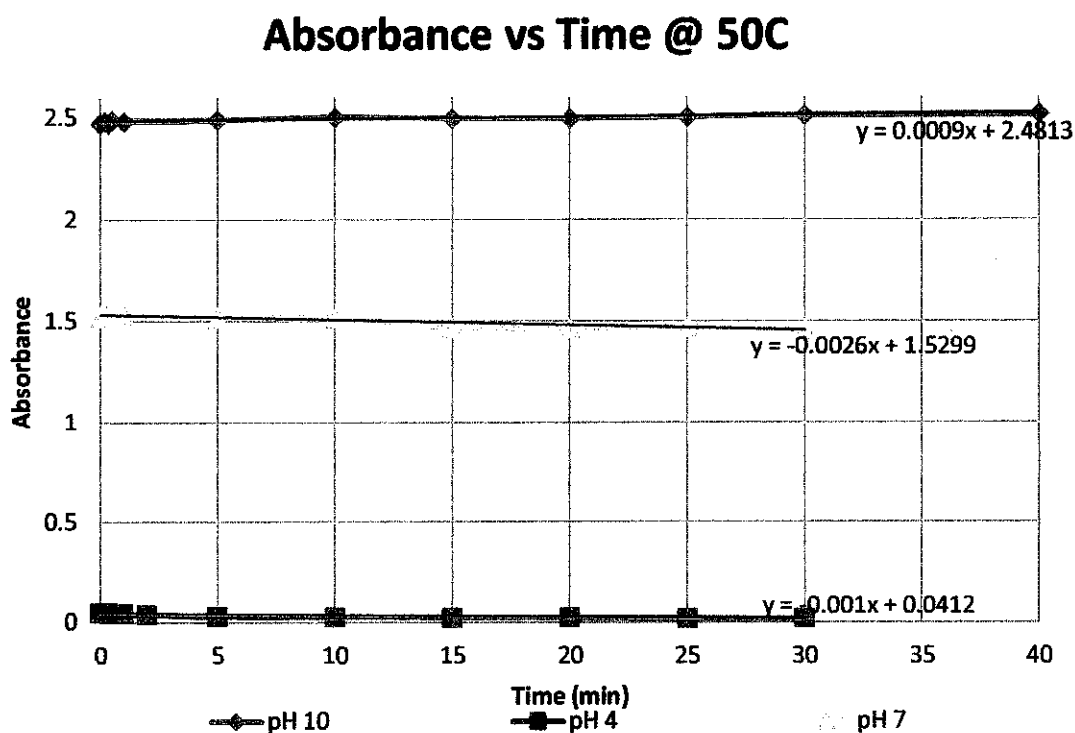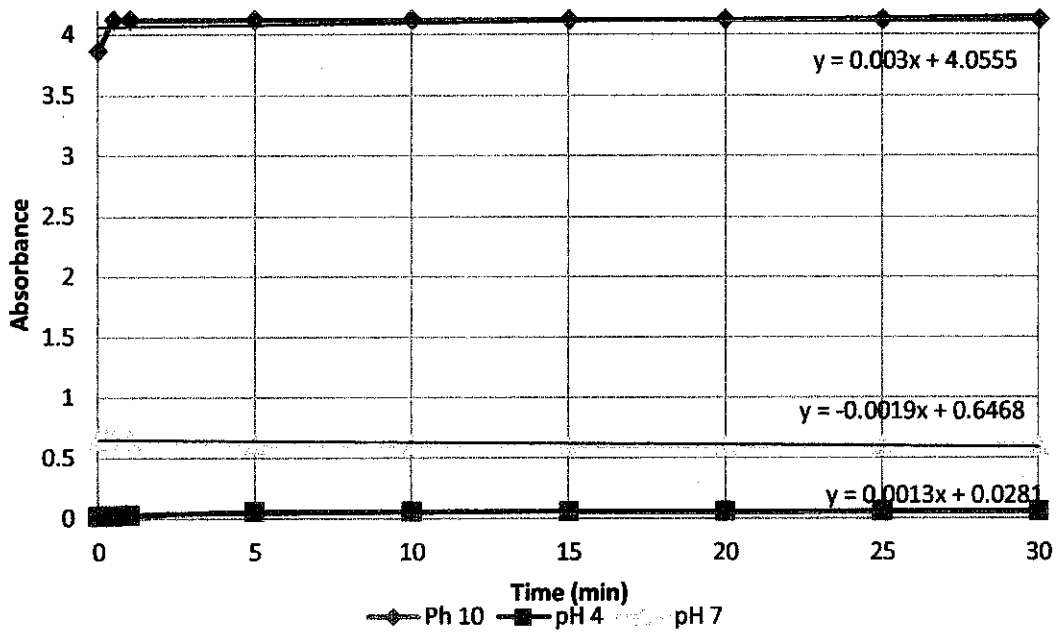Figure 10: Graph for Absorbance versus time using nitrated coke at 75°C

Absorbance vs Time @ 95C
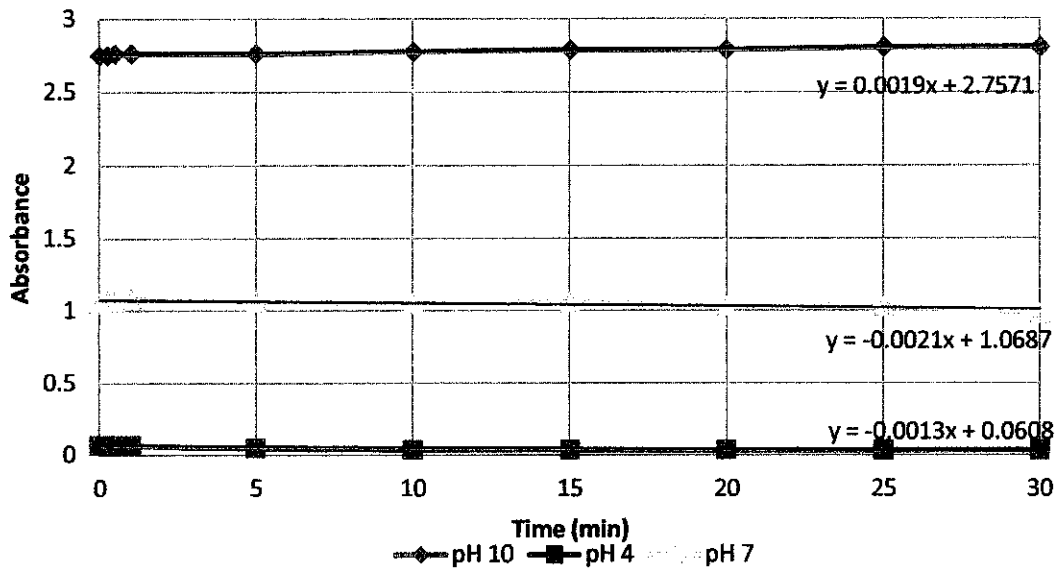
Figure 11: Graph for Absorbance versus time using nitrated coke at 95°C.

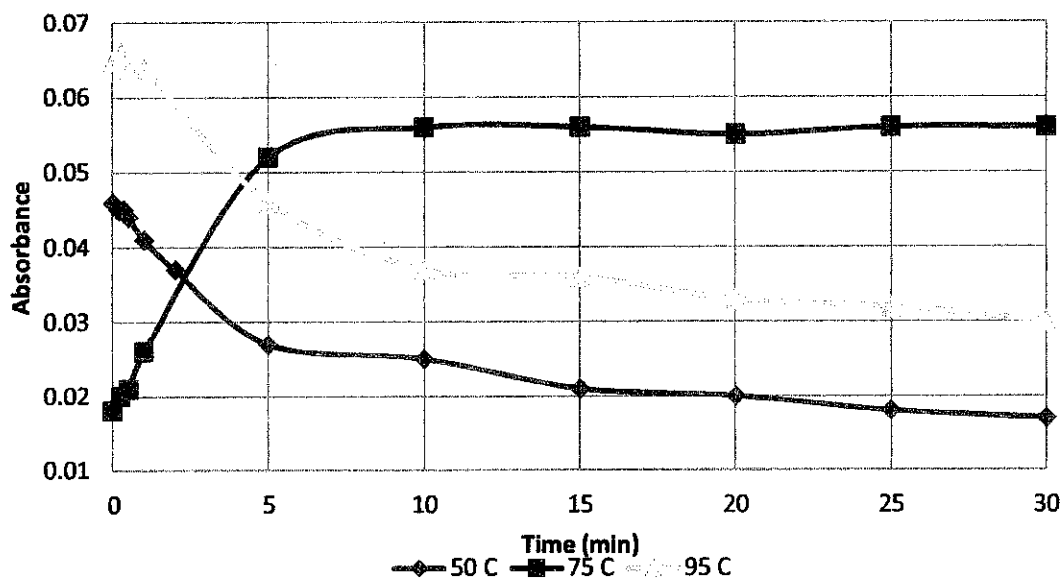28

II.   Graph absorbance versus time. (based on the pH of the solution)

Figure 12: Graph for Absorbance versus time using buffer solution at pH of 4
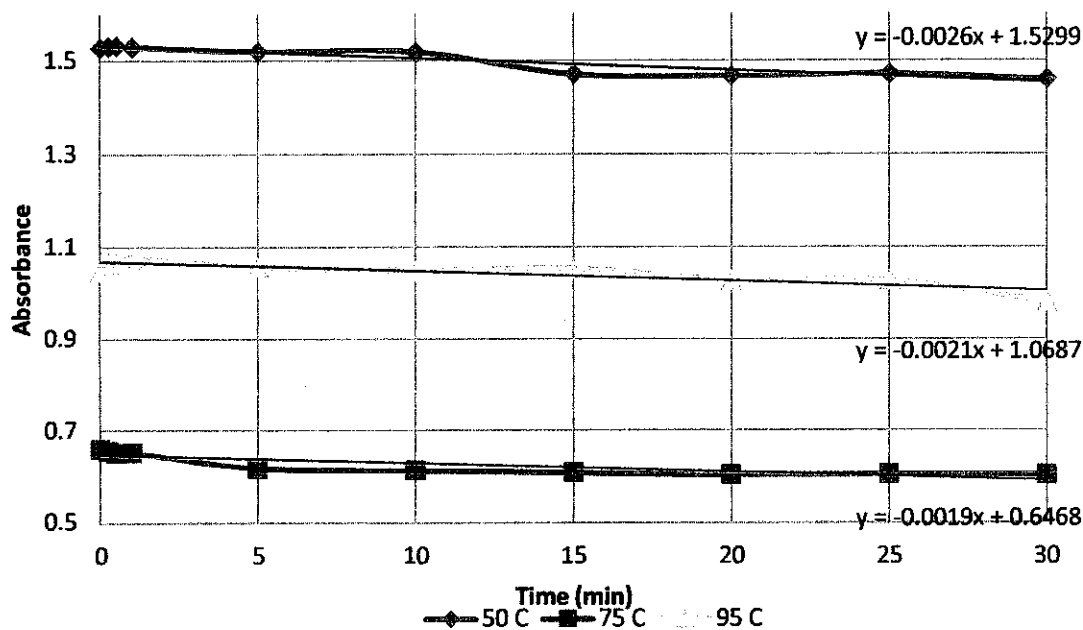

Figure 13: Graph for Absorbance versus time using buffer solution at pH of 7
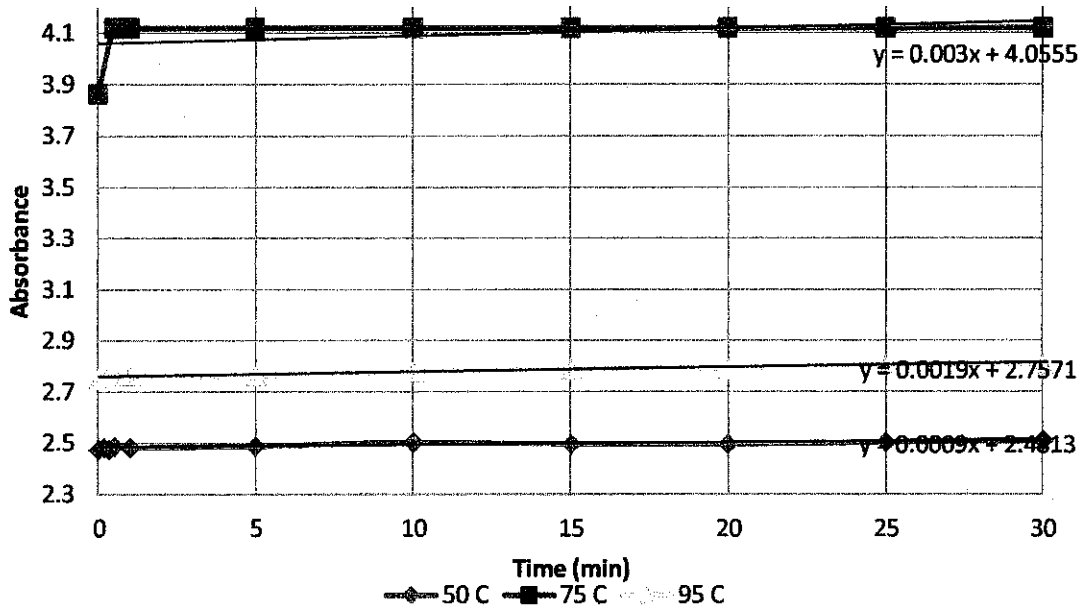
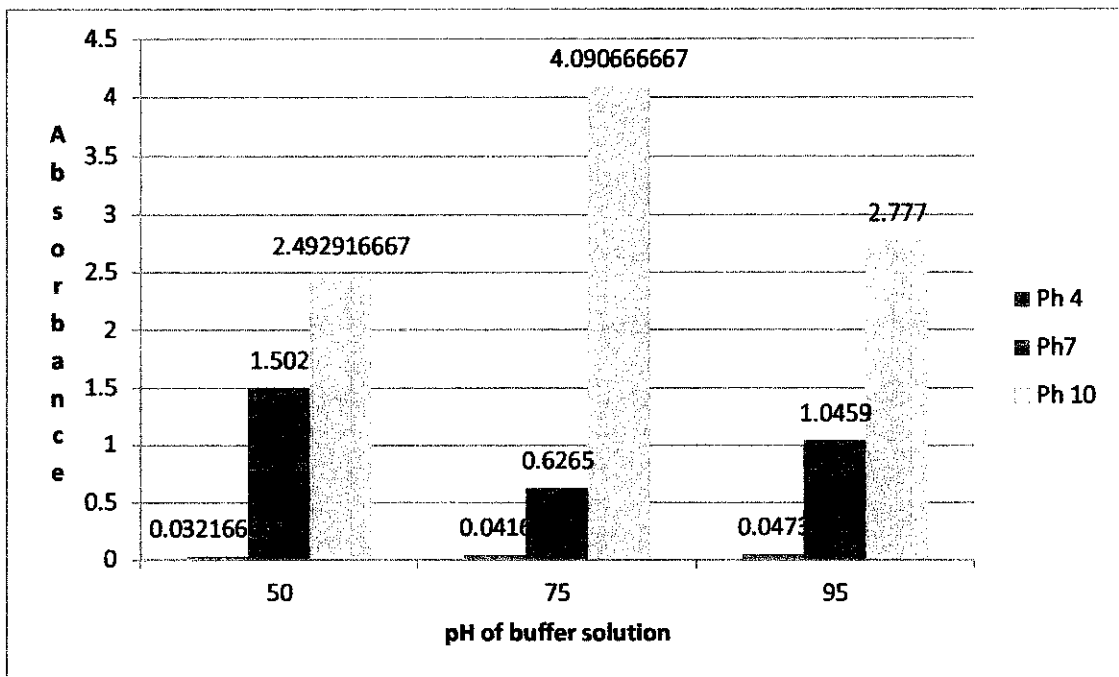Figure 14: Graph for Absorbance versus time using buffer solution at pH of 10

Figure 15: Average Absorbance for respective pH.

4.2 Discussion

Referring to the graph 15 in result section, in overall the absorbance value is higher in an alkaline solution. The observation proved that the nitrated mesophase lost its original hydrophobicity and can be readily dispersed in distilled water and dissolves in high pH which contributing to the high absorption. The absorption at pH 4 is very low since the petcokes only disperse in the solution followed by absorbance in pH 7. The highest absorbance value can be seen when using higher pH of buffer solution. The nitrates coke dissolve in high pH solution.

The characteristic of the nitrated coked itself is acidic that prevent it from dissolve in acid solution. The nitration of cokes has result the introduction of hydrophilic ionizable group. Surface acidity of the nitrated mesophase is due to the acidic oxidized groups. Based on figure 15, absorbance at high pH is increasing with time. The nature of acidic nitrated coke enhances the reaction between the alkaline solutions. In addition, for acidic and neutral pH the absorbance is decreasing with time as the dispersed particle settle down.

Based on figure 13, the absorbance is decreasing gradually with time at the neutral solution. However, in acidic solution of pH 4 (refer to figure 12), the absorbance pattern is quite different. The absorbance of nitrated coke at 75°C is increasing while the others decrease with time.

As a conclusion, the dispersibility patterns of nitrated cokes do changed in different pH of buffer solutions. However, the different characteristic that affect by the nitrated temperatures is not so obvious. Hence, it is recommended that the effect of the nitrated temperature can be neglected. There are several factors and explanations behind these characteristic such as carboxyl and nitro group, effect of mellitic acids and the influence of humic acids. **Detail reasoning and explanations are discussed in section 4.4.**

31

4.3   Additional Result

The 3 types of nitrated coke are then mixed with neutral and acidic solution each in a test tube. The observation and the changes occur in solution is recorded. The results are summarized below:

Buffer solution at pH 4 (Acidic)

1. Overall observation for 3 different samples of nitrated cokes; cokes disperse equally in the solution.
2. The small particle can be seen moving in the solution. The cokes did not contaminate the clear colour of buffer solution. It not dissolves in solution.
3. Light can pass through the solution mixture.
4. It is hard to detect and distinguished the layer. (No obvious layer)
5. The layer keeps on settle down slowly (layer height decrease) with time time.
6. After a certain period of time all the remaining suspension settle down at the bottom of the test tube and the solution becomes clear.
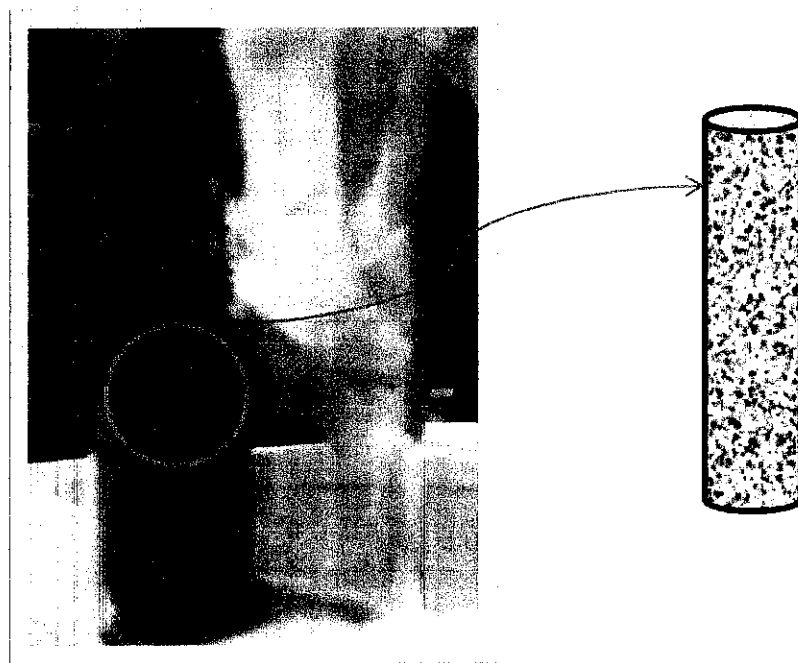
Figure 16: Nitrated Cokes dispersed in low pH (pH 4) - The particle disperses in water. Particle moving downward before it settles down can be seen clearly.

Buffer solution at pH 7 (Neutral)

1. Overall; the mixture solution turns into dark. No light can pass through.

2. The particle movement cannot be observed by naked eye. It seems like some of the cokes dissolve in the solution.

3. Initially, the level of black layers moving downward can be seen.

4. The layers can be distinguished clearly.

5. After a certain period of time, the brownish thin layers appear on the top of black layer. After a certain time the layer remain at certain level and the black colour also remain static under the brownish layer. (See figure 17).

6. The solution is darker in this following manner; **75°C<50°C<95°C.**
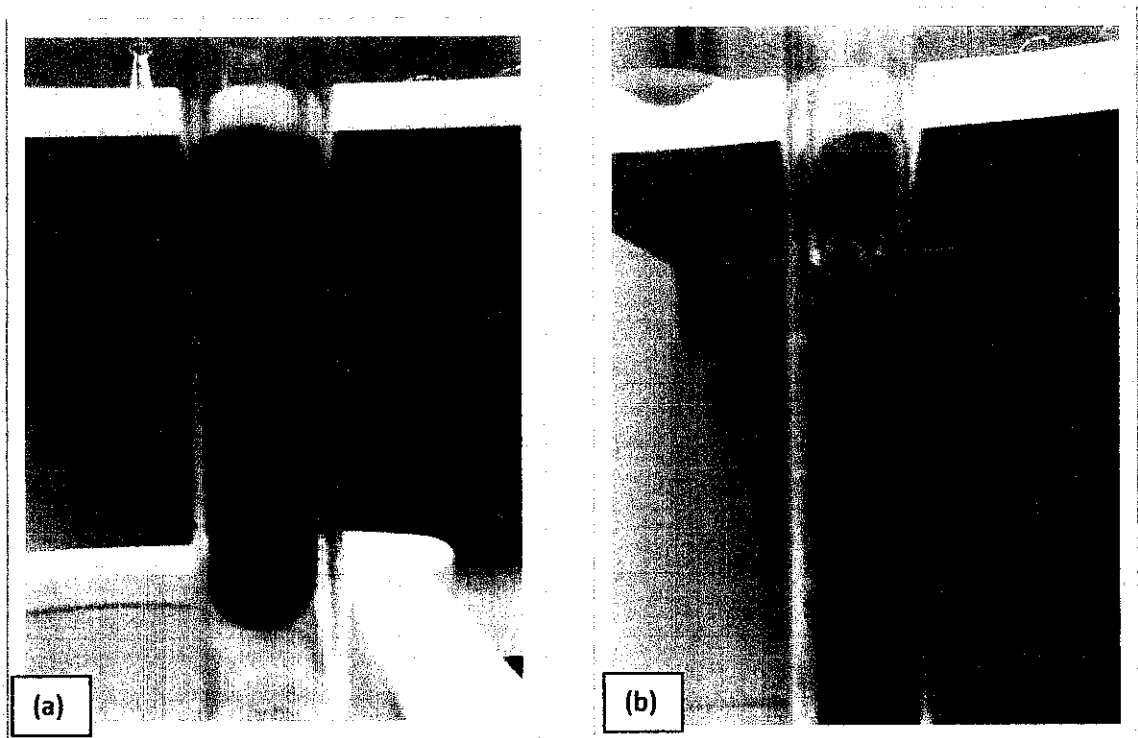
Figure 17: (a) The first picture is showing the nitrated cokes at 95°C. (b) The second picture is showing the nitrated cokes at 75°C. Both in pH 7

Figure 18: Illustration showing the layer obtained after 25 minutes in pH 7. Nitrated cokes seem to be dissolve in the medium solvent before a brownish layer appears on the top of the black solution.

4.4 Scientific Justification

Aromatic nitration is performed using "mixed acid" and involves two phases i.e., the aromatic phase and the mixed acid phase. It is an accepted proposition that the reaction occurs exclusively in the acid phase in which aromatics are sparingly soluble. The rate controlling step involves electrophilic attack of nitronium ion on the aromatic ring. Reaction is known to be irreversible and first order in concentration of the aromatic species and nitric acid. Nitration (lower pH; lower ionic strength) will enhance the humic acid production in poly aromatic hydrocarbons (PAH).

The solubility of nitrated cokes has big influenced by the presence of **humic acids**. The effects of humic substances on the solubility and mobility of organic contaminants has been the subject of numerous studies. In the first phase of study, it was found that humic acids concentration as low as 0.1g/L could enhance the solubilization of aromatics from diesel fuel. While pH and ionic strength did affect the solubility, the concentration of humic acids was the most important factor governing solubility. Literature research stated that humic acids in solution will affect the colour of the solution. The more concentration of humic acids, the darker the solution will be. This is a reasonable explanation on the difference colour of suspensions in settlement time testing (refer to figure 17).

An increase in pH and ionic strength was found to decreases the binding or network of poly aromatic hydrocarbons (PAH) by humic substance (Suzanne et.al 1995).

Suzanne and her teams also claims that the binding of particular PAH compound by humic substances depend not only on the hydrophobicity of the PAH but also on the size of the solute molecule and its ability to fit into hydrophobic cavities in humic substances. Humic acids can suppress the hydrophobic elements in PAH (M.Rebhun, 1998).

On the other hands, Bernard Juetter, (1937) states that active carbons have been reported to give high yields of **mellitic acids** on oxidation. The yield of mellitic acids from coal and all carbonaceous material which has been heated increases with increasing rank. High stability mellitic acids are the end product of the oxidation of polycyclic aromatic hydrocarbons. The appearance of mellitic acid will increase the solubility of nitrates cokes since the acids are water-soluble and colorless compound, (Kurmmo *et. al*, 2005).

Michael Susic, (2003) in his research web blog states that keto groups were present in all of the material, but only humic acids and kerogen showed carboxylate group. Hence, the effect of **carboxyl (-COOH)** group also should be taking into consideration that influencing the solubility of nitrated cokes. Hydrogen bonding also contributes to the solubility of covalent compounds. Carboxylic acids are acidic because of the hydrogen in the –COOH group. When the acids form salts this is lost and replaced by a metal. Sodium ethanoate (IV), for example, has the structure:

$$
\begin{array}{c}
O \\
\parallel \\
CH_3-C \\
\diagdown \\
O^- \ Na^+
\end{array}
$$

sodium ethanoate ....(IV)
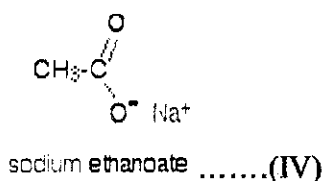
The solubility of carboxylic acids in certain organic solvent increase sharply as the concentration of water in the solvent increase. Water- enhanced solubility has been observed previously for some carboxylic acids, but does not appear to have been investigated in much depth.

Humic, mellitic and carboxylic acids are all acidic in nature. This is the most judicious reason that the nitrated cokes well dissolved in higher pH and only disperse in lower pH medium. It also proved that, treated coke (in this case nitrated cokes) has a potential to be developed as water dispersible solid fuel.

Both dispersed and dissolve nitrated cokes can be manipulated depend on the purpose of usage. However, since the research is more concerning on the liquid that can be sprayed out so that can easily burned out, dissolve nitrated coke in high pH is more preferable. Liquid fuel is more easily to be transported out through pipelines and low handling cost. Apart from that, the effect to the machine and environment should be taken into consideration since it includes high pH.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusions

The result reported has shown that nitrated cokes can possibly be developed as water dispersible solid fuel. The absorbance testing using UV-vis proves that nitrated coke do dissolve in respective solution has unique characteristic for every pH as shown in the results. The reasons behind the solubility of the nitrated cokes have been described thoroughly through this report. The objective of this study has been achieved as per highlighted in the earlier part of this report.

The knowledge of colloid engineering is important in ensuring this research successful. The next step on preceding the research is to conduct the efficiency of colloidal nitrated coke in releasing energy.

5.2 Recommendations

To have a very strong and reliable result, the experiment should be repeated using turbidity machines. The research should be continued to prove the presence of humic acid, mellitic acids and others solubility groups. The research also can be proceeded to liquefy the coke into colloid dispersion. The colloid can be tested in a burner to determine the quality of heat or the energy that can be obtained from new treated water- dispersible cokes.

Determination of calorific value of nitrated cokes is a good starting point for these purposes. The sedimentation of particles should be overcome by adding any chemical that slow down the settling rate or against sedimentation. It is important to ensure the stable durability of water dispersible solid carbonaceous material.

It is also a good approach to have another samples of cokes to be tested instead of using only one source of calcined coked only; (in this experiment the cokes obtained

from PETRONAS Penapisan Melaka only) to ensure the research has high impact on user. In addition, the effect of the high or lower pH on the performance and sustainability of engine if these treated cokes are applied should be also being taken into consideration as well as the effect to the environment.

REFERENCES

Journals and Articles:

B. Ariwahjoedi and B. Rand 1989 *Mesophase Aqua-sol, School of Materials*, Division of Ceramics, Glases and Polymers, University of Sheffield, Sheffield S10 2TZ, UK.

Bernard Juettner, 1937 *Mellitic Acid from Coals, Cokes and Graphites*, J. Am. Chem. Soc., 1937, 59 (1), pp 208–213DOI: 10.1021/ja01280a052

Choudhury, D. P.; Choudhury, S. S. Banerjee A. *1986 Fuel Sci. Technol.*, 5 (4), 195.

C.M.J. Brands, B.L .Wedzicha, M.A.J.S. van Boekel 2002 *Int. Congr. Ser.* 1245, pp 249.

Debapriya Choudhury, Samar S. Choudhury, Raja Sen, Joy Mukherjee, Gora Ghosh, and Sunil K. Srivastava *2007 Role of the Nitro Group on Coal Solubilization in Aqueous Organic Solvents, Energy Fuels* , 21 (2), pp 1006–1013.

D.H. Williams,I. Fleming 1989, *Spectroscopic Methodsin Organic Chemistry, Fourthedition,*Mc.Graw-Hill Book Company Europe, p.1

F. Schulze, Bey 1884, 4, p. 802; C. Friedel and J. M. Crafts, Ann. *chim. phys., [6], I, p. 470*

G.K .Sandhu, K. Singh, B.S. Lark,L. Gerward,Radiat 2002, *Phys.Chem. 65211*

Judith M. Bonicamp, Kelly L. Martin,Gerald R. McBride and Roy W. Clark 1999, *Beer's Law Is Not a Straight Line: Amplification of Errors by Transformation.* Chem Eduacator.

Jun M. Lee, James J. Baker, Jeffery G Rolle, Robert Llerena, A.J Edmon Co. 1997 *1530 West 16th Street Long beach, CA 90813,pp 271.*

Kurmoo M, Estournes C, Oka Y, Kumagai H, Inoue K 2005 *Inorganic Chemistry volume 44,* page 217

Laux, Horst, Iradj Rahimian, and Thorsten Butz 1997, *Thermodynamics and mechanis of stabilization and precipitation of petroleum colloids*. Fuel Processing Technology 53, (1-2) (11): 69-79.

L. M. Ferris, July 1964, *Mellitic Acid from the Oxidation of Graphite with 90% Nitric Acid*, J. Chem. Eng. Data, 1964, 9 (3), pp 387–388.

Leslie M. Ferris, *Mellitic Acid from the Oxidation of Graphite with 90% Nitric Acid*, Oak Ridge National Laboratory, Oak Ridge, Tenn, Journal Of Chemical and Engineering, Vol. 9, No. 3, July 1964

M. Rebhun,, S. Meir, and, Y. Laor, *Using Dissolved Humic Acid To Remove Hydrophobic Contaminants from Water by Complexation—Flocculation Process*, Environmental Science & Technology *1998* 32 *(7), 981-986*

Ramkumar Jayakumar 2008, *Analysis of Power Generation Process Using Petcoke*, Texas A&M University.

S.F Darlow 1960, *The Crystal Structure of Mellitic Acids*, Crystalographic Laboratory, Cavendish Laboratory, Cambridge, England.

S. P. Singh, J. S. Wishnok, M. Keshive, W. M. Deen, and S. R. Tannenbaum, 1996. *The chemistry of the S-nitrosoglutathione/glutathione system PNAS*, December 10, 1996 vol. 93 no. 25 14428-14433

Salvador, S., J. -M Commandré, and B. R. Stanmore 2003, *Reaction rates for the oxidation of highly sulphurised petroleum cokes: The influence of thermogravimetric conditions and some coke properties*. Fuel 82, (6) (4): 715-20.

Suzanne Lesage, Hao Xu, Kent S. Novakowski, Susan Brown and Louise Durham 1995, *Use Oh Humic Acids to Enhanced The removal of Aromatic Hydrocarbons from Contaminated Aquifers*, Proceedings of the 5th annual Symposium on Groundwater and Soil Remediation, Oct 2-6, 1995, Toronto Ontario,

Groundwater Remediation Project, National Water Research Institute, Environment Canada, Burlington, Ontario, L7R 4A6

Tekin, Nalan and Mustafa Cebe, 2005, *Investigation of dissociation properties of oxalic acid–solvent systems by UV-spectrophotometry*. Journal of Molecular Liquids 122, (1-3) (11/15): 65-8.

Wang, Jinsheng, Edward J. Anthony, and Juan Carlos Abanades 2004, *Clean and efficient use of petroleum coke for combustion and power generation*. Fuel 83, (10) (7): 1341-8.

Zhu, Z. Y., J. L. Duan, Y. Maekawa, H. Koshikawa, and M. Yoshida 2004, *Bulk and track etching of PET studied by spectrophotometer*. Radiation Measurements 38, (3) (6): 255-61.

Website/ World Wide Web:

Wikipedia: Petroleum coke, 23th August 2010
   <*http://en.wikipedia.org/wiki/Petroleum_coke*>

Wikipedia: Spectrophotometry, 16th March 2010
   <*http://en.wikipedia.org/wiki/Spectrophotometry#UVandIRspectrophotometers*>

Evaluation of Fly Ash from Co-Combustion of Coal and Petroleum Coke for Use in Concrete, 6th November 2010
   <*http://www.allbusiness.com/manufacturing/chemical-manufacturing-chemical-product/4062280-1.html*>

Beers law <*http://www.apsu.edu/Chem_page/*>

Petroleum coke and the coal industry <*http://www.petcokeconsulting.com*>

Colloid- *http://www.chemistrydaily.com/chemistry/Colloid*

Kinetics Fading of Phenolphthalein in Alkaline Solution, 6th November 2010,
<http://www.uni-regensburg.de/Fakultaeten/nat_Fak_IV/Organische_Chemie/Didaktik/Keusch/che mbox_pheno-e.htm >

Humic Acids, 6th November 2010 *<http://en.wikipedia.org/wiki/Humic_acid>*

The Ultimate Fulvic Acid Humic Acid Liquid Mineral Supplement-
<http://www.supremefulvic.com/>

How Oil Refining Works by Craig Freudenrich, Ph.D.
<http://science.howstuffworks.com/environmental/energy/oil-refining.htm>

Michael Susic, Research Scientist, Structure and Origin of Humic Acids and their
Relationship to Kerogen, Bitumen, Petroleum and, -6 December 2010.
<http://humicacid.wordpress.com/structure-and-origin-of-humic-acids-and-their-relationship-to-kerogen-bitumen-petroleum-and-coal/>

Books and Reports:

Terence Cosgrove, *Colloid Science; Principles, method and applications 2005*, Blackwell
Publishing.

Hidayah Awalluddin, *Preliminary Study of Nitration of PETRONAS cokes for water
dispersible solid fuel*, UTP, July 2009.

Personal Communication:

Shaiful Baharuddin Halim, *Calorific Values of PETRONAS Cokes Nitrated at Various
Temperatures*, Mechanical Engineering, UTP, July 2010.

APPENDICES

Gantt chart of scheduled activities

Semester 1

	Jan				Feb				March				April				May				June			
Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Problem Identification		█	█	█																				
Literature Review			█	█	█	█	█	█	█	█	█	█	█	█	█	█								
Lab Consultation								█	█	█	█	█	█	█	█	█	█	█	█	█				
Experimental Works																					█	█	█	█
Collecting Data																								
Progress Report												█	█											
Analysing Data																					█	█	█	
Final Report																								
Presentation																								

Semester 2

	July				August				Sept				Oct				Nov				Dec			
Week	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
Problem Identification																								
Literature Review	█	█	█	█	█	█	█	█	█	█	█	█												
Consultation																								
Experimental Works						█	█	█	█	█	█	█	█	█	█									
Collecting Data								█	█	█	█	█	█	█	█									
Progress Report							█							█										
Analysing Data									█	█	█	█	█	█	█									
Final Report															█	█	█	█						
Poster / Presentation																					█			

CHNS Analysis Result

Material	Carbon			Hydrogen			Nitrogen			Sulfur		
	1	2	average	1	2	average	1	2	average	1	2	average
Petcoke (Untreated)	39.4	38.35	38.88	4.379	4.441	4.41	1.119	1.043	1.081	0.127	0.134	0.131
Petcoke nitrated at 50 degree celcius	38.15	39.04	38.56	5.1	5.02	5.06	0.941	0.921	0.931	0.087	0.093	0.09
Petcoke nitrated at 75 degree celcius	47.17	46.45	46.81	5.864	5.789	5.827	1.728	1.658	1.693	0.133	0.123	0.128
Petcoke nitrated at 95 degree celcius	47.29	47.93	47.61	5.911	5.936	5.924	1.847	1.822	1.835	0.108	0.1	0.104

Result of Calorific Value Test

Sample	Calorific Value (J/g)		
	1	2	Average
Untreated coke	17104	17092	17098
Petcoke nitrated at 50°C	22419	22402	22410.5
Petcoke nitrated at 75°C	15961	15973	15967
Petcoke nitrated at 95°C	20353	20358	20355.5

The **CHNS** machine works based on the principle that high temperature combustion is used as the means of removing the elements from the material. This analysis will report the (carbon, hydrogen, nitrogen, and sulphur) content in the samples. The parameter for ultimate analysis was set according to ASTM D 3176-89.

To determine the amount of energy stored in the each sample, a **Calorific Value Test** would be done using a LECO AC-350 Bomb Calorimeter. Gross Calorific value of a fuel specimen is the heat produced by a complete combustion of a unit quantity of sample, at a constant volume, in an oxygen bomb calorimeter under standard condition. The parameter for the calorific test was done according to ASTM D 5865-07, Standard test Method for Gross Calorific Value of Coal and Coke.