

**EXPERIMENTAL STUDY ON Al_2O_3 - TiO_2 AND
 Al_2O_3 - CuO HYBRID NANOFLUIDS FOR
LITHIUM ION BATTERY COOLING**

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 Al_2O_3 - CuO HYBRID NANOFLUIDS FOR
LITHIUM ION BATTERY COOLING**

by

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LIST OF SYMBOLS

C_p	Specific heat capacity ($\text{Jkg}^{-1}\text{K}^{-1}$)
h	Heat transfer coefficient ($\text{W/m}^2\cdot\text{K}$)
k	Thermal conductivity ($\text{W/m}\cdot\text{K}$)
K	Kelvin (K)
R	Mixture ratio
V	Voltage (V)
μ	Dynamic viscosity ($\text{mPa}\cdot\text{s}$)
μ_r	Relative viscosity
σ	Shear stress (Pa)
γ	Shear rate (s^{-1})
%	Percentage
θ	Angle ($^\circ$)
λ	Wavelength (m)

LIST OF ABBREVIATIONS

Ah	Ampere hour
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning for Engineers
ASTM	American Society for Testing and Materials
ANN	Artificial Neural Network
BTMS	Battery thermal management system
CNT	Carbon nanotubes
CPU	Central processing unit
CTAB	Cetyl Trimethyl Ammonium Bromide
DC	Direct current
DI	Deionized water
DLS	Dynamic light scattering
DSC	Differential Scanning Calorimetry
EG	Ethylene Glycol
EVs	Electric vehicles
FESEM	Field Emission Scanning Electron Microscopy
GM	General Motor
GO	Graphene oxide
HEVs	Hybrid Electric Vehicles
ICDD	International centre for diffraction data
IEEE	Institute of Electrical and Electronics Engineers
LDPE	Low density polyethylene
LIB	Lithium ion battery
LPM	Litre per minute
MOD	Margin of deviation
MSE	Mean squared error
MWCNT	Multi walled carbon nanotubes
OAFSS	Oxygen acetylene flame synthesis system
PAG	Polyalkylene glycol
PCM	Phase change material
PHP	Pulsating heat pipe
PVP	Polyvinylpyrrolidone

PWP	Pulse wire evaporation
Re	Reynolds number
RSM	Response surface methodological
SDS	Sodium Dodecyl Sulfate
SDBS	Sodium Dodecyl Benzene Sulfonate
SE	Standard error
SLS	Sodium Laureth Sulfate
TEM	Transmission electron microscopes
UPS	Uninterruptible power supply
VCC	Vapor compression cycle

LIST OF APPENDICES

- Appendix A Certificate of participation
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KAJIAN EKSPERIMEN KE ATAS BENDALIR NANO HIBRID Al_2O_3 - TiO_2 DAN Al_2O_3 - CuO UNTUK PENYEJUKAN BATERI ION LITIAM

ABSTRAK

Bateri ion litium (BIL) banyak digunakan dalam kenderaan elektrik dan kenderaan elektrik hibrid kerana ketumpatan tenaga yang tinggi, voltan yang tinggi, kestabilan yang baik, dan kehilangan cas yang rendah ketika tidak digunakan. Walau bagaimanapun, penggunaan BIL pada kadar ketumpatan tenaga tinggi mempunyai risiko seperti landasan terma yang memerlukan sistem pengurusan haba yang berkesan. Penyelidikan ini memberi tumpuan kepada pembangunan bendalir hibrid nano dan menilai prestasi bendalir nano hibrid untuk penyejukan bateri ion litium. Dua jenis bendalir hibrid nano yang mengandungi zarah Al_2O_3 , TiO_2 , dan CuO dikembangkan menggunakan air dan campuran air-Ethylene Glycol sebagai bendalir asas. Zarah bersaiz nano yang terdiri daripada Al_2O_3 , TiO_2 , dan CuO dicirikan menggunakan teknik XRD dan FESEM. Kesan nisbah campuran zarah nano dan kepekatan isi padu pada sifat termofizik dikaji secara eksperimen pada suhu antara 30 hingga 70°C. Berdasarkan data eksperimen, analisis regresi dilakukan untuk memodelkan korelasi baru yang dapat digunakan untuk pengiraan kekonduksian haba dan kelikatan dinamik bendalir hibrid nano TiO_2 - Al_2O_3 dan Al_2O_3 - CuO . Purata saiz zarah hablur Al_2O_3 , TiO_2 , dan CuO yang dikira menggunakan data XRD masing-masing adalah 8, 19, dan 24 nm. Bendalir hibrid nano Al_2O_3 - CuO mencapai peningkatan kekonduksian haba maksimum sebanyak 12.32% untuk nisbah campuran zarah 60:40, sementara bendalir hibrid TiO_2 - Al_2O_3 mencatatkan peningkatan sebanyak 66.5% untuk nisbah campuran 50:50 pada suhu 70°C. Selain itu, hasil kelikatan dinamik menunjukkan bahawa bendalir hibrid nano TiO_2 - Al_2O_3 /air mempunyai

kelikatan dinamik yang lebih rendah berbanding dengan bendalir hibrid $\text{Al}_2\text{O}_3\text{-CuO}$ /air-EG. Model korelasi yang dikembangkan untuk anggaran kekonduksian haba, dan kelikatan dinamik menunjukkan ketepatan yang baik antara data eksperimen dan data yang diramalkan dengan ralat piawai kurang dari 10%. Prestasi termal kedua-dua bendalir nano diuji menggunakan sistem pengurusan termal baru yang dikembangkan berdasarkan sistem penyejukan cecair menggunakan blok penyejukan saluran mini. Kesan kepekatan isipadu bendalir nano dan kadar aliran bendalir terhadap prestasi penyejukan BIL diuji secara eksperimen. Prestasi penyejukan menggunakan bendalir hibrid $\text{TiO}_2\text{-Al}_2\text{O}_3$ menunjukkan peningkatan pekali pemindahan haba sehingga 74.9% berbanding dengan cecair asas. Penggunaan bendalir hibrid $\text{TiO}_2\text{-Al}_2\text{O}_3$ dapat mengurangkan suhu BIL sebanyak $12.35\text{ }^\circ\text{C}$ berbanding dengan bendalir hibrid $\text{Al}_2\text{O}_3\text{-CuO}$ yang hanya dapat mengurangkan suhu sekitar $10.06\text{ }^\circ\text{C}$. Nilai faktor geseran atau “friction factor” yang dikira untuk bendalir hibrid $\text{TiO}_2\text{-Al}_2\text{O}_3$ jauh lebih rendah daripada nilai yang diperolehi untuk bendalir hibrid $\text{Al}_2\text{O}_3\text{-CuO}$. Penggunaan bendalir hibrid mampu mengekalkan suhu BIL pada kadar suhu operasi yang selamat dan berpotensi tinggi untuk digunakan dalam penyejukan modul BIL untuk kenderaan elektrik dan kenderaan elektrik hibrid.

EXPERIMENTAL STUDY ON Al_2O_3 - TiO_2 AND Al_2O_3 - CuO HYBRID NANOFLUIDS FOR LITHIUM ION BATTERY COOLING

ABSTRACT

Lithium ion battery (LIB) is widely used in electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to its high energy density and low charge loss when not in use. However, the use of high energy density LIB has thermal runaway risk, which requires an effective thermal management system. This research focuses on formulating hybrid nanofluids and evaluating the thermal performance of hybrid nanofluids for cooling LIB cells. Two different types of hybrid nanofluid containing Al_2O_3 , TiO_2 , and CuO nanoparticles are developed using water and water/EG as the base fluid. The Al_2O_3 , TiO_2 , and CuO nanoparticles were characterized using XRD and FESEM technique. The effect of nanoparticle mixture ratio and volume concentration on the thermophysical properties are investigated experimentally at temperatures between 30 to 70°C. Based on the experimental data, regression analysis was performed to model new correlations that can be used to estimate the thermal conductivity and dynamic viscosity of TiO_2 - Al_2O_3 /water and Al_2O_3 - CuO /water-EG hybrid nanofluid. The average crystallite size of Al_2O_3 , TiO_2 , and CuO nanoparticles calculated using the XRD data is about 8, 19, and 24 nm, respectively. The Al_2O_3 - CuO hybrid nanofluid achieved the maximum thermal conductivity enhancement of 12.32% for the mixture ratio of 60:40. In contrast, the TiO_2 - Al_2O_3 hybrid nanofluid recorded the maximum thermal conductivity enhancement of 66.5% for the mixture ratio of 50:50 at a temperature of 70°C. Besides, the dynamic viscosity results show that TiO_2 - Al_2O_3 /water nanofluid has lower viscosity compared to Al_2O_3 - CuO /water-EG hybrid nanofluid. The correlation model were developed for thermal conductivity and

viscosity estimation indicates a good agreement between the experiment and predicted data with a standard error of less than 10%. The thermal performance of both nanofluids is tested using a novel thermal management system developed based on a liquid cooling system using mini channelled cooling block. The effect of nanofluid volume concentration and volumetric flow rate on the cooling performance of LIB was tested experimentally. The $\text{TiO}_2\text{-Al}_2\text{O}_3$ hybrid nanofluid showed an excellent cooling performance with 74.9% enhancement in the heat transfer coefficient compared to the base fluid. The use of $\text{TiO}_2\text{-Al}_2\text{O}_3$ hybrid nanofluid reduces the LIB temperature by about 12.35°C compared to $\text{Al}_2\text{O}_3\text{-CuO}$ hybrid nanofluid, which can only reduce 10.06°C . The friction factor computed for the $\text{TiO}_2\text{-Al}_2\text{O}_3$ hybrid nanofluid is significantly lower than the $\text{Al}_2\text{O}_3\text{-CuO}$ hybrid nanofluid. The use of hybrid nanofluid was able to maintain the temperature of the LIBs at safe operating temperature and has a high potential to be used in cooling LIB module for EVs and HEVs.

CHAPTER 1

INTRODUCTION

1.1 Background of study

In recent days, most electronic devices and the transport industry uses lithium ion battery (LIB) for large battery system applications [1]. The issues of energy shortage and environmental pollution have contributed to the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs). LIBs are widely used in EVs and HEVs due to their high energy density, high voltage, good stability, and low charge loss when not in use [2]. European countries such as Norway, Germany, France and the Netherlands are moving towards electric vehicles, which are powered by lithium ion batteries [3].

Generally, LIBs are available in cylindrical and prismatic shapes. One of the common types of cylindrical LIB used in EVs and HEVs is the 18650 type cell. The advancement in LIB technology has contributed to developing high energy density lithium ion batteries to be used widely in the transport industry, including aviation. However, the use of high energy density LIB has thermal runaway risk, which can even lead to fire and explosion [4]. One example of such an incident is the thermal runaway experienced by the lithium ion battery pack in a modified Toyota Prius that caught fire during highway running in the year 2008 [5].

Another similar incident happened in China in July 2016, where the battery pack of an EV bus caught fire after heavy rain due to overheating caused by a loose wire connection [6]. LIB has high sensitivity towards temperature and can suffer both safety and performance if exposed to high or imbalanced temperatures [7]. The LIB module's optimum operating temperature is between 20°C to 40°C [2]. The temperature increase above the optimum limit may risk a thermal runaway due to heat generated during the charging or discharging period. Besides, overheating and uneven cell temperature

distribution in the LIB module and battery pack lead to degradation and failure of cells [8]. Therefore, a practical battery thermal management system (BTMS) is vital to increase LIB's performance and lifespan.

There are various BTMS, including air cooling, liquid cooling, phase change material cooling, and hybrid cooling. Among the four cooling systems, the liquid cooling system was the most efficient thermal management for LIB module. Companies such as Tesla and General Motors (GM) are among the pioneers to employ active liquid cooling systems for their EVs. Tesla used ethylene glycol as the refrigerant and pumped it into a ribbon shaped channel that interfaces with the 18650 batteries [9]. This system uses a forced convection heat transfer mechanism as its battery thermal management system. Meanwhile, GM uses five individual channels to flow the coolant in parallel flow and maintain their prismatic LIB cell temperature. However, both systems used by Tesla and GM have an opportunity for improvement due to the cooling medium's low thermal conductivity.

An efficient cooling system requires a coolant with superior transport properties to achieve the desired cooling performance. Conventional coolants such as water, transformer oil, and ethylene glycol possess a low thermal conductivity, limiting their application in liquid cooling systems [10-12]. Improving the working fluid's thermophysical properties is an effective way to enhance the convective heat transfer mechanism. Maxwell first discovered thermal conductivity enhancement of working fluid by the suspension of solid particles in the year 1881 [13]. The thermal properties of the cooling medium play an important role in maintaining uniform battery temperature and standard temperature levels in the battery thermal management system. After years of continuous research by various researchers and scientists around the world, this technology further evolved into nanotechnology by the development of

nanofluids. The word 'nanofluid' was first introduced by Choi et al. [14], who described it as a suspension of nanometer-sized particles less than 100 nm in a base fluid. After years of continuous research by various researchers and scientists worldwide, this technology further evolved into hybrid nanofluid by the dispersion of two different nanoparticles or nanocomposites in the base fluid such as water, ethylene glycol, or a mixture of both [15,16].

Hybrid nanofluid is the second generation of nanofluid achieved by dispersion of two different nanoparticles or nanocomposites in any base fluid such as water, ethylene glycol or oil [9,13]. Hybridization is a novel technique used to integrate two different materials into a single element that possesses superior properties and characteristics. The suspension of two different types of nanoparticle in the base fluid significantly enhance the heat transfer performance of the base fluid. Example of nanoparticles used in the preparation of hybrid nanofluid includes a stable metal such as gold and copper, metal oxides, metal nitrides, and carbon material such as diamond and graphite [17].

The present study focuses on developing hybrid nanofluids as a cooling medium in the battery thermal management system for 18650 LIB cells. Two different types of metal oxide based hybrid nanofluids were developed using water and water/EG mixture as the base fluid. A novel battery thermal management system was designed employing an indirect cooling method for the 18650 LIB cells. The battery module consists of 10 LIB cells arrange in a 2S5P arrangement. The cooling block used in the research is designed and fabricated from aluminium material. The hybrid nanofluid performance was evaluated using the developed test rig for the LIB module at a constant current discharge rate of 1C.

1.2 Problem statement

Thermal runaway has been a major issue that limits the application of LIB. In most EVs and HEVs, cylindrical 18650 LIBs are used as the power source to drive the vehicle's mechanical system. One of the main reasons for the thermal runaway of LIB cells is due to overheating of the battery during the discharging period. The heat generation for LIB is mainly due to the ohmic heat and side reaction. A LIB module is considered safe if the battery's operating temperature is between 15 to 35°C and the temperature difference between each cell is less than 5°C. However, if the temperature difference between LIB cells in a module exceeds 5°C or the average battery temperature goes beyond 35°C, the risk of thermal runaway is very high.

An efficient cooling strategy is needed to ensure that the LIB operates within the optimum range and has even temperature distributions among the cells. The actual EV uses a secondary loop cooling system for the BTMS. For instance, car manufacturer Tesla use Glycol-based cooling in their BTMS, but it is not too efficient in maintaining the battery temperatures due to its low thermal conductivity. Moreover, the secondary loop liquid cooling system has several limitations, such as complex design, increased weight, and risk of leakage. Besides, most of the research work available on liquid cooling BTMS system for LIB were only focused on mono nanofluids. Mono nanofluid either have good thermal properties or better rheological properties. It does not possess all favourable properties required for a specific application as there is no synergistic effect.

Hybrid nanofluid is an advanced version of nanofluid being researched worldwide for its thermophysical properties. Most of the studies available on hybrid nanofluid are primarily focused on the effect of nanoparticle volume concentration and temperature on thermal conductivity and dynamic viscosity. However, very limited

studies are available on the composition or the mixture ratio of the nanoparticles and the effect on the thermophysical properties of the hybrid nanofluid. A suitable mixture ratio is required to develop a stable hybrid nanofluid with excellent thermophysical properties. The stability of hybrid nanofluids is a critical factor that often limits the thermal performance and applications of nanofluids. Unstable nanofluids tend to lose their heat transfer potential and worsens the flow behaviour during the cooling process. To my best knowledge, there is no heat transfer performance study conducted using hybrid nanofluid as a coolant for lithium ion battery thermal management system. This research will serve as a breakthrough for potential applications of hybrid nanofluid for cooling LIB in EVs and HEVs.

1.3 Objectives

The objectives of this study are listed below:

1. To formulate and examine the thermophysical properties of Al_2O_3 - CuO /water-EG and TiO_2 - Al_2O_3 /water based hybrid nanofluid.
2. To investigate the effect of nanoparticle mixture ratio and volume concentration on the thermophysical properties of hybrid nanofluid
3. To examine the thermal performance of BTMS of cylindrical LIB cells by experimental measure using Al_2O_3 - CuO /water-EG and TiO_2 - Al_2O_3 /water based hybrid nanofluid.
4. To investigate the effect of nanofluid volume concentration and volumetric flow rate on the thermal performance of BTMS for cylindrical LIB cells at a constant current discharge rate.

1.4 Scope of work

The scope of the present study is mainly focusing on the formulation of hybrid nanofluid at different nanoparticle mixture ratios and volume concentrations. This study is limited to two types of base fluid which is water and ethylene glycol. The experimental investigation is limited to the thermophysical properties as these are the vital property that influences the heat transfer performance of a working fluid. Moreover, the temperature range for the thermophysical property evaluation is limited between 30 – 70°C because the nanofluid's main application is for LIB cooling and the temperature of LIB during the discharging process is within the proposed range. The current discharge rate during the experimental work on heat transfer performance of hybrid nanofluid on cooling LIB were maintained at 1C as this is the safe discharge rate according to the battery specification. The volumetric flow rate of the hybrid nanofluid during the forced convection experiment is varied between 150 – 350 ml/min. All conclusion made from this study is based on the mentioned scope and limitation.

1.5 Thesis outline

Chapter 1 of the thesis consists of the introduction section and the historical background of the research work. The problem statement of the research work is highlighted and explain in this particular chapter. Also, the four main objectives of the study are presented in this chapter.

Chapter 2 of this thesis covers the literature reviews of the previous research works related to the current research project. This chapter highlights the major finding of the previous study and the research gap between the past and the present study. The literature review section is focused mainly on the experimental works related to convective heat transfer mechanism, BTMS for cylindrical LIBs, thermophysical

properties of hybrid nanofluid, and development of correlation equation to predict thermophysical properties.

Chapter 3 of the thesis consist of the methodology for the entire research work. The methodology can be divided into four main parts, which is on the preparation of hybrid nanofluid, characterization of the nanoparticles, evaluation of the thermophysical properties, and the experimental work on the cooling strategy for LIB module using hybrid nanofluid. The detail of the materials and equipment used in the study are explained in this section.

Chapter 4 consist of the results and the discussion based on the results obtained for the thermophysical properties evaluation of the hybrid nanofluids. The results on the dispersion stability of hybrid nanofluid and the characterization of the Al_2O_3 , TiO_2 , and CuO nanoparticles are discussed. This chapter also presents the regression model developed for the estimation of thermal conductivity and dynamic viscosity of both $\text{TiO}_2\text{-Al}_2\text{O}_3/\text{water}$ and $\text{Al}_2\text{O}_3\text{-CuO}/\text{water-EG}$ hybrid nanofluid. The second half of this chapter mainly consists of the results and discussion on the thermal performance of the LIB cooling using $\text{TiO}_2\text{-Al}_2\text{O}_3/\text{water}$ and $\text{Al}_2\text{O}_3\text{-CuO}/\text{water-EG}$ hybrid nanofluid. The results and discussion on the effect of nanofluid volume concentration and cooling block material on LIB cooling are also discussed in this chapter.

Chapter 5 is the last chapter of this thesis which contains the conclusions of the entire research findings. This chapter will sum up all the findings and their correlations with solid statements and evidence, which will be useful for future research works. A list of future recommendations will be listed in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter explains the fundamental of hybrid nanofluid, its preparation technique, and application for convective heat transfer mechanism. This chapter also reviews the previous research work focusing on different base fluids and nanoparticles used in the research work related to hybrid nanofluids. There will be several subsections items that are divided to coordinate this chapter with information on the past research works conducted on LIB thermal management system using nanofluids. The detail on lithium ion battery and the thermal management system will be reviewed and presented in this chapter. A critical review will be included on the effect of nanoparticles on the thermophysical properties of water and water/EG mixture. The last section of this chapter shows a summary of the previous research findings that can be used as a comparison for the present study.

2.2 Hybrid nanofluid and its applications

Hybrid nanofluid has high potential in various industrial applications such as electronic cooling, automotive, and manufacturing. For the past decade, researchers from different fields have studied the industrial applications of nanofluids, mainly mono nanofluid, for cooling purposes. Hybrid nanofluid has good potential as a substitute for mono nanofluids which consist of a suspension of a single material in the base fluid. Electronic cooling is one of the potential applications of hybrid nanofluid. Cooling of electronic components is vital as it increases the life span and performance of the electronic component. Advance working fluid such as hybrid nanofluid that possesses

superior thermal properties will ensure the temperature of the electronic devices is maintained under normal conditions.

One example of the application of nanofluids in electronic cooling is the work done by Nazari et al. [18], in which they compared the thermal performance of water, EG, alumina nanofluid, and CNT nanofluid in cooling of Central Processing Unit (CPU) of a computer. They manage to reduce the temperature of the CPU by 22 % using CNT's water based nanofluid as working fluid. Besides the electronic cooling application, hybrid nanofluid can also be used as nano lubricants in machining operations such as drilling, milling, turning, and grinding. For instance, Zhang et al. [19] developed $\text{Al}_2\text{O}_3/\text{SiC}$ hybrid nanofluid as a nano lubricant for grinding hardened Nickel based alloy. The outcome of their study showed that the use of $\text{Al}_2\text{O}_3/\text{SiC}$ hybrid nano lubricant lowered the specific grinding energy and the roughness of the machined surface.

In the automotive industry, low efficient heat exchangers are used as radiators to cool down the automobile engines. Conventionally, water and ethylene glycol mixture are used as a coolant in automobile radiators. However, these conventional fluids have a lower thermal conductivity which reduces the cooling performance. Hybrid nanofluid gained the interest of many researchers around the world due to the enhancement in heat transfer characteristics.

The hybridization of metallic nanoparticles at low volume concentration is an effective technique to enhance the heat transfer rate without affecting the production cost. This has been proven by Suresh et al. [20], who found that the heat transfer coefficient increases with Reynolds number in his experimental work using Al_2O_3 -Cu/water based hybrid nanofluid. The authors also mentioned that the Nusselt number of hybrid nanofluid is enhanced by about 13.56% relative to water. The uniqueness of hybrid nanofluid is that we can vary the mixing ratio between the nanoparticles.

Different composition of nanoparticles results in the enhancement of the heat transfer coefficient. Hybrid nanofluid was found to increase the heat transfer coefficient for convective heat transfer mechanism in both turbulent and laminar flow.

In an experimental work conducted by Sundar et al. [21] for turbulent flow in a circular tube, the use of MWCNT-Fe₃O₄/water hybrid nanofluid was able to enhance the Nusselt number by 31.1 % for a nanoparticle volume concentration of 0.3 %. For hybrid nanofluid, the friction factor and pressure drop usually increase due to the increase in dynamic viscosity of the hybrid nanofluid suspension. However, the remarkable enhancement in the thermal conductivity and heat transfer coefficient of hybrid nanofluid can compensate for the increase in friction factor and pressure drop. Moreover, the low volume concentration hybrid nanofluid does not affect the flow behavior of the base fluid.

2.3 Preparation method for hybrid nanofluid

The preparation of hybrid nanofluid can be achieved via two different methods, which is one step method and two step method [11]. The one-step method is a preparation method in which the process of producing the nanoparticles and dispersion in base fluids were performed simultaneously. This method is considered one of the most effective methods to achieve a homogenous suspension of nanofluids with minimal particle aggregation [22]. However, the application of the one-step method is limited because it can only be used to produce nanofluids in small quantities. The two-step method is a method where the nanoparticles are manufactured or purchased separately before being suspended in base fluid [11]. The benefit of using the two step method is that it can be employed for mass productions [4]. In most of the previous research work related to hybrid nanofluids, the two step method is employed to prepare

hybrid nanofluids. A detailed explanation of the techniques, process parameters, and equipment used in the preparation of hybrid nanofluid are discussed in the next subsections.

2.3.1 One step method

One step method is one of the most suitable methods of preparation of hybrid nanofluid for metal nanoparticles with high thermal conductivity. The main reason is to prevent oxidation of the metals during the preparation process and enhance the stability of the nanofluid. In one step method, synthesizing the nanoparticles and dispersion in the base fluid is performed simultaneously in a single step [10]. This means that the number of steps involved in the preparation process is reduced to one step, and other processes such as drying, storing of nanoparticles, and the dispersion process can be avoided. However, one major problem in this method is the capability for mass production. One step method is significantly not suitable for mass production.

The pulse wire evaporation (PWE) method is an example of one step method used in the preparation of nanofluid. The experimental setup for the PWE method involves a high voltage DC power supply with a gap switch, a capacitor bank, and a condensation chamber. The procedure for the PWE process is initiated by directing a high voltage ($\approx 300\text{V}$) pulse through a thin wire, which evaporates into plasma and condensed into nanopowders in the condensation chamber. Then a nanofluid with the required volume concentration is filled in the exploding bottle in the PWE equipment to produce a hybrid nanofluid. According to Azwadi et al. [15], this method is one of the most popular among other one step preparation methods for hybrid nanofluid. Figure 2.1 shows the graphical illustration of the single step method using PWE technique.

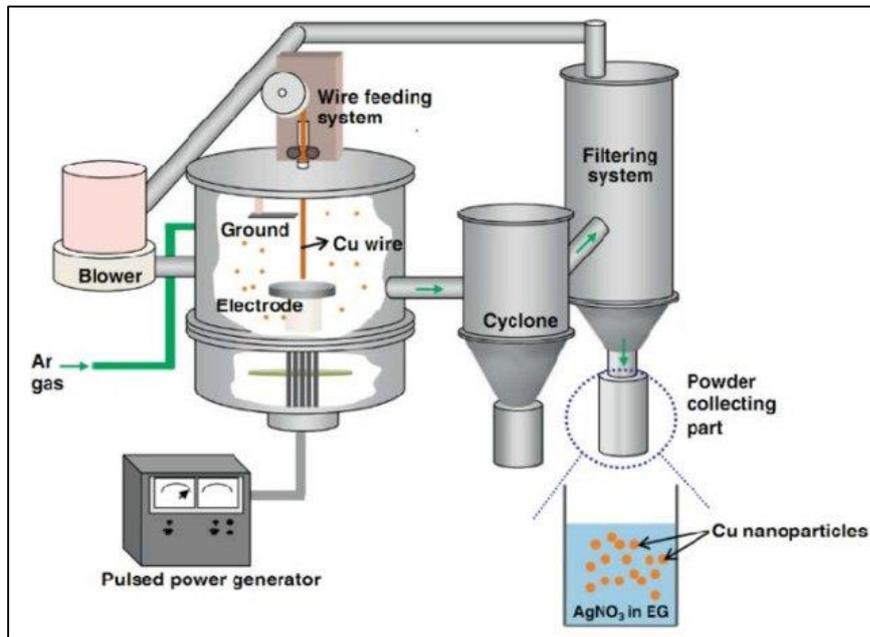


Figure 2.1 PWE preparation method [23]

In the PWE method, there are several factors that affect the size of the nanoparticles obtained. One of the factors that affect the particle size is the level of superheat applied to the thin wire. According to Lee et al. [24], as the amount of superheat applied to the wire is increased, the size of the nanoparticles obtained tend to decrease significantly. Besides that, the authors also mentioned that the size of the particles reduces with an increase in the pressure of the inert gas and the wire diameter. PWE method was used by Munkhbayar et al. [25] to synthesize a hybrid nanofluid consist of multi-walled carbon nanotubes (MWCNTs) and silver (Ag) nanoparticles using water as the base fluid. In their study, the authors treated the MWCNTs with nitric and sulphuric acid to enhance the dispersibility of the nanoparticle in the base fluid. The outcome of their study revealed that the thermal conductivity and dispersion stability of MWCNTs/AG nanofluid is improved using the PWE method. Besides, the authors highlighted that the TEM image characterization shows that the particle size of MWCNTs is less than 100nm.

Another method of synthesizing hybrid nanofluid based on single step method is by using an oxygen acetylene flame synthesis system (OAFSS). The OAFSS system also known as AFSS, which is acetylene flame synthesis system without the presence of oxygen. This method is used by Hung et al. [26] to prepare hybrid carbon nanofluids (HCNFs). The AFSS uses acetylene flame as the carbon source nebulizer, synthesizer, torch, collector, and pipeline of filtered water were integrated to complete the AFSS process hardware. The acetylene was regulated at a flow rate of 2.5 LPM and gas pressure of 1.5 kg/m^2 , while the water flowed into the synthesizer to generate mist. The final product of HCNFs was produced by the combustion and condensation process. Figure 2.2 shows the schematic of the AFSS.

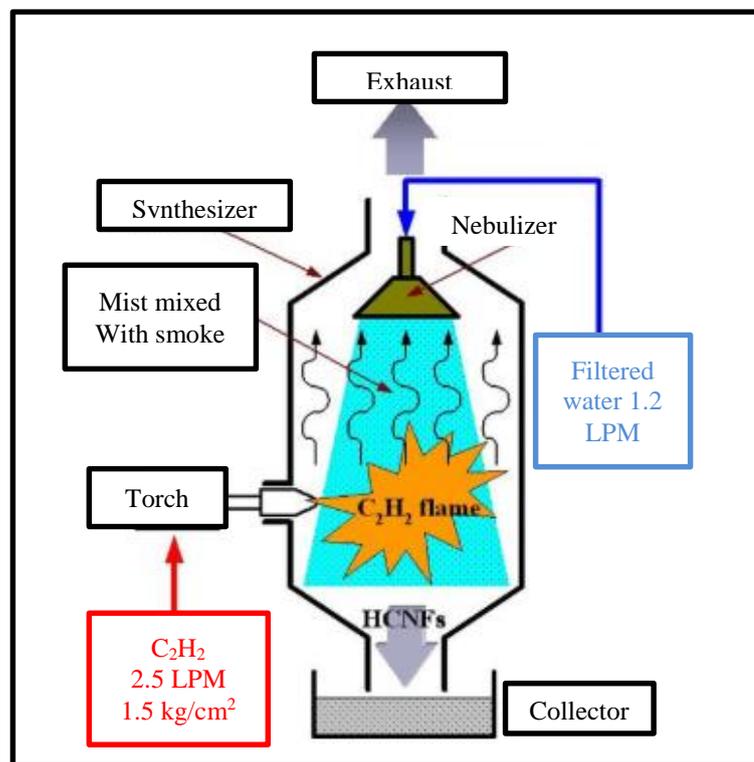


Figure 2.2 Experimental setup of the AFSS [26]

2.3.2 Two step method

The two step method is the most prominent method used by various researchers in the development of hybrid nanofluids. This method differs from the one step method

because the process of synthesizing the nanoparticles/nanocomposites and dispersing them in the base fluid are performed separately. Besides synthesizing the nanoparticles or nanocomposites separately, the nanoparticle can also be purchased directly from various manufacturers and dispersed in the base fluid. The advantage of the two step method is that it can be used to produce hybrid nanofluid in large quantity. Usually, two step method involve intermediate processes such as ball milling [27], wet mixing [28], mechanical stirring [29], ultrasonication [30], thermochemical synthesis [20,31], mechanical alloying, sol-gel method [32], wet chemical method [33], annealing [34], and wet chemical reaction technique [35].

The selection of the manufacturing process depends on the characteristics and properties of the nanomaterial and the base fluid. For instance, Akilu et al. [28] produced SiO₂-CuO/C nanocomposite using a wet mixing method and then ultrasonicated in the base fluid using ultrasonication technique for 1h. They prepared hybrid nanofluid in four different volume concentrations and tested their thermophysical properties. Their experimental results on the pH value and zeta potential show that the pH values lie between 8-9 and zeta potential between -33 and -48 mV. The authors mentioned that the SiO₂-CuO/C hybrid nanofluid with 0.5% volume concentrations has good stability with a zeta potential of -48 mV. This proves that the two step method still able to produce hybrid nanofluid with good stability.

Another combination of a simple two step method is the use of mechanical stirring and ultrasonication technique or a homogenizer. This is a simple and efficient technique to disperse the nanoparticles in any base fluid such as water, water/EG, and oil. This method is suitable when it does not involve the step of synthesizing the nanoparticles because nanoparticles are readily available these days from commercial sources. Using this method involves various process parameters such as stirring

duration, stirring speed, ultrasonication frequency, sonication period, and temperature control. Figure 2.3 shows the schematic of the two step method using mechanical stirring and ultrasonication.

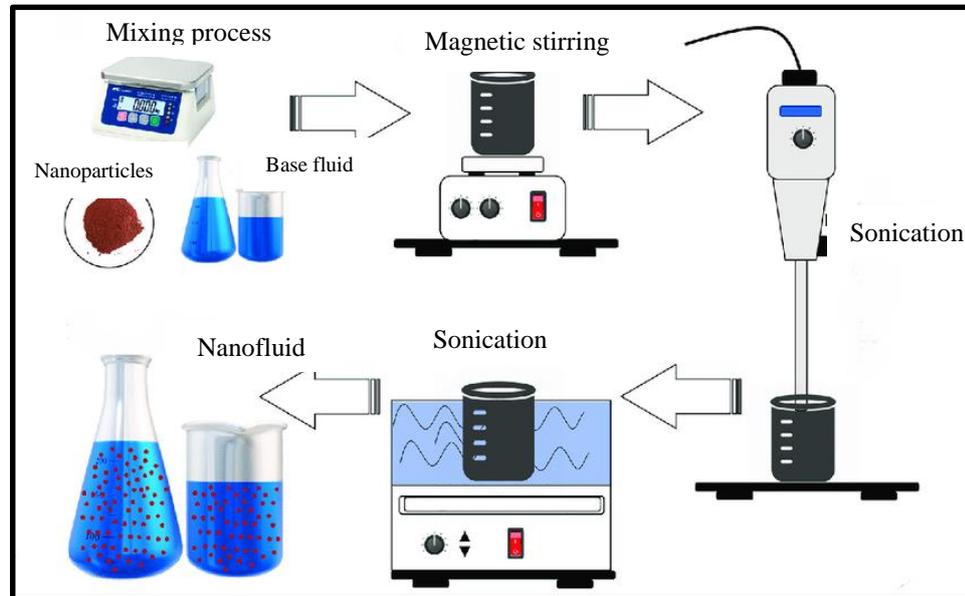


Figure 2.3 Schematic of two step method [11]

Ramadhan et al. [36] used a similar approach to prepare a tri-hybrid nanofluid using TiO_2 , SiO_2 , Al_2O_3 nanoparticles and water/EG mixture as the base fluid. The authors employed a different period of sonication from 0.5 to 10 hours and evaluated the stability of the prepared nanofluid. They found that the hybrid nanofluid sample sonicated for 5 and 10 hours exhibited good stability for 10 days. In another research work on hybrid nanofluid by Hong et al. [37], the authors prepared both mono and hybrid nanofluid by first employing mechanical stirring for 30 min at 500 rpm and then sonicated using a probe sonicator (FS-1200 N) at a frequency of 20 kHz and 80%. The TiO_2 nanoparticle and graphene nanoplatelets used in their study were supplied by US Research Nanomaterials, Inc. and Cheap Tubes Inc., respectively. During the ultrasonication process, the authors placed ice cubes in the beaker to maintain the nanofluid temperature of less than 40°C . Higher temperatures can result in the degradation of the materials dispersed in the nanofluid. They concluded that an

ultrasonication period of 1.5 hours is sufficient to produce a hybrid nanofluid with excellent stability.

The use of sol-gel method to synthesize the nanoparticles before dispersion in a base fluid is also an interesting technique in two step method. Shriram et al. [38] employed the sol-gel technique with ultrasonication to synthesize the TiO₂ nanoparticles. The precursor solution is a mixture of 10 ml titanium isopropoxide, 30 ml isopropanol, and 250 ml of distilled water. The researchers used high frequency ultrasonicator (UP 1200 Chromtech Ltd., Taiwan) to initiate the gel formation and hydrolysis reaction. The end product, in the form of precipitates was washed with ethanol and dried at a temperature of 120°C for 8 hours. According to the authors, the particle size of the TiO₂ is controlled by the dilution of titanium isopropoxide with isopropanol. As for the dispersion of the TiO₂ in the base fluid, the same ultrasonic homogenizer UP 1200 is used to disperse the nanoparticles homogeneously.

The thermochemical method is also used to synthesize nanoparticles. This process involves several intermediate processes such as spray-drying, oxidation of precursor powder, reduction by hydrogen and finally homogenization. For instance, Suresh et al. [20] prepared the Al₂O₃-Cu nanocomposite using the thermochemical method and ball milling technique to produce a homogenous mixture of nanocomposites. An ultrasonic vibrator (40 kHz) was then used by the authors to suspend the nanocomposite powder homogeneously in DI water. The authors successfully prepared the Al₂O₃-Cu/water based hybrid nanofluid using the two-step method.

Most of the works of literature available on hybrid nanofluid showed that two step method is widely used for the preparation of hybrid nanofluid rather than the one step method. Table 2.1 shows a summary of the methods used by various researchers

for the preparation of hybrid nanofluid based research papers searched in science direct using keyword, preparation of hybrid nanofluid.

Table 2.1 Hybrid nanofluid preparation method used in various studies

Hybrid nanofluid	Process involved	Method	Reference
γ -Al ₂ O ₃ /MWCNTs	Solvothermal/ mechanical stirring	Two step	[15]
Al ₂ O ₃ /Ag	Mechanical stirring/ultrasonication	Two step	[39]
Cu-Al ₂ O ₃	Chemical reduction/ultrasonication	Two step	[40]
TiO ₂ -SiO ₂	Mechanical stirring/ultrasonication	Two step	[29]
f-MWCNTs-Fe ₃ O ₄	Mechanical stirring/ultrasonication	Two step	[41]
Al ₂ O ₃ -TiO ₂	ultrasonication	Two step	[42]
SiO ₂ -Cu	Mechanical stirring/ultrasonication	Two step	[43]
Ag-MWNT	Chemical reduction/ball milling	Two step	[44]
Al ₂ O ₃ /CuO	Mechanical stirring/ultrasonication	Two step	[45]
MWCNTs-SiC	Mechanical stirring/ultrasonication	Two step	[46]
Cu/TiO ₂	Chemical reduction/ultrasonication	Two step	[47]
Al ₂ O ₃ -Ag	Sol-gel/ultrasonication	Two step	[33,48]
Al-Zn	Ball milling/magnetic stirring	Two step	[27]

2.3.3 Addition of surfactant

One of the significant limitations of preparing hybrid nanofluid using two step method is stability issues. The stability problem is due to the existence of robust Van der Waals and cohesive forces between the nanoparticles. The best way to enhance the stability of hybrid nanofluid is by adding surfactant during the preparation process. Surfactants are substances that lower the surface tension between a liquid and solid by creating a self-assembled molecular cluster (micelle) in a solution and adsorb to the interface between the liquid and solid. Surfactants can be classified into four different categories which is anionic, cationic, non-ionic, and amphoteric [11].

These surfactants are widely applied in laundry detergents, household appliances, and personal care products. The selection of surfactants depends on the type of material and the nature of the base fluid. Some examples of surfactants used commonly in the preparation of hybrid nanofluids are Polyvinyl Pyrrolidone (PVP), oleic acid, Sodium Dodecyl Benzene Sulfonate (SDBS), Cetyl Trimethyl Ammonium Bromide (CTAB), and Sodium Laureth Sulfate (SLES). Surfactants are very useful in the preparation of hybrid nanofluids, but the ratio of the surfactant used must not affect the thermophysical properties of the hybrid nanofluid.

Hong Wei et al. [49] investigated the effect of different surfactants such as PVP (non-ionic), CTAB (cationic), SDS (anionic), SDBS (anionic), and Triton X-100 (non-ionic) on the stability of TiO_2 -GnPs suspended in Water/EG mixture. The authors concluded that the addition of CTAB at 1:10 ratios could produce a stable hybrid nanofluid. In another recent work by Nurul et al. [50] on the effect of surfactant on the dispersion stability of Al_2O_3 - SiO_2 /water hybrid nanofluid, the authors used SDS, CTAB, and PVP to stabilize the hybrid nanofluid. They mentioned that the addition of surfactant is crucial to disperse the nanoparticles homogeneously in water. The outcome of their study revealed that SDS showed promising results on the enhancement of nanofluid stability even though there is a slight increase in the viscosity because of the increment in solid-phase concentration.

The use of surfactant not only enhance the stability of hybrid nanofluid but also increases the heat transfer performance. This was investigated by Hormozi et al. [48] in their study on the effect of surfactants on the thermal performance of hybrid nanofluid in a helical coil heat exchanger. The authors used SDS and PVP surfactant in three different concentrations (0.1, 0.2 and 0.4 wt.%) to prepare Al_2O_3 -Ag water based hybrid nanofluid and tested the heat transfer performance using the heat exchanger. Their

experiments showed that the use of anionic SDS and PVP surfactant resulted in a maximum thermal performance enhancement of 16% and 6.425%, respectively, compared to the distilled water. However, the authors also mentioned that the use of SDS surfactant at a concentration of more than 0.1 % wt. resulted in a decrease in the Nusselt number due to the adverse effect on nanofluid stability.

The effect of surfactant on the stability of nanofluid can be observed visually by the sedimentation technique. Asadi et al. [51] prepared $Mg(OH)_2$ -water nanofluid by adding SDS, Oleic acid, and CTAB at a volume fraction of 0.02% and then the mixture was sonicated for 30 minutes. They kept the prepared sample for 30 days and observed the sedimentation of nanoparticles by visual inspection. Based on Figure 2.4, it is evident that the addition of surfactant shows a significant effect in improving the stability of the nanofluid because the nanofluid sample without surfactant shows a huge separation layer between the water and the $Mg(OH)_2$ nanoparticles. According to the author's visual sedimentation analysis for a period of 30 days, the nanofluid sample with the inclusion of CTAB exhibited the best stability compared to the other samples.



Figure 2.4 Stability of nanofluid from literature [52]

The effect of adding surfactant in nanofluid preparation enhances the stability and affects the thermal conductivity of nanofluid. In a study conducted by Xia et al.

[53] on the effect of surfactant on the stability and thermal conductivity of Al_2O_3 /water based nanofluid, the authors found that the use of non-ionic PVP surfactant shows better stability for nanofluid compared to ionic SDS surfactant. However, as they increase the surfactant ratio to a maximum of 4:1 ratio, the stability of nanofluids deteriorates, and the nanoparticles are completely deposited. The poor stability of nanofluid is due to the high concentration of surfactant. Also, the author reported a decrease in the thermal conductivity of nanofluid as the surfactant is added. This happens due to the longer alkyl chain length of PVP. Besides, another interesting fact observed in their study is that excessive use of dispersion agents raises the supersaturated adsorption and caused flocculation. Nevertheless, the use of surfactants in the preparation of hybrid nanofluid is unavoidable, even though the use of surfactants have some minor effect on the thermophysical properties of hybrid nanofluid.

2.4 Thermophysical properties of hybrid nanofluid

The performance of a working fluid in the convective heat transfer system is mainly dependent on the thermophysical properties of the fluid. Thermophysical properties are the parameters that describe the heat transfer phenomena based on Fourier law. For hybrid nanofluid, the four important thermophysical properties that determine the heat transfer performance are thermal conductivity, viscosity, specific heat capacity and density. This section will discuss the details of each thermophysical property and the instrument used to evaluate the properties and various parameters that affect the thermophysical properties. Various literature will be reviewed and discussed in these sections. The sequence of each property discussed is based on the property, which is highly researched, followed by the fewer discussed one based on the literature available.

2.4.1 Thermal conductivity

The thermal conductivity of a substance can be easily defined as the ability to conduct heat. The common symbol used to denote thermal conductivity is k , while the standard international unit is watts per meter kelvin (W/m.K). In general, the thermal conductivity of solid materials is higher than of liquid. This has been fundamental to the development of nanofluids. In the field of nanofluid, nanosized particles are suspended in a base fluid to enhance the overall thermal conductivity of the base fluid. A similar concept is used in the development of hybrid nanofluid where two different nanoparticles or nanocomposites are dispersed in water or water/EG mixture to enhance the thermal conductivity.

Thermal conductivity of hybrid nanofluid can be measured using the transient hot wire method based on the ASTM D5334 and IEEE 442-198 standards. One of the prominent instrument used by various researchers to measure the thermal conductivity of hybrid nanofluid is the KD2 Pro thermal analyzer [29], [54–58]. The device often used with a thermal bath to measure the thermal conductivity of nanofluid at various temperatures. Figure 2.5 shows the KD2 Pro thermal analyzer (Decagon devices inc.) used by Redhwan et al. [59] to measure the thermal conductivity of SiO₂ and TiO₂ Polyalkylene glycol (PAG) based nanofluid at temperatures between 300 – 370 K. A KD2 Pro thermal analyzer is a battery operated devices consist of a needle sensor that measures the thermal conductivity. According to Hamid et al. [29], who used the same device to measure the thermal conductivity of hybrid nanofluid, the sensors must always be calibrated first at room temperature using standard glycerine (0.285 W/mK) before the actual measurement. This ensures that the reading of the sensor has high accuracy and minimal deviation ($< \pm 5\%$).



Figure 2.5 KD2 Pro thermal analyzer [59]

There are various factors that affect the thermal conductivity of hybrid nanofluid, as illustrated in Figure 2.6. Among all the factors, nanoparticle concentration and nanofluid temperature are the most crucial factors that alter the thermal conductivity of hybrid nanofluid. Most of the researchers working in the field of hybrid nanofluid examined the enhancement of thermal conductivity of hybrid nanofluid by varying the nanoparticle volume concentration and the nanofluid temperature.

Thermal conductivity of nanofluid increases linearly with an increase in particle volume concentration [61]. Roozbeh et al. [62] prepared water based graphene oxide(GO)/Al₂O₃ hybrid nanofluid at a volume concentration between 0.1 – 1.0% and examined the thermal conductivity at temperatures between 25 – 50°C. Their results showed that the thermal conductivity of hybrid nanofluid increases with an increase in volume concentration and temperature. The authors reported a maximum thermal conductivity enhancement of 33.9% for the GO/Al₂O₃ hybrid nanofluid at 1% volume concentration and 50°C. They mentioned that the increment of thermal conductivity was attributed by the Brownian motion and increase in the kinetic energy of the molecules.

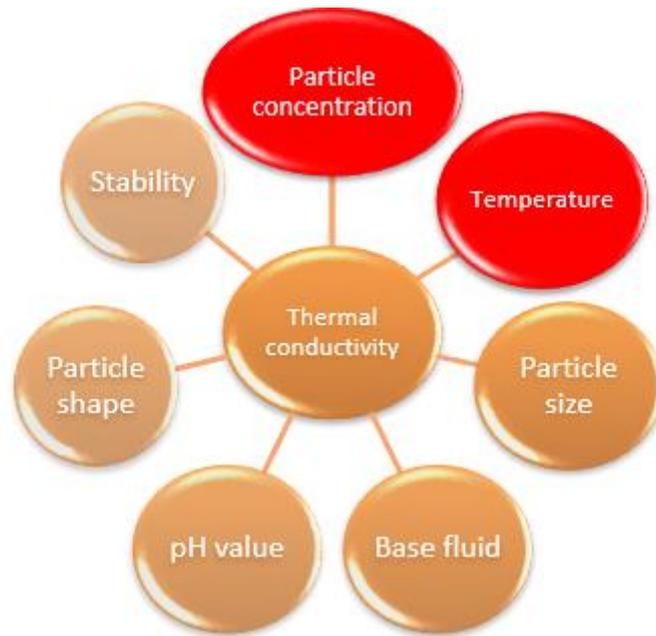


Figure 2.6 Factors affecting thermal conductivity of hybrid nanofluid [60]

Hemmat et al. [61] studied the effect of Ag-MgO nanoparticle volume concentrations on the thermal conductivity of Ag-MgO/water hybrid nanofluid by using transient hot wire method. They maintained the ratio of Ag and MgO nanoparticles at 50:50 and varied the volume concentration of Ag-MgO nanoparticles in water from 0 – 2%. The experimental results on their thermal conductivity values showed that the increase in nanoparticle volume fraction significantly enhanced the thermal conductivity of hybrid nanofluid.

Harandi et al. [62] synthesized MWCNTs-Fe₃O₄/EG hybrid nanofluid and experimented the effect of both volume concentration (0.1, 0.25, 0.45, 0.8, 1.25, 1.8, and 2.3%) and temperatures (30°C, 40°C and 50°C) on the thermal conductivity. A KD2 Pro thermal property analyser with the KS-1 probe sensor was used in their study to measure the thermal conductivity. They reported a maximum thermal conductivity enhancement of 30% for hybrid nanofluid with a volume concentration of 2.3% and nanofluid temperature of 50°C. In addition, their study concluded that the augmentation of thermal conductivity ratio with higher nanoparticle volume fraction was more

significant at high temperatures compared to lower temperatures. This is due to the increase in thermal conductivity caused by the distinctive arrangement of nanoparticles in the base fluid, which increases the contact area for conduction between the molecules inducing higher rates of heat transfer during the collision by the Brownian motion.

Sahid et al. [63] conducted an experimental study on the properties of TiO₂-ZnO/water-EG hybrid nanofluid prepared at volume ratios of 70:30, 80:20, and 90:10. The hybrid nanofluid prepared with 90% TiO₂ and 10% ZnO found to be the most stable compared to other ratios. The authors obtained results where the thermal conductivity of hybrid nanofluid increased with an increase in TiO₂ nanoparticle proportion in the base fluid. They observed the maximum thermal conductivity of TiO₂-ZnO/water-EG hybrid nanofluid at 70°C for a volume ratio of 90:10. The experimental results reported by the authors clearly show a potential influence of TiO₂ nanoparticles in improving the thermal conductivity of hybrid nanofluid.

Hamid et al. [55] tried to improve the thermal conductivity of TiO₂-SiO₂ suspended in water/EG (60:40) mixture by varying the nanoparticle volume concentration from 0.5 to 3%. They measured the thermal conductivity using KD2 Pro thermal analyzer while the nanofluid temperature is varied using a thermal bath. The authors observed that the TiO₂-SiO₂ hybrid nanofluid at all concentrations exhibited higher thermal conductivity than the base fluid. Besides, the highest and lowest thermal conductivity enhancement was noticed to be approximately 3.9% and 22.1%, respectively. The outcome of their study on thermal conductivity is shown in Figure 2.7.

Similar researchers experimented with the thermal conductivity of TiO₂-SiO₂/water-EG based nanofluid at mixture ratios of 20:80, 40:60, 50:50, 60:40, 80:20 and constant volume concentration of 1%. They revealed that the hybrid nanofluid with