Characterization of Functionalized Graphene for Improvements in Drilling Fluid Properties

By

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CERTIFICATION OF APPROVAL

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Approved By:

…….
(AP Dr Suzana Bt Yusup)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2014

CERTIFICATION OF ORIGINALITY

I hereby 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 to the extent of my knowledge and information.

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(DEIVANKUMAR A/L CHANDRAN)

ABSTRACT

The introduction and basic mechanism of drilling mud were outlined. A novel process based on functionalizing graphene using certain functional group (carboxylic) is reviewed to determine the compound with the best performance. Focus of this project will be on optimizing the performance of graphene addition into rubber seed ester base oil for producing drilling mud.

In chapter one, background of drilling fluid is generally discussed. Followed by the problem statement where the significance of the project is highlighted. The objectives and scope of study for this project is also elaborated in this chapter. Finally the relevancy and feasibility of project are discussed.

Chapter two is the literature review part, where this chapter plays an important role to help the understanding of the concept for the project. As a preliminary literature review in proposal, it is divided into four sections which are drilling mud, graphene, vegetable ester based oil, chemical processes and physical process (ball milling).

For chapter three, methodology of the project is discussed. This chapter includes a brief summary of methodology (five stages), followed by equipment used in each stages, Gantt chart for FYP 1, FYP 2 and a finalized methodology diagram

In chapter four, the project proposal has concluded. In this chapter, the dire need for this project as a way to promote sustainable petroleum exploration is highlighted. Some explanation on the nature of graphene as a relatively new material and the difficulties in its synthesis is mentioned.

ACKNOWLEDGEMENT

First and foremost, I would like to thank God for his protection throughout the conduction of my Final Year Project. It was with His protection that I was able to finish the project successfully.

Besides, I would use this opportunity to show my deepest appreciation to Dr Suzana Yusuf for her constant advice, support, assistance and guidance to me in Final Year Project for Universiti Teknologi PETRONAS. Without her, I would not have completed the project with ease. She assigned me with a very interesting topic that applied my chemical engineering knowledge which I have learnt in the past 4 years of my bachelor degree. I also benefitted a lot in terms of knowledge through the constant discussions with her.

I would also like to mention about my feeling of gratitude towards the lab technicians who helped me with the lab application and lab working procedures in order for me to conduct my final year project in a conducing environment and manner.

Lastly, a special thanks to my beloved parents who supported me and encouraged me during this Final Year Project. They are the pillar of strength for me to complete this project.

Thanks to this opportunity, now I have a deep understanding of how the biodiesel and drilling fluid functions and this is really great for me as I plan to venture in this industry in the future. Lastly, I would like to thank UTP Chemical Engineering department for coordinating and aiding the evaluation milestones of this course and the continuous support.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Drilling fluid, or better known as drilling muds are materials pumped down hole as part of the procedure to remove cuttings and keep drill bits clean. They are commonly used while drilling natural gas or oil wells and on exploration drilling rigs, drilling fluids are also used for much simpler operations such as water wells. Three main categories of drilling fluids are water-based mud (dispersed or non-dispersed), gaseous drilling fluid where a wide range of gases can be used or non-aqueous mud, usually called oil-based mud.

Oil-based mud (OBM) can be where the base fluid is of a petroleum product. Oil-based mud are used for various reasons, including increased lubricity, greater cleaning abilities with less viscosity and enhanced shale inhibition. Oil-based mud also withstand greater heat without breaking down. The reason this typical mud is not preferred in most cases nowadays is due to cost and environmental considerations.

By using the traditional oil based muds, differential pressure forms a layer on the wellbore called a filter cake, which both keeps the oil from flowing out and drilling fluids from invading the tiny, oil-producing pores. When the drill bit is removed and drilling fluid displaced, the formation oil forces remnants of the filter cake out of the pores as the well begins to produce. But sometimes the clay won't be fully removed, thus the well's productivity is limited. Furthermore, oil based muds carry with them a heavy environmental penalty and are slowly being phased out in many countries [9].

Synthetic based mud (SBM) are often regarded as the ultimate drilling fluid due to oil having non-polar attributes which hinders the reaction with water sensitive clays and shales. Clay and shale formations remain stable in a SBM environment provided that the salinity of the SBM brine phase is higher than the salinity of the in situ shale pore fluid, to maintain osmotic backflow from the shale to the SBM. This rectifies and avoids shale hydration problem which may pose a serious threat in drilling operations.

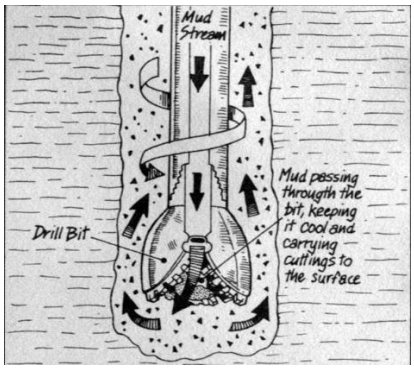


Figure 1-Working Representation of Drill Bit and Drilling Mud

A research done by Rice University lab chemists and scientists from M-I SWACO discovered that microscopic, pliable flakes of graphene can form a thinner, lighter filter cake. Aside from making the filter cake much thinner, which would give a drill bit more room to turn, the mud contained less than half as many suspended solids[2]; this would also make drilling more efficient as well as more environmentally friendly.

In order to be used as a component in drilling mud, Graphene oxide (GO) is to be esterified with alcohol to produce the required quality (easy dispersion in water), also known as Functionalized Graphene Oxide (FGO). This is because graphene is hard to disperse in water, whereas untreated GO tends to coagulate in saltwater[2].

FGO is to be blended with base fluid which is produced via the hydrolysis and esterification of various oils. Among the candidates are rubber seed oil, Jathropha curcas seed oil and Palm Fatty Acid Deposit oil. These vegetable ester based oils has reported higher rate of penetration, lower cutting disposal cost, less drilling complications and less damage in event of spillage [8].

1.2 Problem Statement

i. Effect of ball milling and its effect on particle size will be determined
ii. **1 criteria** will be investigated for their influences on the drilling mud performance:
    - Nanoparticle loading (wt%)

1.3 Objective

The objective of this project is to:

i. To study the effect of ball milling on FGO particle size
ii. To study the effect of different FGO loading percentage on rheological properties of blended compound

1.4 Scope of Study

The scope of study will cover starting from the utilization of various FGO batches followed by using ball mill to vary the particle size of each batch up to the formulation/ratio of base fluid with FGO and determination of the various properties of this new compound.

3 factors (reaction parameters):

a. Graphene Nanoparticle Size
b. COOH-Functionalized Batch (2 Batches)
c. Loading Percentage (0wt% to 1wt%)

Responding aspects:

a. Changes in graphene nanoparticle size after ball milling
b. Rheological properties of base oil produced after FGO addition

1.5 Relevancy of the Project

The relevancy of this project can be construed in three important criteria or level of focus. Firstly, it is my personal interest that drives me to pursue this project as it would set a pathway for my career in future and would expand my horizon in terms of my expertise in a more diverse field. Apart from that, it is also very relevant with my course of study and enables me to master the key syllabus in addition to providing real time experience to deepen my understanding about this project. In terms of the Chemical Engineering and the industry as whole, this project mainly comprises of the research and development aspect. It sets the foundation in assessing the strength and performance of the bio-based drilling fluid. The project will determine the most suitable formulation of the vegetable oil based drilling fluid and will be taken account as a possible alternative drilling fluid compared to conventional diesel based mud. The study of the capability of vegetable esters as an alternative option for drilling fluid can open opportunity for an environmentally friendly drilling operations.

1.6 Feasibility of the project within the Scope and Time Frame

The project's feasibility within the scope is mainly to be set as a guideline for preliminary exclusion of the unsuitable base oil and formulations. The time frame of 28 weeks can only provide a guideline whether rubber seed oil can be used as continuous phase. Furthermore the real focus in this project is to determine effects of blending graphene into a sample base oil. The whole prospect of full mud formulation study is very comprehensive and through and would require a much larger time frame to provide a definite alternative bio-based drilling fluid. Since this project is the 1st phase in the study of graphene suitability and formulation, the blending compatibility can be identified based on the scope of data analysis. The project will be feasible in terms of assessing the performance of graphene additive based drilling fluids and recommendations for further optimizing the formulations to be feasible and compared with conventional drilling fluids.

CHAPTER 2

LITERATURE REVIEW

2.1 Drilling Mud/Fluid

Used to aid the drilling process of wells in various locations on earth. There are several types of drilling fluid based on composition and usage, mainly Synthetic Based Mud (SBM), Water Based Mud (WBM), and Oil Based Mud (OBM). The main functions of drilling fluids includes keeping the drill bit cool and clean during drilling activities, providing hydrostatic pressure to prevent formation fluids from entering into the well bore, carrying out drill cuttings, and suspending the drill cuttings during down time. The drilling fluid used for a particular job is selected to avoid formation damage and to limit corrosion. (Apaleke, Al-Majed, & Hossain, 2012)[1]

Figure 2-Drilling mud formulation. Color depends on type

Three important factors that determine the type of drilling fluid suitable for a specific type of well are as follows [5]:

- Cost
- Technical performance
- Environmental impact

Selecting the correct type of fluid for the particular conditions is crucial to a successful drilling operation.

This section illustrates some of the elements considered to ensure the efficiency and effectiveness of project progress.

2.2 Graphene

Graphene is an allotrope of carbon by the structure of a planar of sp2 bonded atoms with a molecule bond length of approximately 0.142 nanometers (nm). Layers of graphene stacked on top of each other form graphite, with a determined inter planar spacing of 0.335nm. In simpler context, it consist of single highly dense packed layer of carbon atoms that are bonded together in a hexagonal patterned honeycomb lattice.

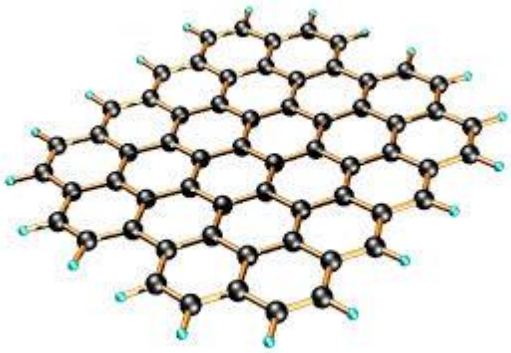


Figure 3-Typical graphene sheet honeycomb lattice

This is the thinnest (one atom thick) and lightest compound known to man. Among its remarkable properties is being the strongest material ever discovered (reported to be 100-300 times stronger than steel), performs as the best conductor of heat at room temperature and best conductor of electricity[6] .

Currently graphene is being intensely studied by many researchers and research bodies from a diverse pool of discipline (thermodynamics, electronics, material science, biotechnology, among the few) all over the world. The biggest advantage of studying this compound is the limitless supply of raw materials to produce it. Carbon is the fourth most abundant element in the universe and the basis of all known life form which means it could also be an ecologically friendly, sustainable solution for limitless number of applications[7].

Some problems faced afflicting research on this compound is the high costs and complex procedures required to synthesize high quality graphene, issues which are gradually being

addressed by the scientific community. Cost is not a very significant issue in the oil and gas industry, especially if graphene laced mud can increase the profit margin and reduce operating costs.

2.3 Vegetable Oil Esters

Mineral oil-based drilling mud is toxic, does not biodegrade easily and thus has a lasting impact on the coastal, terrestrial, and marine habitats. Base fluids for mineral oil-based mud development (usually diesel) have a limited source of supply. In addition, their use is subjected to more and more constrains due to increasing evolution of environment legislations.

One of the ways to avoid these problems while keeping the advantages of oil-based mud is to substitute diesel in mud with vegetable or animal oils. Vegetable oils are undoubtedly becoming a promising alternative to replace diesel due to their renewable nature and environmentally friendly combustion as well. They have almost negligible sulphur content, offer no storage difficulty and has good lubrication properties. Due to their abundance of waste vegetable oil generated annually, developing countries can use this to their advantage to solve their ecological problems and hence improve their economy. In Nigeria this day, the environmental acceptance of a non-water soluble drilling mud base fluid depends on both its toxicity as measured from traditional bio-assays and on its biodegradability under aerobic and anaerobic conditions (Fadairo, Tozunku, Kadiri, & Falode)[6]

A study done on effects of palm oil derived esters as base fluid for drilling mud (Tapavicza & Salleh, N.A.) found that quantity of low viscosity ester based oil is halved within a month and could degrade almost completely (<1wt%) within 112 days. This performance is far better than mineral oil which has degraded only up to 60wt% in 112 days[10].

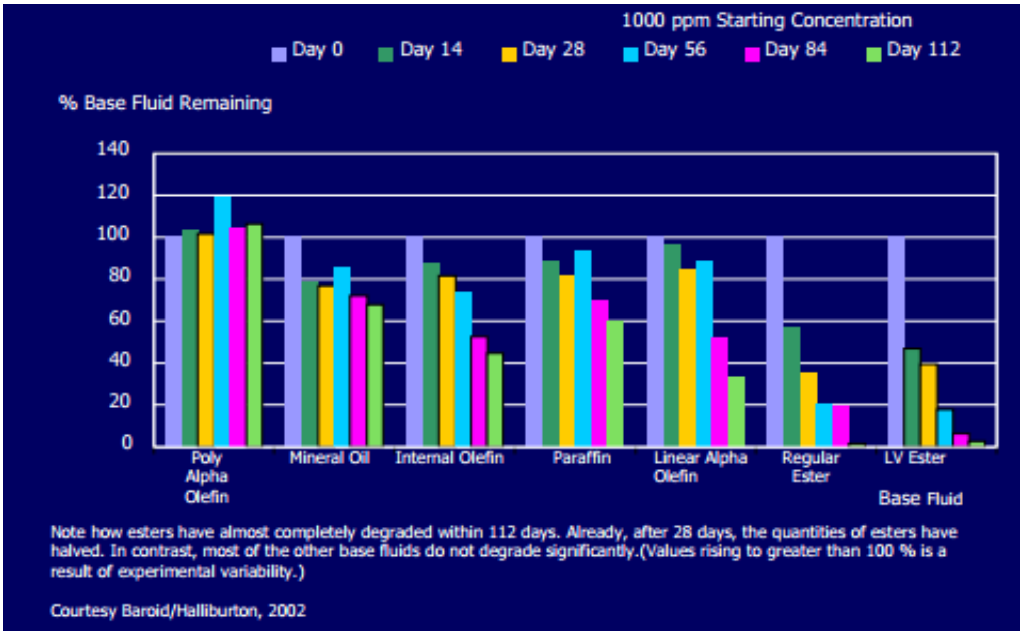


Figure 4-Ester degradation vs time of various base fluids

2.4 Chemical Process

This section shows all about producing the functionalized graphene oxide required for this project. Although we are not going to synthesize the compound, it is crucial to understand how it is produced.

2.4.1 Production of Graphene Oxide (GO)

One of the most promising method of producing GO is by oxidizing it using modified Hummers Method (Chen, Yao, Li, & Shi, 2013)[3]. From the comparative studies, this modification is purposely chosen for this research as it does not decrease the yield of product, yet eliminates the evolution of NO2/N2O4 toxic gasses and simplifying the disposal of waste water because of the inexistence of Na+ and NO3- ions. This allows for a more feasible commercialization scope.

First, graphite powder (3.0g) is mixed with conc. H2SO4 (70mL) while stirring in an ice bath. Next KmNO4 (9.0g) is slowly added under vigorous agitation while maintaining T<20oC. The solution is transferred to an oil bath where the temperature is set at 40oC, vigorous stirring for 30 minutes followed by addition of 150mL water, T=95oC, stirring

for 15 minutes followed again by 500mL water and a slow addition of hydrogen peroxide (15mL, 30%). The solution should turn dark brown to yellow.

Later on the solution is filtered and washed with 1:10 HCl (aq) to remove metal ions. This GO aqueous dispersion is dried in air and diluted to 600mL, followed by a session in the dialysis membrane unit for a week to remove remaining metal species. After that, the precipitate is diluted in 1.2L, stirred overnight, and bath sonicated for 30 minutes to exfoliate into graphene oxide (GO). The solution is centrifuged at 3000rpm for 40 minutes. The yield is 92±3 weight percent of graphite powder used. The approximate time spent in producing graphene oxide is about 1.5 days.

2.4.2 Production of Functionalized Graphene Oxide (FGO)

As stated earlier, graphene oxide alone couldn't be blended into base oil as there will be some complications while dispersing. To solve this, we functionalize GO. One way to achieve this is by using alcohol for esterification. An example series of procedures to produce FGO is shown as following.

GO produced earlier is covalently attached to poly vinyl alcohol by a carbodiimide esterification reaction (Salavagione, Gómez, & Martínez, 2009)[7].

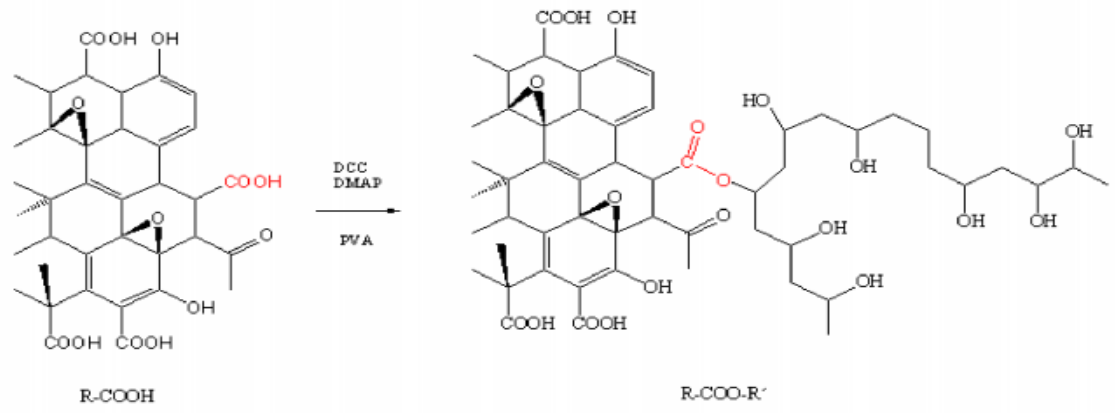


Figure 5-Carbodiimide Esterification reaction

The graphite oxide produced earlier (50mg) is added to dimethylsulphide (DMSO) of 10mL and bath sonicated for 24 hours to exfoliate + disperse GO. Next, 100mg, 0.48mmol of N,N dicyclohelylcarbodiimide is added with 5mg, 0.04mmol and bath sonicated for 4 hours. Later on, 50-150kg/mol PVA (50mg) in DMSO (10mg) which is bath sonicated for 60 mins is added into the mixture. The solution is further bath sonicated at room temperature for 2 days. The FGO mix produced has to be precipitated by adding 40mL acetone to mixture, solid filtered through nylon membrane (0.45μm), washed with water (2L) Remove excess PVA. Final result is f-(PVA)GO.

Estimated time duration needed for FGO synthesis is around 4 days using the method highlighted by this author. They concluded by stating that the best performances are achieved for attached polymers with molecular weight between 50 and 150 kg/mol.

2.5 Physical Process

2.5.1 Ball Milling

The chosen technique to vary particle size is by ball milling. This method needs to have a certain optimum range because inadequate milling intensity will result in little changes of nanoparticle size while excessive milling produce damages to the shape of the carbon nanotubes (CNTs). Optimum ball milling intensity produces short and open-ended carbon nanotubes with less damage on its structure.

A study carried out by Tucho et. al. (2010)[11] used a planetary ball milling equipment and managed to successfully reduce nanoparticle size with operating condition of 510RPM for 3 hour duration. They concluded by saying moderate high speed at short milling duration gives remarkable changes in the atomic structure of nanoparticles.

CHAPTER 3

METHODOLOGY

Due to the limitation of time and the demand for high quality results, the author will only use one manipulated variables for assessment with base oil which is nanoparticle loading percentage. This project basically consist of 2 parts. The first part uses 2 different batches of FGO-COOH and is subjected to ball milling and particle size analyzing. The batch with smaller particle size is chosen for our next stage which is using 5 different particle size of FGO. All of the samples will later be blended with one type of base oil (rubber seed ester oil). Both stages will be conducted via experimental procedure. All experimental works will start and end during FYP2.

Study of FGO Batch towards Drilling Fluid Properties

The FGO samples required for this project is obtained from Platinum Nanochem Sdn. Bhd. There will be 2 samples used (2 separate batch functionalized with carboxylic group). The goal at this stage is to study the effect (if any) of the variation in FGO loading percentage to base oil properties. Samples are to undergo preliminary round of Power Spectral Density analysis (PSD) in UTP material analysis lab to establish physical properties. After that, nanoparticles will be dispersed in rubber seed ester base oil and the thermal conductivity/viscosity will be analyzed.

Figure 6-Typical commercial high quality graphene oxide (GO)

A summary of the methodology is as follows:

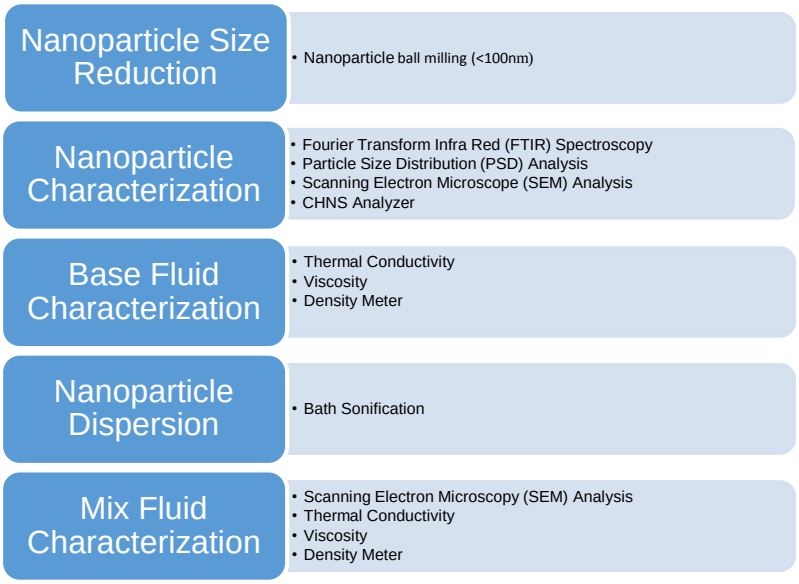


Figure 7-Summary of project methodology

3.1 Nanoparticles Size Reduction

The first equipment to be used is the ball miller. This is a small scale lab version which allows the user to set the spin duration, rotation per minute (RPM) and spin cycle. For our purpose we set the rotation speed to 500RPM (total 3 hours). The goal here is to reduce the particle size into a consistent unit for our base oil mixing later.

Figure 8-Planetary Ball Milling equipment

3.2 Nanoparticle Characterization

3.2.1 FTIR Spectroscopy

Infrared spectroscopy is one of the core of organic chemistry. One can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. It is an easy way to identify the presence of certain functional groups in a molecule. This is important to ensure our sample is not contaminated with anything which may affect our results later on. Used after ball milling.

Figure 9-FTIR Spectroscopy Set Up

3.2.2 Particle Size Analyzer

In order to determine the particle size of ball milled sample, a particle size analyzer (PSA) is used. This equipment uses the technique of laser diffraction to measure the accurate size of sample particles. It does this by measuring the intensity of light scattered as a laser beam passes through a dispersed particulate sample. This data is then analyzed to calculate the size of the particles which has created the following scattering pattern.

Figure 10-Mastersizer 2000 Particle Size Analyzer

3.3 Base Fluid Characterization

For this part, we will be analyzing the thermal conductivity, viscosity and specific gravity of the base fluid sample. This is to later determine the change in characteristics of base fluid after blending of nanoparticles.

Figure 11-Anton Paar 4500M Density Meter

3.4 Nanoparticle Dispersion

Ultrasonication procedures are important to ensure that FGO has been completely dispersed in base oil and does not form sedimentation. Ehsan et. al. (2013) suggested dispersion of nanoparticles in base oil for 1 hour at high intensity [12]

Figure 12-Branson 8510-DTH Branson Model 8510 Digital Sonicator with Heating

For this project we are using a bath sonicator apparatus located in UTP Block P. A range of 0 to 1wt% graphene is added into base oil samples and sonicated for duration of an hour.

3.5 Mixed Fluid Characterization

The final product of this project. To be tested for its thermal conductivity, surface tension, kinematic viscosity:

Thermal conduction in fluid

The equipment used for assessing the thermal conductivity of fluid is as follows:

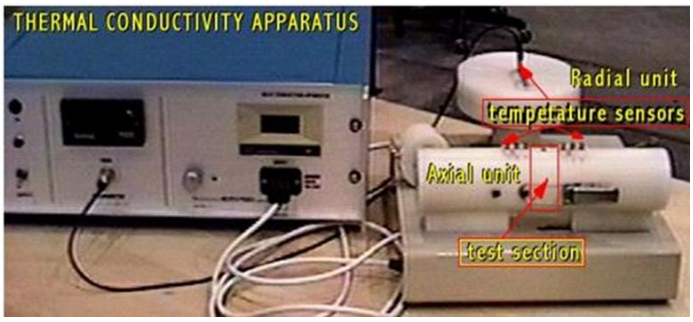


Figure 13-Heat conduction unit H940 (P.A. Hilton Limited)

Heat conduction within a fluid is tested using Fourier's law. Equation is given as follows:

$$k = -\frac{q_c}{A}\frac{dx}{dT}$$

In radial heat conduction of a cylinder, dx is changed to dr and area A is the cross sectional area of the path of conduction. Now for measurements made at steady state conditions, dr becomes Dr, and dT is changed to DT so we can obtain,

$$k = -\frac{q_c}{A}\frac{\Delta r}{\Delta T}$$

Conservation of energy principle is used to find heat by conduction and is given by:

$$q_c = q_{gen} - q_{lost} = \frac{V^2}{R} - q_{lost}$$

V and R are the voltage and resistance units of the heater element in apparatus. In this mechanism there are heat transfers other than that transferred by conduction through the fluid under test. These heat "losses" are defined as incidental heat transfer. This can be caused by:

- Heat radiation from plug

- Heat losses to surrounding by radiation and convection from exposed end of plug
- Heat conduction through the o-ring seals

The following are needed specifications for calculation purposes.

- Nominal resistance of heating element, R = 55 □
- Radial clearance between plug and jacket, r = 0.30mm
- Area of conducting path through fluid, A = 0.0133 m^2

By determining the q_c for each sample (0wt%, 0.2wt%, 0.4wt%, 0.6wt%, 0.8wt% and 1wt%) we can find the thermal heat conduction coefficient and plot a Thermal Conductivity vs Loading % curve.

Viscosity in fluid

The equipment used for assessing the viscosity of fluid is as following:

Figure 14-Brookfield CAP 2000+ Viscometer

The viscosity of mixed fluid (centipoise) for a range of nanoparticle loading percentage (0%, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%) is measured and the graph of viscosity (cp) vs nanoparticle loading (%) is plotted.

3.6 Gantt Charts

Table 1-Generalized Gantt Chart FYP 1

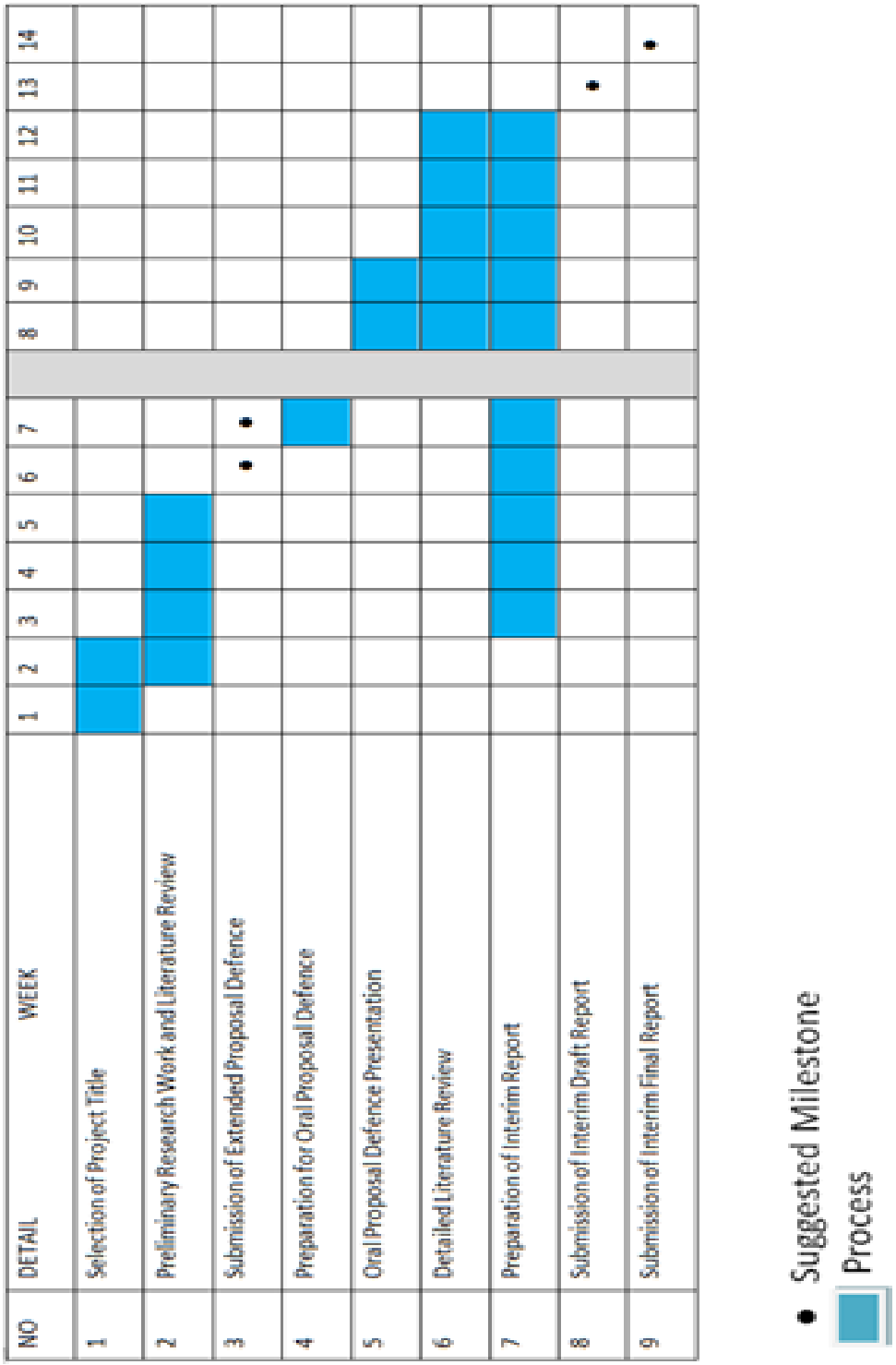
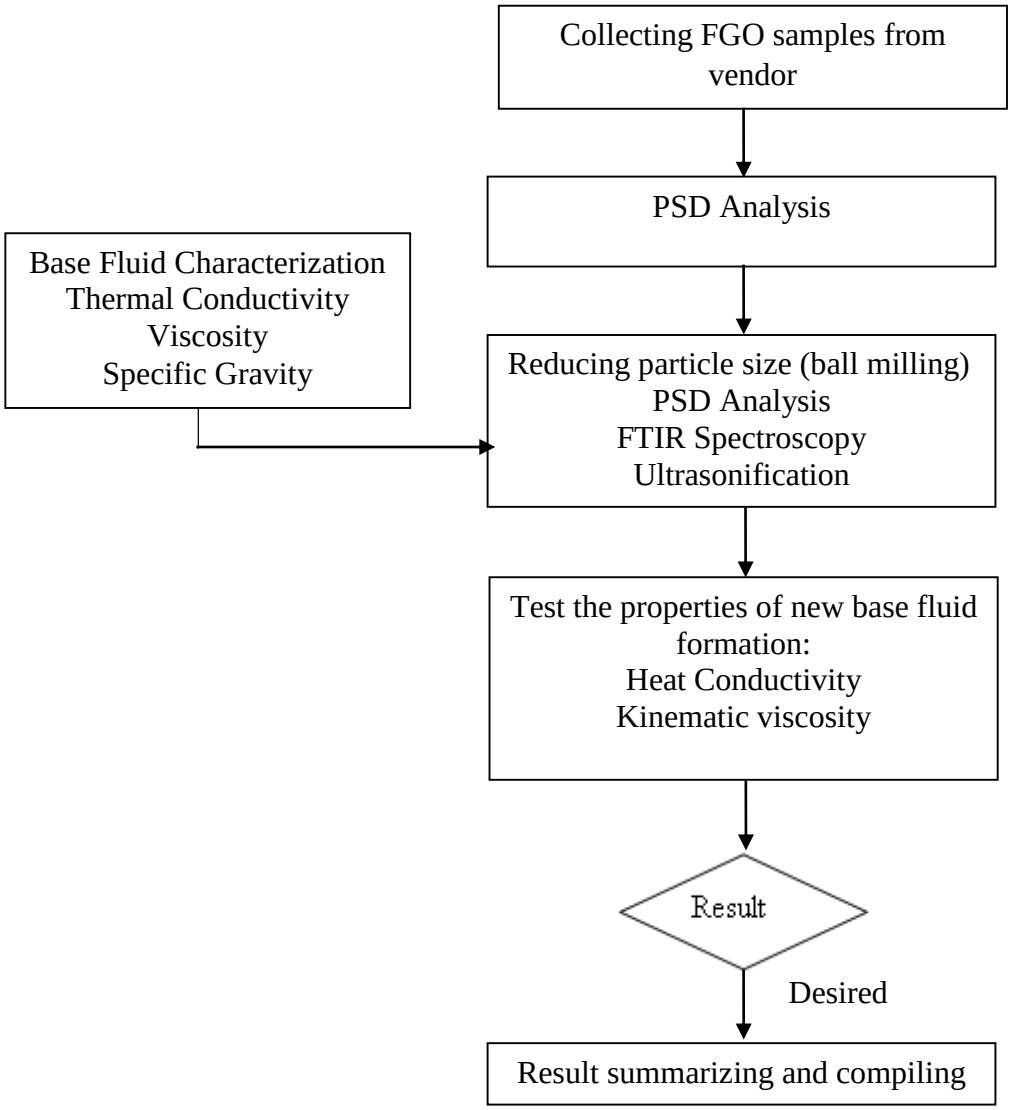


Table 2-Gantt Chart for FYP 2

No	Detail\Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Continue Research Methodology/Literature Review	■	■	■	■										
2	Analysis of Data and Present Findings			■	■										
3	Collecting FGO samples	■	■												
4	Power Spectral Density analysis (PSD)		■	■		■									
5	Ball milling			■	■										
6	Ultrasonification				■	■									
7	Cavitation					■	■								
8	Submission of Progress Report							■	■						
9	Preparation for Pre-SEDEX								■	■					
10	SEDEX									■	■				
11	Preparation of Dissertation										■				
12	Submission of Dissertation											■			
13	Viva												■	■	■
14	Preparation of Technical Paper												■	■	■
15	Preparation of Final Dissertation													■	■
16	Submission of Final Dissertation/Technical Paper														

3.7 Finalized Methodology Diagram



CHAPTER 4

RESULT AND DISCUSSION

4.1 Nanoparticle Characterization

Ball milling of carbon nanotubes is carried out referring to the study conducted by Tucho et al. (2010), and following their recommendation, 500RPM and 3 hours of total duration of intense ball milling experiment was carried out. However, based on previous experience from other UTP's postgraduate and undergraduate students who use this equipment, they have found out that traces of zirconium oxide is left in their sample analysis if the samples were ball milled for very long periods of time. This may caused by high intensity impact between the milling balls and the walls of the retention container, which scrapes off traces of zirconium oxide into the samples.

In order to prevent contamination of zirconium oxide into our samples, the sample is left to run at a 20 minute interval for 8 repetitions at a total time of 3 hours. This could also prevent deformation of the structure of the carbon nanoparticles due to high temperature as a result of extreme intensity from the collision of the retention container.

4.1.1 Particle Size Distribution (PSD)

The figures below shows the average particle size distribution of graphene nanoparticle functionalized group –COOH Batch 1 and Batch 2, and ball-milled graphene nanoparticles functionalized group –COOH Batch 1 and Batch 2.

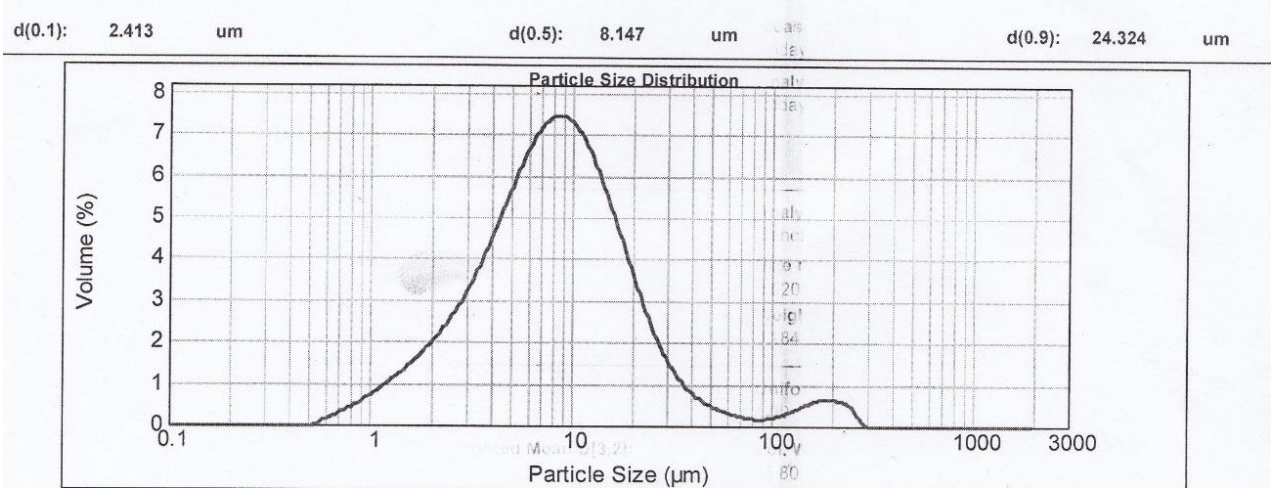


Figure 15-Particle size distribution of graphene nanoparticle functionalized group – COOH Batch 1

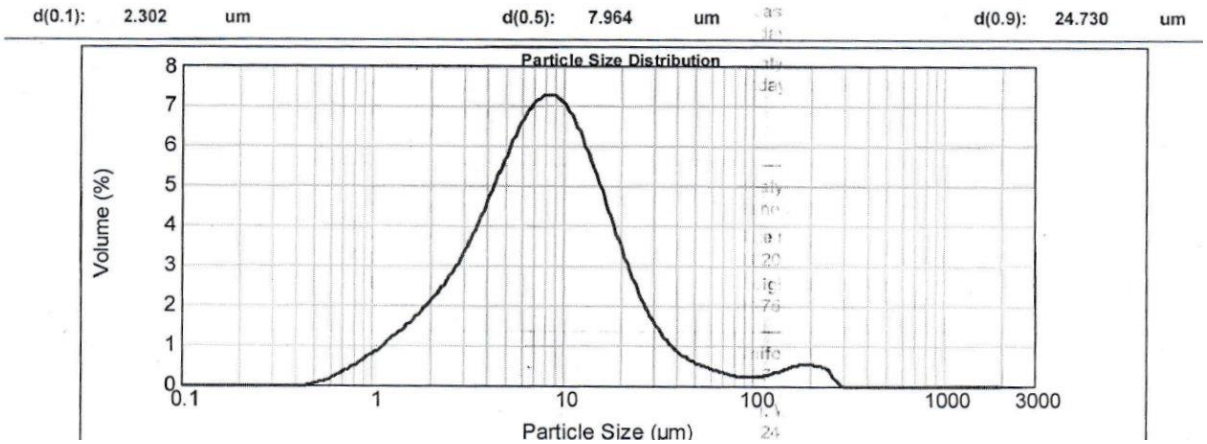


Figure 16-Particle size distribution of graphene nanoparticles functionalized group – COOH Batch 2

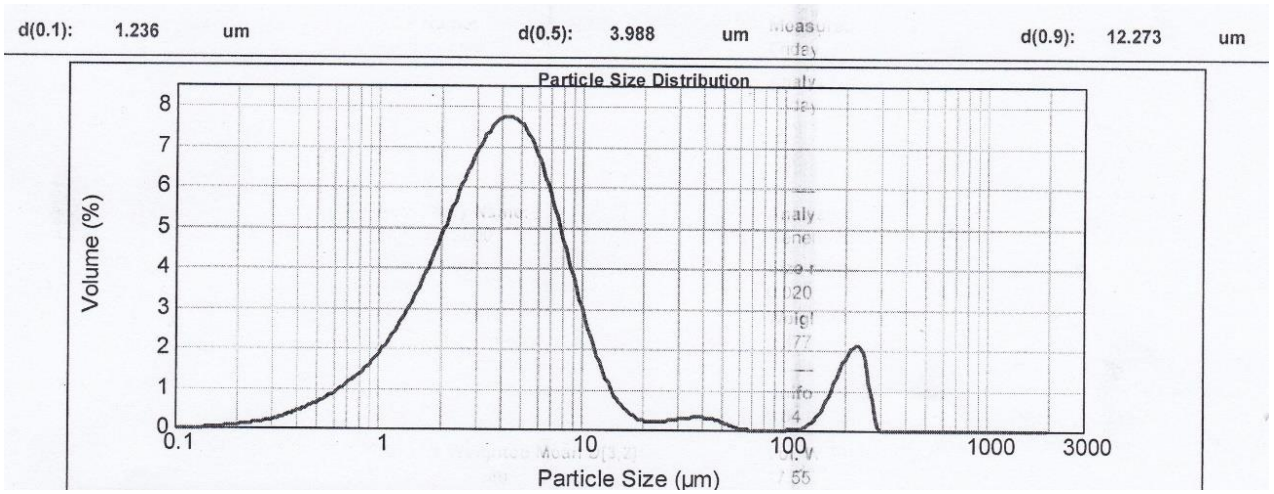


Figure 17-Particle size distribution of ball milled graphene nanoparticles functionalized group –COOH Batch 1

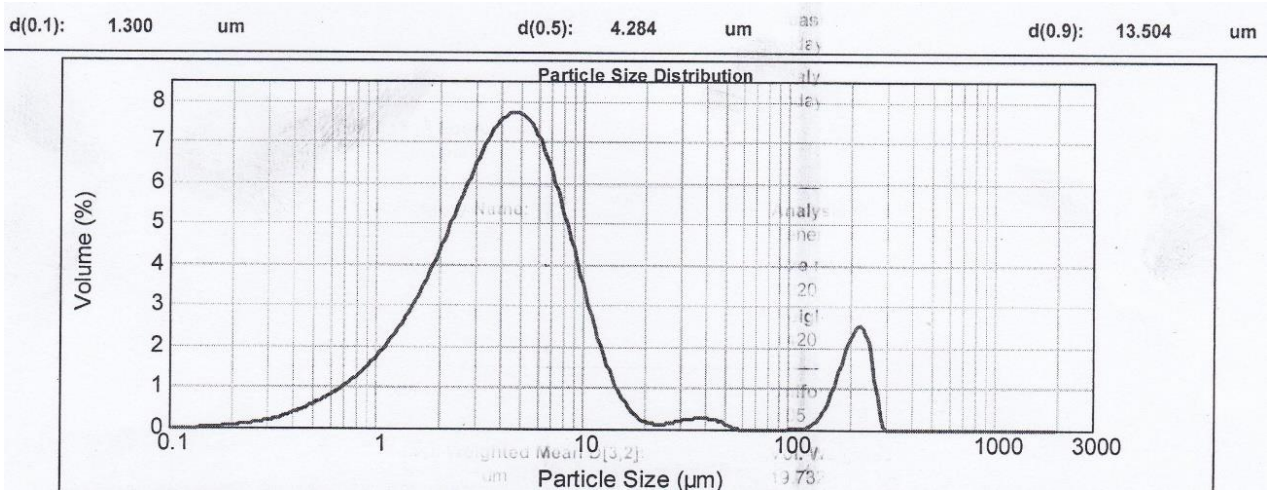


Figure 18-Particle size distribution of ball milled graphene nanoparticles functionalized group –COOH Batch 2

Table 3-Summary and comparisons between findings of particle size distribution of carbon nanotubes (CNTs)

Condition	**Before Ball Milling**		**After Ball Milling**	
PSD (µm)	**Batch 1**	**Batch 2**	**Batch 1**	**Batch 2**
d(0.1)	**2.413**	**2.302**	**1.236**	**1.300**
d(0.5)	**8.147**	**7.964**	**3.988**	**4.284**
d(0.9)	**24.324**	**24.730**	**12.273**	**13.504**
Comparison (Before and After)				
Batch 1 (0.1, 0.5, 0.9)	**48.8%, 51.0%, 49.5%**			
Batch 2 (0.1, 0.5, 0.9)	**43.5%, 46.2%, 45.4%**			

Figure 14 and Figure 15 displays the results of CNTs before ball-milling of Batch 1 and Batch 2 respectively. In Figure 14, 10% of the total population measured is averagely 2.413µm, 50% is 8.147µm and 90% of the total population giving a measurement of 24.324µm averagely. Similarly in Figure 15, 10% of the total distribution yields an average of 2.302 µm, 50% is 7.964µm and 90% of the total population gives 24.730µm averagely in readings.

Figure 16 and Figure 17 displays the results of CNTs after ball-milling of Batch 1 and Batch 2 respectively. In Figure 16, 10% of the total population measured is averagely 1.236µm, 50% is 3.988µm and 90% of the total population giving a measurement of 12.273µm averagely. Similarly in Figure 17, 10% of the total distribution yields an average of 1.300 µm, 50% is 4.284µm and 90% of the total population gives 13.504µm averagely in readings.

Values which are more important to our purpose is 90% distribution. By calculating the percentage reduction in size ([before-after]*100/before), we found out that batch 1 has a 49.5% size reduction whereas batch 2 has a 45.4% size reduction. Therefore we can conclude that our samples have reduced by up to half in size using the operating conditions stated above.

4.1.2 FTIR Spectroscopy Analysis

Figure 18 and Figure 19 below show Fourier Transform Infrared Spectroscopy (FTIR) analysis result of ball milled graphene nanoparticles functionalized group–COOH Batch 1 and Batch 2. A table of characteristic IR absorptions (refer to Appendix) is used in order to determine the presence of the bonds and functional group in the samples.

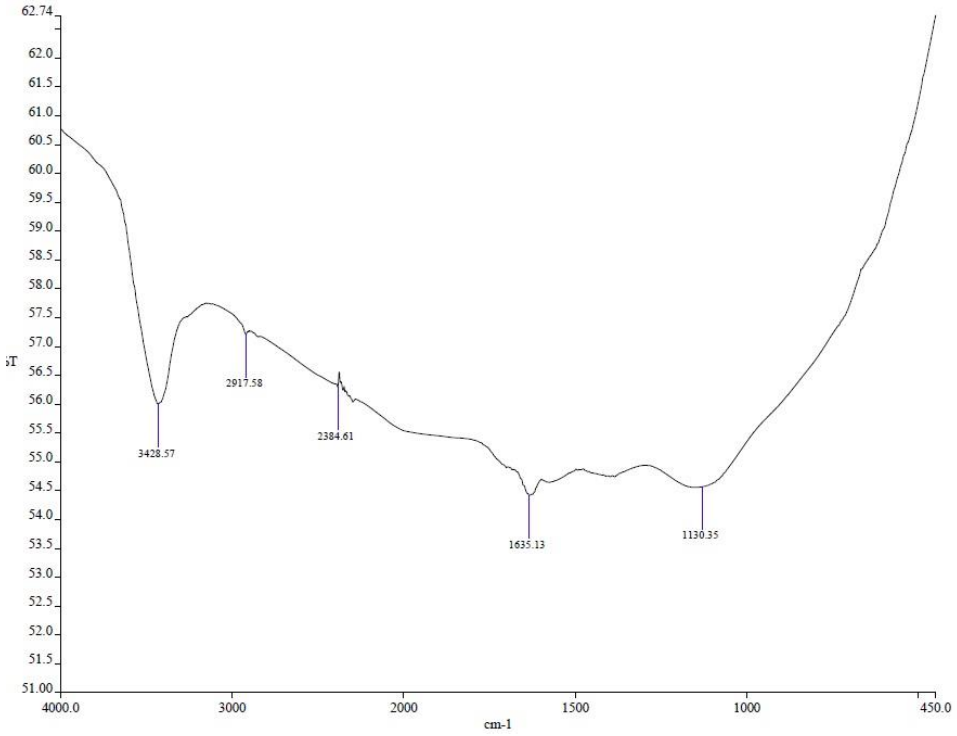


Figure 19-IR spectroscopy graph of ball milled carbon nanoparticle functionalized group –COOH Batch 1

In Figure 18, observed is a broad peak with wavelength 3428.7 cm-1 which shows presence of O-H stretch bond or H-bonds which shows the possible presence of alcohol or phenol groups. A small peak can be seen at wavelength 2917.58 cm-1 showing the presence of O-H stretches with carboxylic acids as its main functional group. The analysis shows medium peak at 1635.13 cm-1 containing carboxylic acid functional group as well. Another smaller broader peak at 1130.35cm-1 also show C-O stretch bonds containing carboxylic acid group.

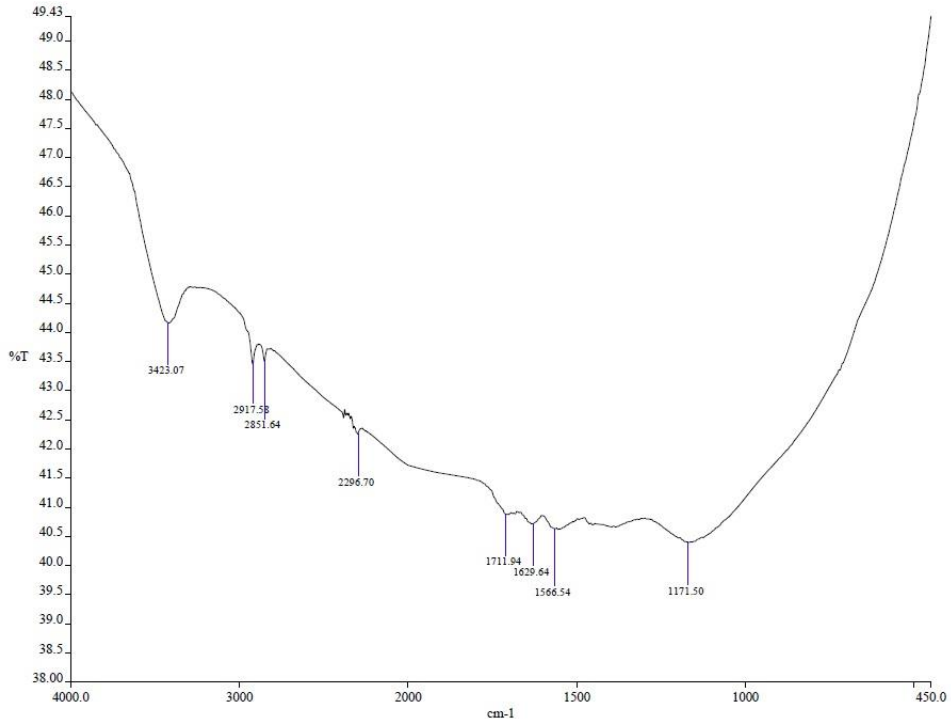


Figure 20-IR spectroscopy graph of ball milled carbon nanoparticle functionalized group –COOH Batch 2

Similarly in Figure 19, observed is a medium peak at 3423.07 cm-1 identified having O-H stretch bonds or H bonds with functional group of either alcohols or phenols. As compared to Batch 1, an extra peak at frequency of 2851.64 cm-1 falls under the category of alkanes with C-H bonds. At frequency 1711.94 cm-1 and 1629.64 cm-1, the peak shows the presence of carboxylic acid functional groups in the sample. However, an extra peak at 1566.54 cm-1 C-C bonds with ring formations with possible aromatic functional groups present within in the sample.

4.2 Base Fluid Characterization

Sample being analyzed is rubber seed oil obtained from UTP Biochemical Lab Department. The goal is to determine the characteristics of base oil before CNT dispersion.

4.2.1 Density Meter

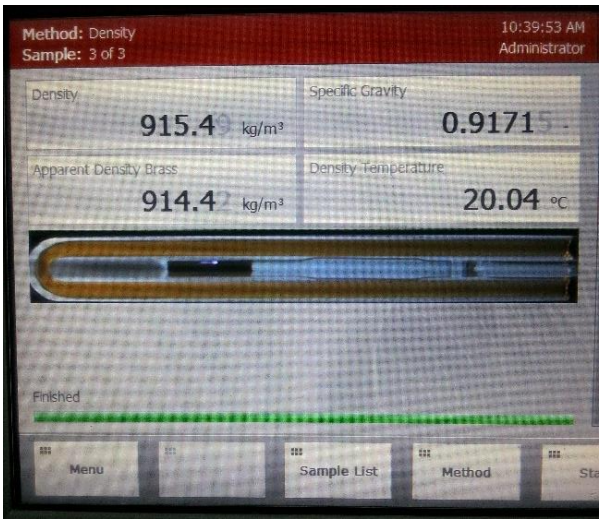


Figure 21-Density readout of sample at T=20℃

Figure 22-Density readout of sample at T=25℃

As observed from the readings above, the specific gravity of oil changes from 0.9171 to 0.9144 for the varying temperatures, which is a reduction of only 0.3%. Therefore we can conclude this base fluid is thermally stable.

4.3 Mixed Fluid Characterization

4.3.1 Thermal Conductivity

The initial calculations to determine q generated are as follows:

$$q_{gen} = \frac{V^2}{R} = \frac{60^2}{55} = 65.45W$$

This value is similar for all the samples. Next we find the Δt which for 0wt% is 10.8°C (value set by user) followed by determination of q_{loss} from calibration which is 1.5W. Therefore,

$$q_c = q_{gen} - q_{lost} = 65.45W - 1.5W = 63.95W$$

From this we can find the heat transfer coefficient as follows:

$$k = -\frac{q_c}{A}\frac{\Delta r}{\Delta T} = \frac{63.95 \times (0.3 \times 10^{-3})}{0.0133 \times 10.8} = \frac{0.1288W}{m\,℃}$$

Summary of the calculations for all 6 samples are tabulated below:

Table 4-Calculation summary for thermal conductivity vs loading percentage

	0wt%	0.2wt%	0.4wt%	0.6wt%	0.8wt%	1.0wt%
q_{gen}	65.45W	65.45W	65.45W	65.45W	65.45W	65.45W
q_{lost}	1.5W	1.55W	1.55W	1.08W	1.41W	1.68W
q_c	63.95	63.9	63.9	64.37	64.04	63.77
ΔT	10.8	11.2	11.0	11.0	10.7	10.5
k	0.134	0.129	0.131	0.132	0.135	0.137

A graph of k vs loading is plotted to observe the general trend as shown next:

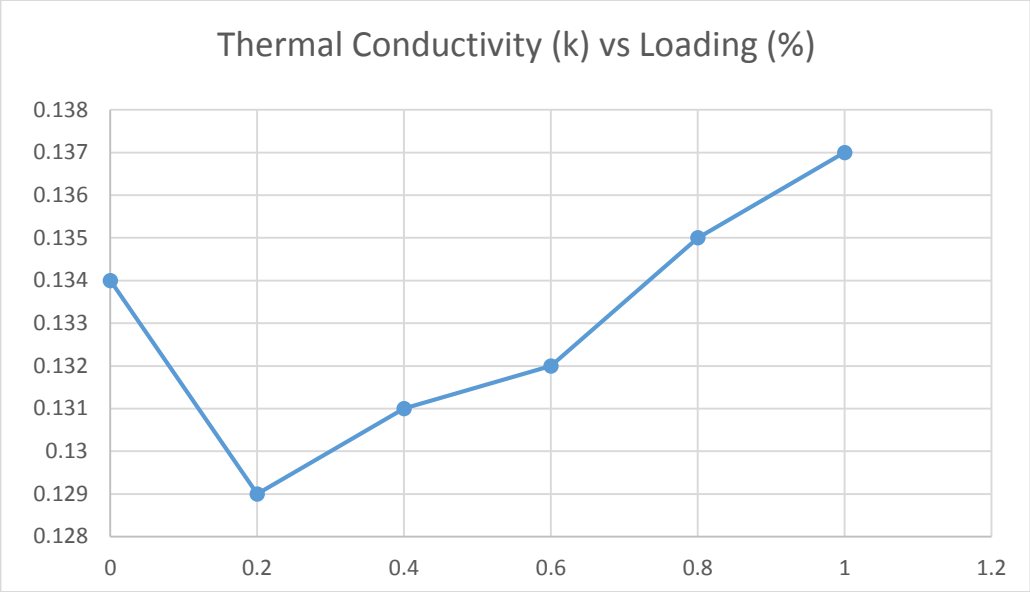


Figure 23-Thermal Conductivity vs Loading curve

Data shows that at 0.8wt% loading and above, the thermal conductivity of rubber seed ester base oil is higher as compared to 0wt% loading, but the range of data is not very significant for us to draw conclusion.

4.3.2 Viscosity

Spindle 3 set up is used for viscometer as it has the best viscosity range we are measuring. Apparatus is run for one minute each at a varying speed of 100RPM, 150RPM, and 200RPM. The results are as shown below:

Table 5-Viscosity of mixed fluid (Spindle 3: 100 RPM)

Temp/Loading	0wt%	0.2wt%	0.4wt%	0.6wt%	0.8wt%	1.0wt%
25°C	1163cp	705cp	1395cp	1043cp	923cp	1080cp
30°C	555cp	787cp	1065cp	1027cp	1056cp	1065cp
35°C	322cp	967cp	1155cp	1065cp	1013cp	458cp
40°C	510cp	818cp	1065cp	1005cp	1102cp	705cp
45°C	780cp	893cp	585cp	1155cp	1102cp	360cp

Table 6-Viscosity of mixed fluid (Spindle 3: 150 RPM)

Temp/Loading	0wt%	0.2wt%	0.4wt%	0.6wt%	0.8wt%	1.0wt%
25°C	575cp	565cp	795cp	470cp	535cp	605cp
30°C	380cp	665cp	785cp	520cp	655cp	650cp
35°C	480cp	520cp	720cp	660cp	660cp	525cp
40°C	395cp	600cp	640cp	670cp	625cp	525cp
45°C	655cp	665cp	530cp	670cp	650cp	270cp

Table 7-Viscosity of mixed fluid (Spindle 3: 200 RPM)

Temp/Loading	0wt%	0.2wt%	0.4wt%	0.6wt%	0.8wt%	1.0wt%
25°C	383cp	465cp	458cp	446cp	521cp	450cp
30°C	454cp	480cp	611cp	278cp	416cp	547cp
35°C	356cp	379cp	349cp	461cp	451cp	169cp
40°C	244cp	476cp	356cp	443cp	450cp	221cp
45°C	450cp	472cp	311cp	383cp	454cp	101cp

In order to further analyze the data obtained, a set of line graphs are prepared as shown:

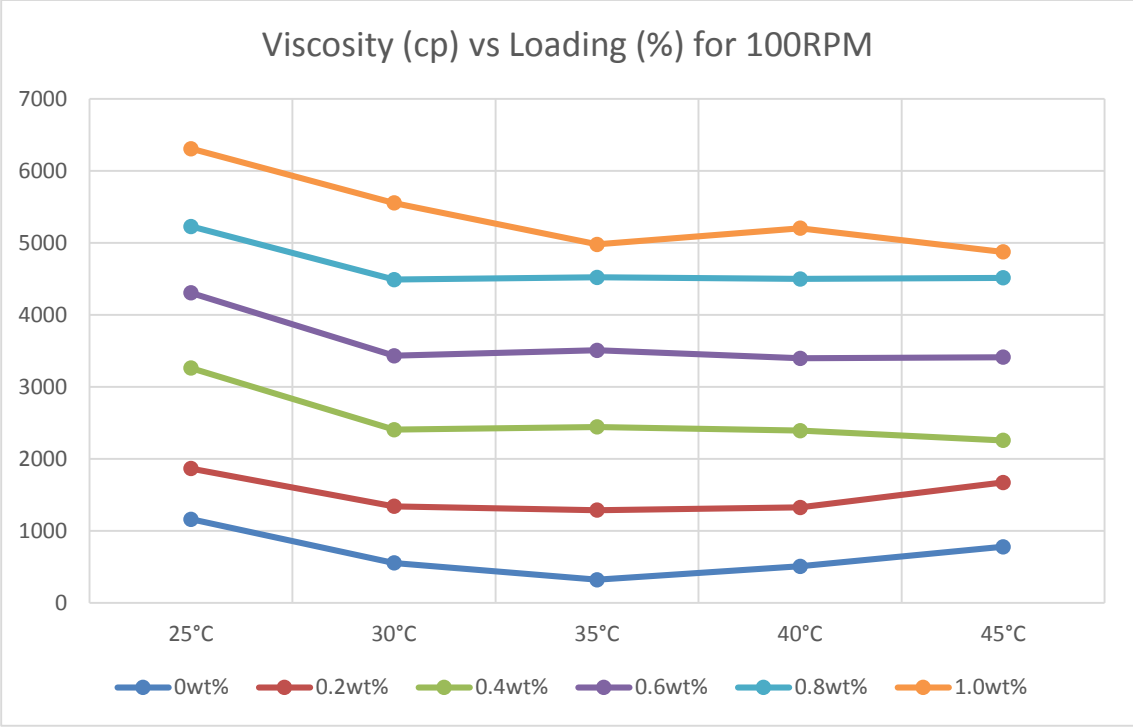


Figure 24-Viscosity (cp) vs Loading (%) curve for 100RPM

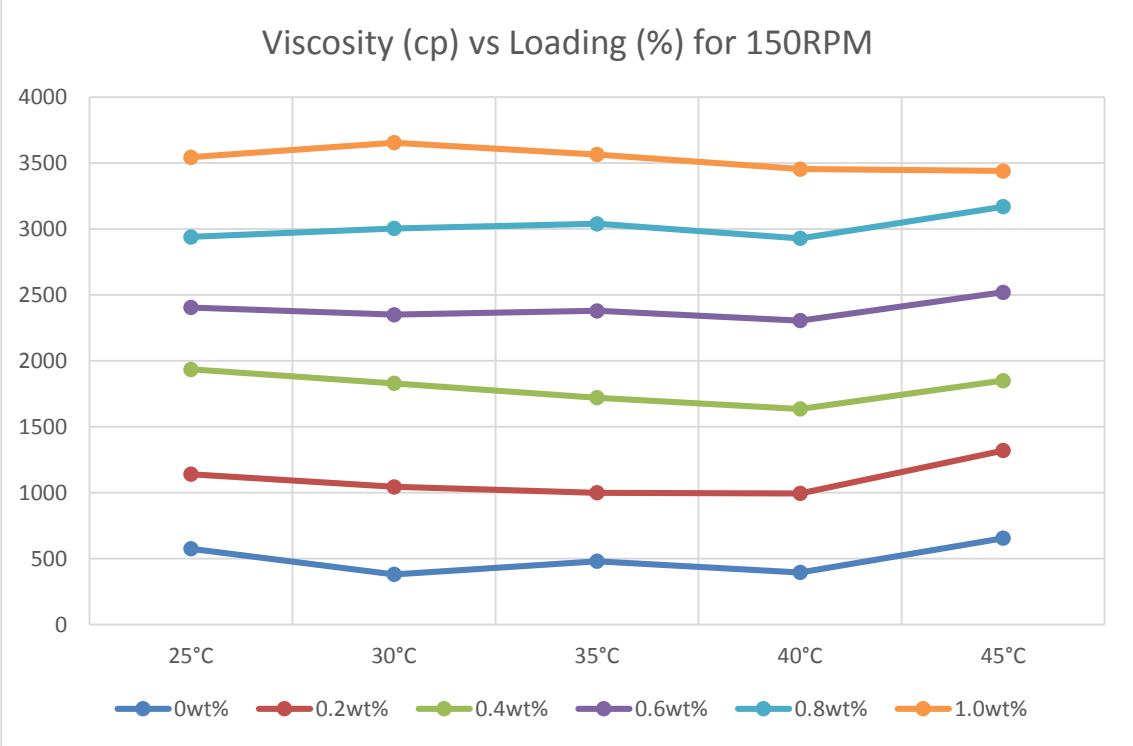


Figure 25-Viscosity (cp) vs Loading (%) curve for 150RPM

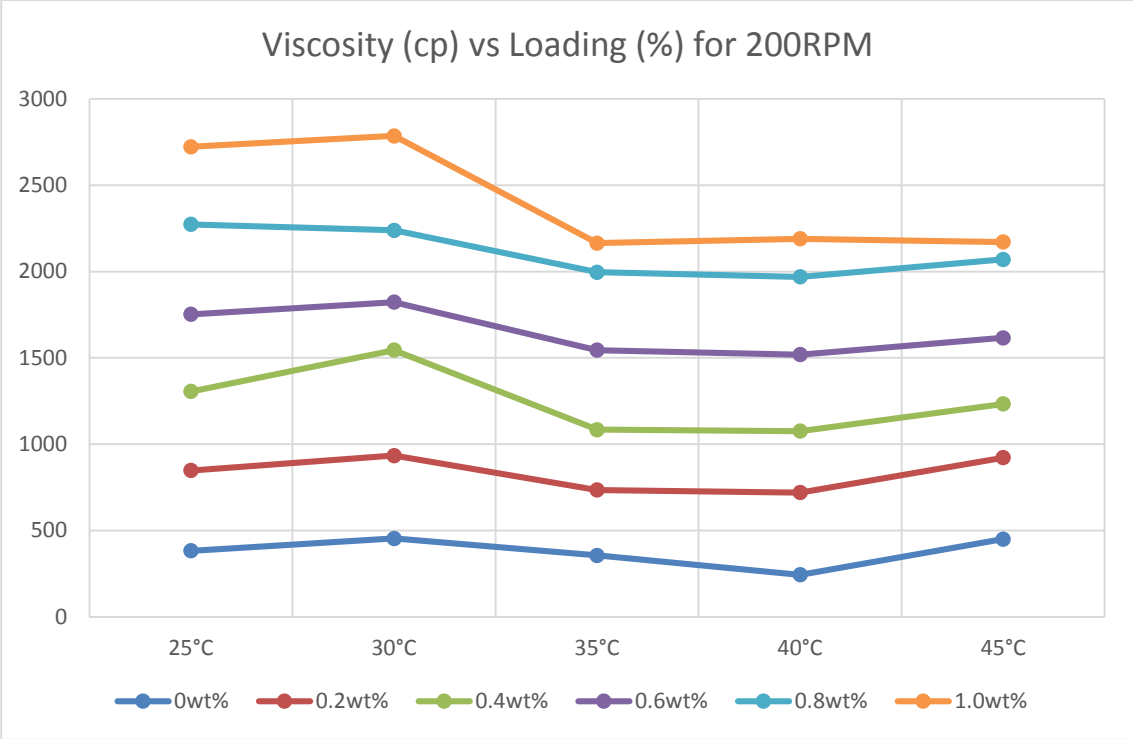


Figure 26-Viscosity (cp) vs Loading (%) curve for 200RPM

Viscosity analysis shows that rubber seed ester base oil becomes more viscous with the addition of nanoparticles, and the trend is consistent with all 3 impeller speed settings.

Literature review has demonstrated to us that nanoparticle addition generally increases the thermal conductivity and improves the rheological properties of the base fluid compare to a pure base fluid. Further in depth discussion will be discussed once more experimental results are obtained.

CHAPTER 5

CONCLUSION/RECOMMENDATION

5.1 Conclusion

The problems associated with the increasing demand for petroleum exploration and the accompanying environmental pollution has been the issues of considerable concern. Graphene, owing to their particular properties, are on the verge of creating a vast revolutionary change in various fields including in the oil and gas sector.

We found out that nanoparticle size can be reduced up to 49.5% through ball milling for 3 hours using a planetary ball miller. Density test of rubber seed oil shows only 0.3% change in density when heated from 20°C to 25°C. We also observed that viscosity of base oil increases as loading percentage increases, and the trend is similar for all 3 impeller speed.

The main challenge comes from the fact that graphene is a relatively new material, hence prior research articles for this project are quite limited. Graphene is also extremely expensive and only a few organizations/universities produce this material in small scale for research purposes. This is because the production process is tedious and causes environmental concern if done in a large scale. [4] Thus through more research, it is believed that a breakthrough discovery is slated for the future.

5.2 Recommendations

Further research could be done by using different types of nanoparticles such as Al_2O_3 particles or Multi-Walled Carbon Nanotube (MWCNT) dispersed into the same base oil and the rheological properties be tested and compared with each other. A more detailed study on nanoparticle size effect could also be conducted using batches of various particle sizes to determine its effect on the thermal conductivity and rheological properties of the fluid for the ratio which gives the best results.

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APPENDICES

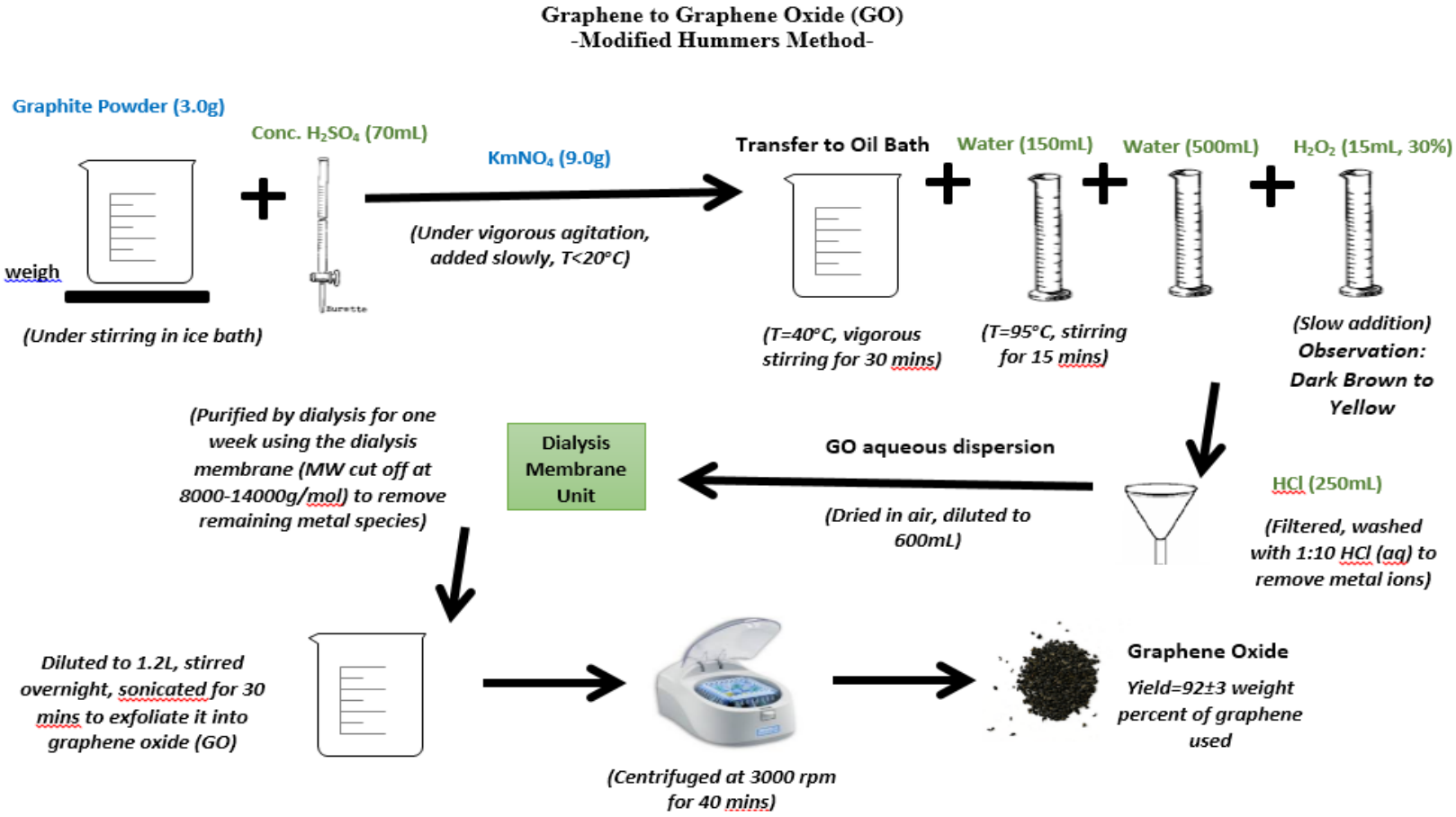
Appendix 1 : Table of Characteristic IR Absorptions

Table of Characteristic IR Absorptions

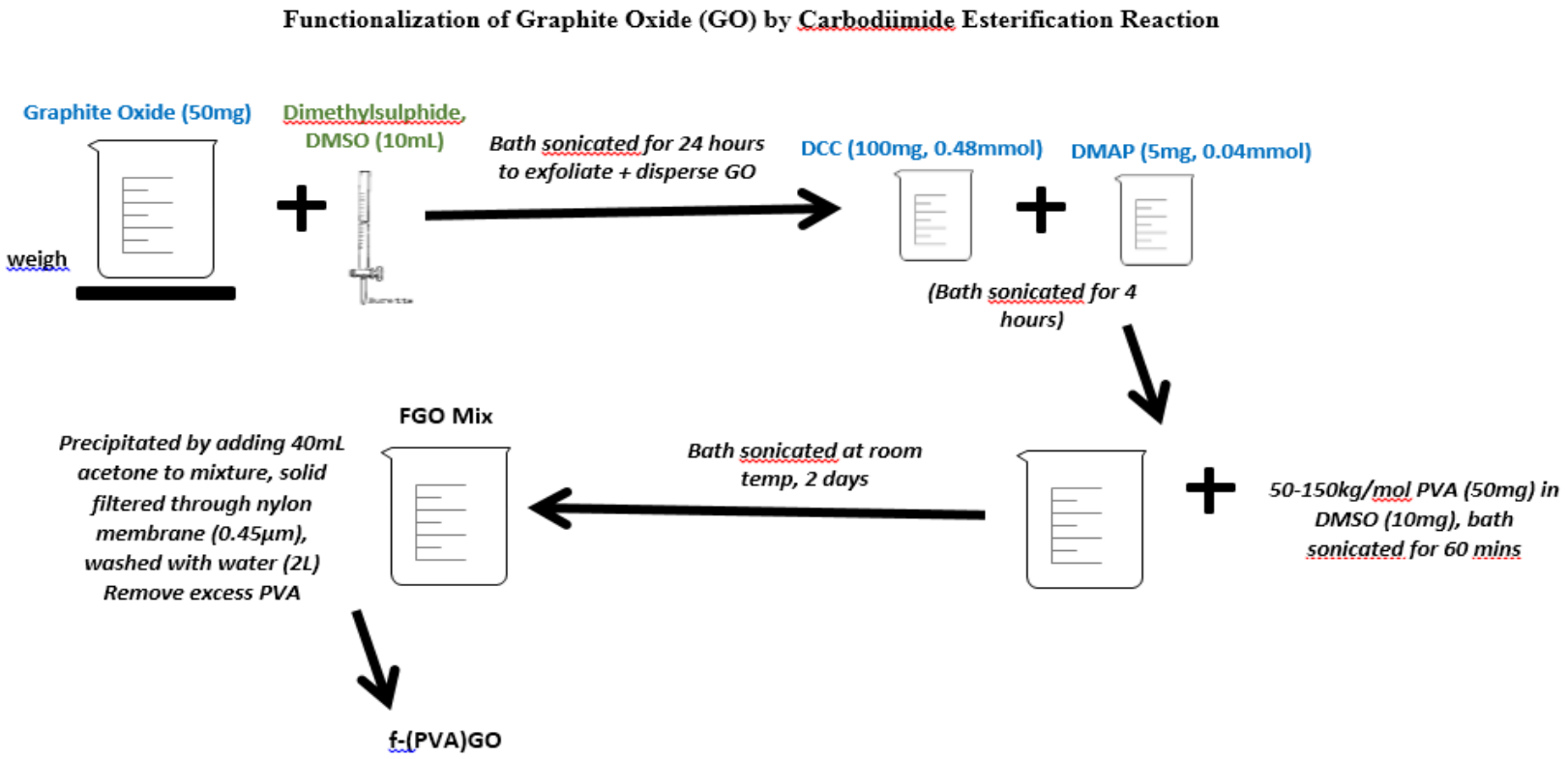
frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Appendix 2: Graphical Representation of GO Production Process



Appendix 3: Graphical Representation of FGO Production Process



Legend:
DCC: N,N dicyclohexylcarbodiimide
DMAP: 4-dimethylaminopyridine
PVA: Polyvinyl Alcohol