

Improving the quality of heating oil with zeolite NaA

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**A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering)
Department of Chemical Engineering, School of Engineering,
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การปรับปรุงคุณภาพของน้ำมันถ่ายเทความร้อนด้วยซีโอไลต์เอ



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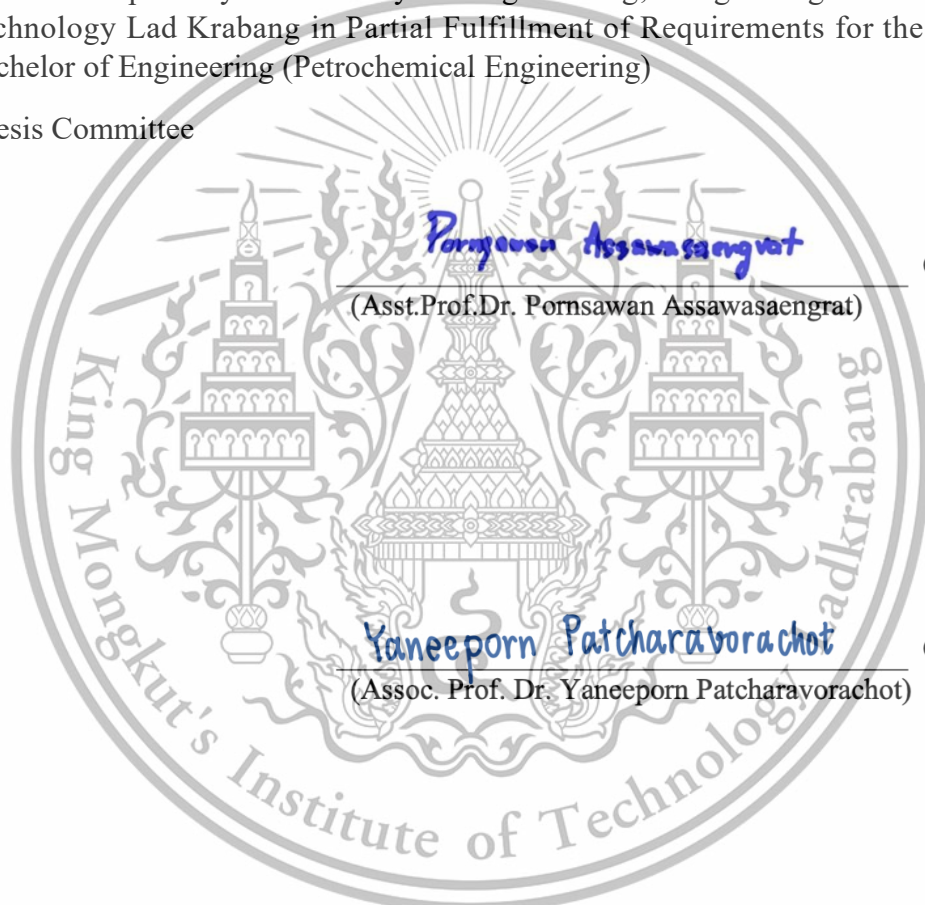
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Abstract

This research aimed to investigate improving the quality of heating oil with zeolite NaA. Palm oil was selected for heating oil due to its high flash point and environmentally friendly compared to synthetic and mineral oil. The effect of the concentration of zeolite NaA suspended in palm oil on the specific heat capacity (C_p), viscosity (μ), viscosity index (VI), thermogravimetric analysis (TGA), and density (ρ) of palm oil was investigated. The zeolite NaA was synthesized by crystallization technique, and X-ray diffraction analysis was performed to confirm zeolite NaA crystallinity. The size of zeolite NaA was measured using a particle size analyzer. The synthesized zeolite NaA size was 4000 nm after the grinding process for 180 min yielded an average zeolite size of 632 nm. Zeolite NaA size 632 was added to palm oil at concentrations of 0.25, 0.5, 0.75, and 1 wt%. The viscosity of palm oil suspended with zeolite NaA at 40 °C was measured as 39.70, 40.02, 40.06, 40.68, and 41.31 cSt, respectively. The viscosity measured at 100 °C was 6.44, 8.42, 8.44, 8.46, and 8.47 cSt, respectively. The viscosity index was highest when mixed with 0.5 wt% of zeolite NaA, which was 195. The density of palm oil slightly increased with increasing zeolite NaA concentrations. The specific heat capacity of palm oil increased when zeolite NaA was added. It has been shown that zeolite NaA allows palm oil to store heat energy better than pure palm oil, enabling it to release and absorb more heat during heat transfer. Thermogravimetric analysis, when adding zeolite NaA to palm oil, showed that palm oil could endure more heat and has a long service life.

เรื่อง	การปรับปรุงคุณภาพของน้ำมันถ่ายเทความร้อนด้วยซีโอไลต์เอ	
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บทคัดย่อ

งานวิจัยนี้ศึกษาการปรับปรุงคุณภาพน้ำมันถ่ายเทความร้อนด้วยซีโอไลต์เอ ศึกษาน้ำมันปาล์มเป็นน้ำมันถ่ายเทความร้อนเนื่องจากมีค่าจุดวาบไฟที่สูงและเป็นมิตรกับสิ่งแวดล้อมเมื่อเปรียบเทียบกับน้ำมันสังเคราะห์และน้ำมันแร่ โดยศึกษาผลของความเข้มข้นของซีโอไลต์เอที่แขวนลอยในน้ำมันปาล์มซึ่งส่งผลต่อค่าความจุความร้อนจำเพาะ ค่าการเปลี่ยนแปลงน้ำหนักของสารโดยอาศัยคุณสมบัติทางความร้อน (TGA) ค่าความหนืด ค่าดัชนีความหนืด และค่าความหนาแน่น โดยทำการสังเคราะห์ซีโอไลต์เอด้วยเทคนิคการตกผลึก และวิเคราะห์ความเป็นผลึกของซีโอไลต์เอด้วยเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ วิเคราะห์ขนาดของซีโอไลต์เอด้วยเครื่องวิเคราะห์ขนาดอนุภาค พบว่าขนาดของซีโอไลต์เอที่สังเคราะห์ได้ 4000 นาโนเมตร เมื่อนำไปผ่านการบดที่ 180 นาที ได้ซีโอไลต์มีขนาดเฉลี่ย 632 นาโนเมตร ผสมซีโอไลต์เอขนาด 632 นาโนเมตร ลงในน้ำมันปาล์มที่ความเข้มข้น 0.25, 0.5, 0.75 และ 1 wt% วัดค่าความหนืดของน้ำมันปาล์มที่แขวนลอยด้วยซีโอไลต์เอที่อุณหภูมิ 40 องศาเซลเซียส มีค่าเท่ากับ 39.70, 40.02, 40.06, 40.68 และ 41.31 cSt ตามลำดับ วัดค่าความหนืดที่อุณหภูมิ 100 องศาเซลเซียส มีค่าเท่ากับ 6.44, 8.42, 8.44, 8.46 และ 8.47 cSt ตามลำดับ และที่ความเข้มข้นของซีโอไลต์เอ 1 wt% มีค่าความหนืดสูงสุด โดยค่าความหนืดของน้ำมันปาล์มเพิ่มขึ้นเมื่อความเข้มข้นของซีโอไลต์เอเพิ่มขึ้น และความหนืดของน้ำมันปาล์มลดลงเมื่ออุณหภูมิเพิ่มขึ้น ค่าดัชนีความหนืดมีค่ามากที่สุดเมื่อผสมซีโอไลต์เอที่ความเข้มข้น 0.5 wt% ซึ่งมีค่าเท่ากับ 195 ส่วนความหนาแน่นของน้ำมันปาล์มเพิ่มขึ้นเล็กน้อยเมื่อความเข้มข้นของซีโอไลต์เอเพิ่มขึ้น ค่าความจุความร้อนจำเพาะของน้ำมันปาล์มเพิ่มขึ้นเมื่อเติมซีโอไลต์เอ แสดงให้เห็นว่าน้ำมันปาล์มสามารถรับกักเก็บพลังงานความร้อนได้ดีขึ้นซึ่งทำให้น้ำมันสามารถปลดปล่อยและดูดซับความร้อนได้มากขึ้นในระหว่างกระบวนการถ่ายเทความร้อน การวิเคราะห์การเปลี่ยนแปลงน้ำหนักของสารโดยอาศัยคุณสมบัติทางความร้อนเมื่อเติมซีโอไลต์เอในน้ำมันปาล์มพบว่าน้ำมันปาล์มสามารถทนความร้อนได้มากขึ้นและสามารถใช้งานได้นานขึ้น

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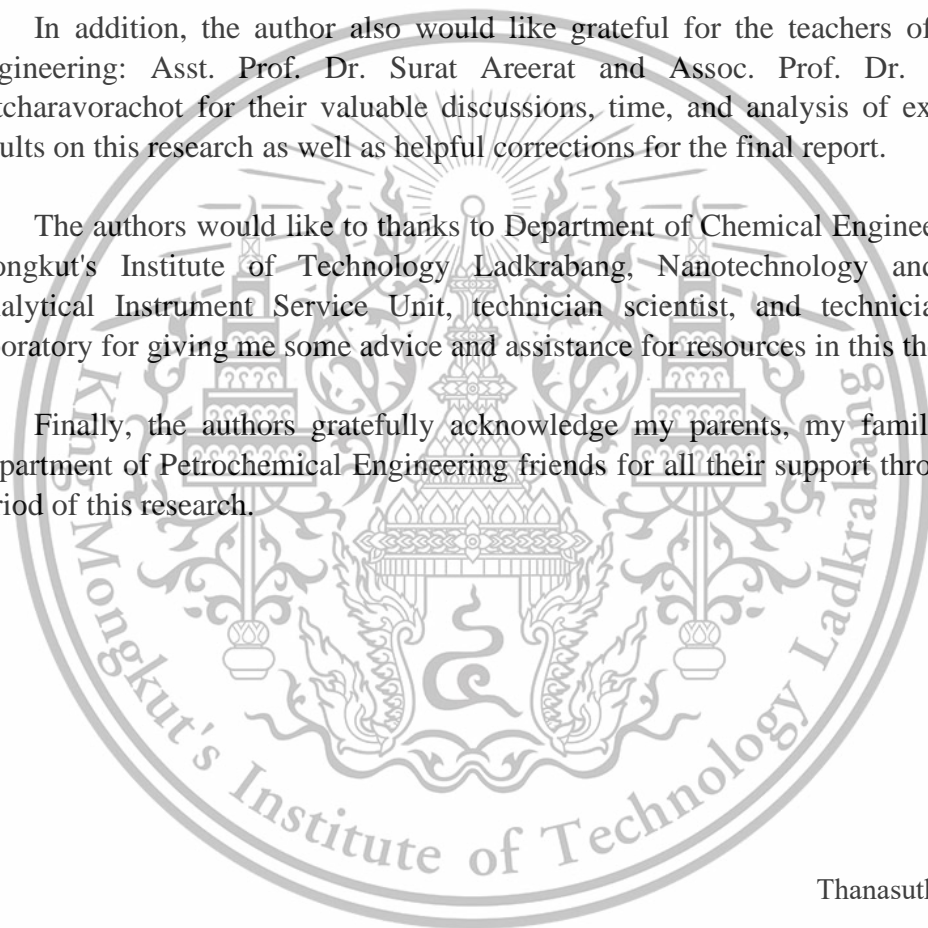
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CONTENT

ABSTRACT	I
ACKNOWLEDGEMENTS	III
CONTENT	IV
LIST OF FIGURES	V
LIST OF TABLES	VI
CHAPTER 1 INTRODUCTION	1
1.1 Background of the research and its significant	1
1.2 Objective	2
1.3 Scope of work	2
1.4 Expect output	2
CHAPTER 2 LITERATURE REVIEW	3
2.1 Heat transfer oil.....	3
2.2 Nanofluid	4
2.3 Application of nanofluid	14
CHAPTER 3 MATERIAL AND METHODS	15
3.1 Material.....	15
3.2 Equipment.....	15
3.3 Method	16
CHAPTER 4 RESULTS AND DISCUSSION	18
4.1 Characteristic of Zeolite NaA particle	18
4.2 Kinematic viscosity (μ) and viscosity index of nanofluid	19
4.3 Density of nanofluid (ρ)	21
4.4 Specific Heat capacity (c_p).....	22
CHAPTER 5 CONCLUSION	25
REFERENCE	26
APPENDIX	28
APPENDIX A	29
APPENDIX B	32
BIBLIOGRAPHY	34

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LIST OF FIGURES

	Pages
Figure 2-1. Schematic diagram of the apparatus for the VEROS method.....	4
Figure 2-2. Two-step method for nanofluids production.	5
Figure 2-3. Thermal conductivity of nanomaterials (a) metallic, (b) carbon-based particle, (c) metal oxides and (d) base fluid for synthesis nanofluids. ^[1]	8
Figure 2-4. Parameters effecting dynamic viscosity of nanofluid.	10
Figure 3-1. Image of the setup of the experiment equipment for reflux.....	16
Figure 4-1. XRD patterns of the synthesized zeolite NaA sample.	18
Figure 4-2. The influence of griding time on size of zeolite NaA particle.	19
Figure 4-3. Comparison of kinematic viscosity at 40 °C and 100 °C.	20
Figure 4-4. Comparison of viscosity index.....	21
Figure 4-5. Density of nanofluid at different concentration of nanoparticles.....	21
Figure 4-6. The specific heat capacity of nanofluid at different concentration of nanoparticles.	22
Figure 4-7. Thermogravimetric analysis (TGA) of nanofluid at different concentration of nanoparticles with respect to temperature.	23
Figure 4-8. Derivative thermogravimetric analysis (DTGA) of nanofluid at different concentration of nanoparticles with respect to a) Temperature b) Time.....	24
Figure A-1. Dissolve 13.89 g of sodium metasilicate pentahydrate with 37.17 g of deionized water using a magnetic stir to the homogenous liquid mixture.....	29
Figure A-2. Dissolve 3.4 g of sodium hydroxide in 34 g of deionized water using a magnetic stir to clear liquid.....	29
Figure A-3. Add 6 g of sodium aluminate to the sodium hydroxide solution.....	29
Figure A-4. Gradually drop sodium metasilicate pentahydrate solution into sodium aluminate solution and mix the solution for 1 hour using a magnetic stirrer until the solution is in gel form.	30
Figure A-5. Put the solution into round bottom flask and reflux at 110°C for 1 hr.	30
Figure A-6. Separate obtained zeolite NaA and solution using Buchner repeat this step until pH < 9. After separation, put Zeolite NaA into oven at 110 °C for 24 hr.....	31
Figure A-7. Zeolite NaA disperse into palm oil base fluid at difference particle loading (0.25%, 0.5%, 0.75% and 1.00 wt%) by stir in magnetic bar. After that, put into sonicate bath to stability zeolite NaA.	31
Figure B-1. Comparison of griding time on size of zeolite NaA particle a) 30 min b) 1 hr c) 3 hr.	32
Figure C-1. Settling characteristic a) 30 min b) 1 hr. c) 3 hr. d) 1 day and e) 3 Days. 33	33

LIST OF TABLES

	Pages
Table 2-1 Summary effect of heat transfer oil degradation	4
Table 2-2. Summary of reviewed experimental studies on thermal-physical properties and viscosity of oil-based nanofluid.	11



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CHAPTER 1

INTRODUCTION

1.1 Background of the research and its significant

Nowadays, thermal oils are widely used as industrial heat transfer fluids in many process applications such as heat exchangers, cooling system drilling, lubricating process, and solar application. Most commonly used thermal fluids should be suitable for various temperatures. However, mineral or synthetic oils are petroleum-based and tend to cause resource depletion. The emergent concern to reduce the use of petroleum derivative mineral oil has led to the research for eco-friendly heat transfer fluid due to the mineral oil-based heat transfer fluid have the lowest biodegradation rate, a high potential for bio-accumulation, toxicity to all organisms and synthetic organic fluids and mineral oils are considered to be very expensive^[2]. Therefore, the synthesis of heat transfer fluid from vegetable oil is an alternative because there is a renewable source, environmentally friendly, less toxic, and economical in reducing waste treatment costs due to its inherently higher biodegradability and high flash point^[3].

Ramasamy et al. (2021)^[4] investigated palm kernel oil had heat transfer potential when compared with Therminol 66 was classified as synthesis oil. Palm kernel oil properties are closely matched with synthetic oil and offer the following properties: thermal conductivity (k) $0.142 \text{ Wm}^{-1} \text{ K}^{-1}$, the dynamic viscosity (μ) of 5.2 mPa s , specific heat (C_p) $2.4 \text{ kJ kg}^{-1} \text{ K}^{-1}$, and density (ρ) 852 kg m^{-3} . Therefore, palm oil is an alternative to heat transfer fluid. The exciting issue of palm oil is thermal stability lower than heat transfer oil commercial grade.

Many research groups have worked on nanoparticle suspending in oil as a based fluid to enhance thermal stability. For example, Sunil et al. (2019)^[5] attempted to improve the thermal stability of rice bran oil by dispersing CaO nanoparticles. The result shows that rice bran oil's thermal stability is considerably enhanced by 18.2% and 25% due to adding 0.25 wt% and 0.50 wt% of CaO-nanofluids, respectively. Furthermore, Ilyas et al. (2017)^[6] investigated the dispersion of multi-wall carbon nanotubes (MWCNTs) in thermal oil. The result shows that the nanofluids with high concentrations of nanotubes can operate at higher temperatures than pure thermal oil.

The stability of Nanofluid is a primary issue concern due to the decreased efficiency of Nanofluid in engineering applications by studies on the interaction of nanomaterial, which is called agglomeration among particles. Ilyas et al. (2017)^[7] revealed that different techniques were applied to stabilize nanoparticles in liquids, such as ultrasonication, high-pressure homogenizer, and surfactant addition. Surfactant addition is the most simple and economical method of preparing stable nanofluids. Javed et al. (2018)^[8] was observe CuO nanoparticle dispersion in palm oil. The result shows that oleic acid groups present in the waste palm oil are role surfactants that will stabilize the CuO nanofluid by coating on the surface of CuO nanoparticles. The oleic acid groups on the surface of CuO nanoparticles will reduce the attractive forces between the particles and thereby increase repulsive forces, stabilizing particles for extended periods. Assadian et al. (2018)^[9] found that CuO NPs have shown high cytotoxicity and can cause DNA damage, induction of oxidative stress, and cell death. Therefore, we chose to study zeolite NaA as a nanoparticle dispersed in palm oil as a based fluid because zeolite NaA is non-toxic, safe for humans, and the production and

processing of zeolite NaA can be relatively inexpensive compared to other types of nanoparticles. Lieut et al. (2015)^[10] and Esmaeili et al. (2016)^[11] investigated silica that can be prepared from biomass such as rice husk and *Hordeum Vulgare* ash, considered to be biomass utilization.

Palm oil is used as a based fluid due to the friendly environment, highly stable, and oleic acid group in palm oil coat on the surface of nanoparticles against aggregation of nanoparticles. In this study, we have synthesized zeolite NaA nanoparticles using the crystallization technique and dispersed them in palm oil using a two-step method by varying the concentration of zeolite NaA to measure thermal stability and properties of palm oil, including viscosity (μ), viscosity index, density (ρ) and specific heat capacity (C_p). However, the synthesis of zeolite nanofluid using palm oil as a based fluid for thermal-physical properties studies has yet to be reported in the literature. Therefore, our research focuses on improving the quality of heating oil with zeolite NaA.

1.2 Objective

To study improvement the quality of heating oil with zeolite NaA.

1.3 Scope of work

1.3.1 Synthetic zeolite NaA from sodium metasilicate and sodium aluminum

1.3.2 Vary different particle concentrations 0.25%, 0.5%, 0.75% and 1.00 wt% that affect heat transfer properties.

1.3.3 Study parameter about characteristics of heat transfer oil such as viscosity (μ), specific heat capacity (C_p), thermogravimetric analysis (TGA), viscosity index (VI) and density (ρ).

1.4 Expect output

Palm oil is a potential heating oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Heat transfer oil

Heat transfer oil is a liquid that transfers heat by transporting and storing thermal energy and heating or cooling on another side of a process. Type of heat transfer oil has two kinds: mineral oil and synthetic oil. Properties of Heat transfer oil include low viscosity, high viscosity index, high thermal stability, antioxidation, common corrosion, and high heat transfer properties.

2.1.1 Degradation of heat transfer oil

2.1.1.1 Oxidation

Oxidation is oxygen reaction with oil from sludge. Sludge typically forms when the oil breaks down due to oxidation, forming a thick, sticky substance. This substance can accumulate in the heating system, increase viscosity, increase the power required to pump, and increase the total number of acids (TAN) that increase corrosion equipment. After oxidation, the color of heat transfer oil turns yellow until brown when increasing sludge. To prevent oxidation by adding antioxidants and regularly replacing the oil to prevent it from breaking down due to age.

2.1.1.2 Fouling

Fouling can occur when contaminants or impurities accumulate on the surfaces of the system. These contaminants can come from various sources, including the environment, heating system, or oil. They can include substances such as dirt, dust, and other particulates and byproducts formed when the oil breaks down due to oxidation or other factors. The fouling substances can reduce the oil's ability to flow and mix, making heat exchange more difficult.

2.1.1.3 Thermal cracking

Thermal cracking is the decomposition of a product at high temperature. The two degradation products are "low boilers" and "high boilers. The low boiler is the product of decay which lowers molecules' weight to the original molecule weight, decreasing the thermal's a flash point and viscosity. The high boiler is a product of decomposition in which molecules are polymerized, increasing the molecule's weight and increasing density. The thermal cracking prevented heat transfer oil, and it is essential to use an oil with high thermal stability and operate the system within the recommended temperature range. Summary effect of heat transfer oil degradation are reviewed in Table 2-1.

1. A cylinder containing a heat transfer fluid such as water or ethylene glycol, or oil is rotated so that a thin film of the liquid is constantly being transported over the top of the chamber.
2. A piece of the metallic material as the source of the nanoparticle is evaporated by heating on a crucible.
3. Evaporated particles contact the fluid overhead and condense as nanoparticles.
4. The fluid is cooled at the base of the chamber to prevent any unwanted evaporation of the liquid.

The advantage of this method is that an accumulation of nanoparticles in a base fluid is minimized, leading to increased fluid stability. It has not used surfactant in any prepared nanofluid, but the limitation of the one-step method is suitable for only a low vapor pressure fluid such as ethylene glycol and water-based fluid. Furthermore, the one-step process is unsuitable for vegetable oil as a base fluid because vegetable oils like coconut and palm oil are high in saturated fatty acids. In Figure 2-2 indicated nanofluids are prepared by two step methods. Zhou et al.(2009)^[14] discover the two-step method is preparing the nanofluid, in which nanoparticles are first, followed by a second step in dispersing nanoparticles in the base fluid. Then the suspensions were homogenized by magnetic stir. It is necessary to use ultrasonic or add surfactants to the liquids to reduce the effect of nanoparticle accumulation in the base fluid.

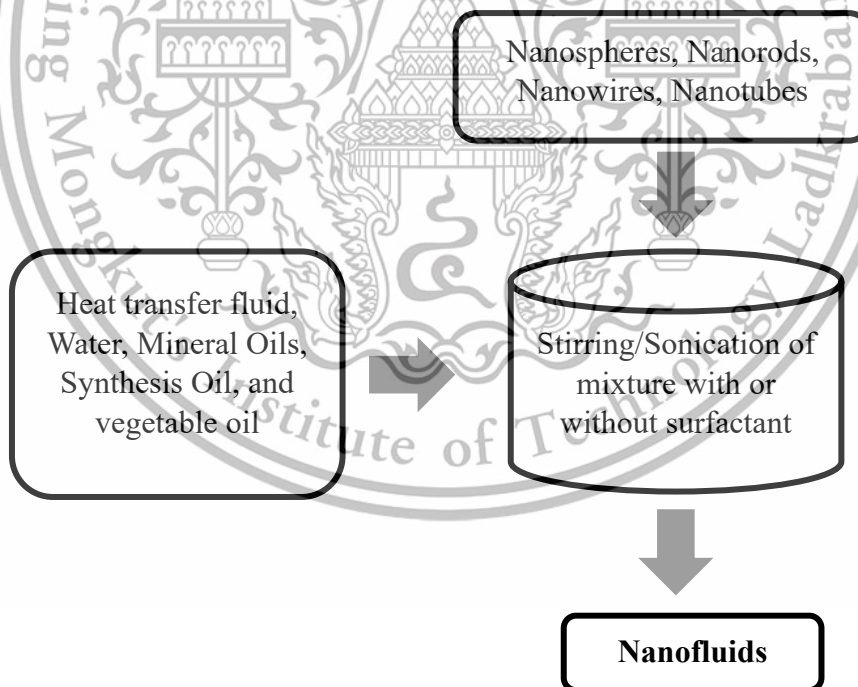


Figure 2-2. Two-step method for nanofluids production.

The standard nanofluid based fluid are water, ethylene glycol, and oil. Water-based fluid and ethylene glycol are also suitable for heat transfer, but the limitation is the narrow range of temperature and the need to pressurize to avoid evaporation. Oil-based fluids have a much broader operational temperature application, and the advantage of oil-based is high stability against thermal degradation. Nanofluid is helpful in many applications such as hybrid-powered engines, engine cooling/vehicle thermal management, domestic refrigerators, chiller, heat exchangers and grinding machining, and boiler flue gas temperature reduction.

2.2.2 Stability of nanofluid

The stability of nanofluid is the most difficult to widespread application of nanofluid for Industrial purposes. The stability of nanofluids is defined as the ability to resist permanent deformation, i.e., the resultant of attraction and repulsion forces (between particle and particle and particle–fluid interface) over a certain period. The effectiveness of nanofluids highly depends on the suspension stability of nanoparticles dispersed in the base fluid. Nanoparticles tend to destabilize and form aggregation caused by various forces, for instance, Van der Waal attraction force, magnetic force, electrostatic force, bouney and gravitational force. These forces act against the stability of the colloidal suspension and cause the formation of large clusters leading to the deterioration of nanofluid performance. The predisposition of nanoparticles to form groups causes nanofluid suspension destabilization. The tendency of accumulation is attributed to the higher surface area and surface activity of nanofluids with the addition of nanoparticles. Therefore, the such propensity to agglomeration must be prevented to prepare stable nanofluid maintaining stable dispersion of N.P.s in the base fluid. Several factors affect the stability of nanofluid suspensions, such as the dielectric constant of base fluids, the concentration of nanoparticles, pH value, particle shape and size, temperature, zeta potential, and stabilizing additive. The degradation of nanofluid suspension stability due to nanoparticle dispersion is a chemical phenomenon, i.e., adding more solid particles in the base fluid lowers the suspension stability. Therefore, techniques are necessary to improve the dispersion of nanofluid. Stabilization of nanofluid can be obtained by physical and chemical methods.

2.2.2.1 Physical stabilization

Different physical methods are commonly utilized to stabilize N.F. suspensions, such as ultrasonic vibration, magnetic stirring, and homogenization are widely employed for homogenous dispersion of colloidal mixture. Ultrasonication of colloidal suspensions provides homogenous distribution of nanoparticles within the variety and reduces the average cluster size, which remarkably influences the nanoparticle's heat transfer properties.

Asadi et al. (2019) ^[15] reviewed the remarkable impact of ultrasonication treatment on colloidal dispersion and heat transfer characteristics of N.F.s. In addition, they reported a notable effect of variation in ultrasonication time and power on the effective dispersion of nanoparticles into base fluids. However, beyond a specific limit of the ultrasonication period, dispersion characteristics tend to deteriorate significantly. On the other hand, Chen and Guo (2011) ^[16] revealed that the average particle size of N.P.s remains constant after an optimum period of effective ultrasonic vibration in the colloidal suspension.

2.2.2.2 Chemical stabilization

Chemical techniques for stabilization, i.e., electrostatic, steric, or electro-steric strategies, include surface functionalization, surfactant inclusion, pH control, polymer addition, and acid treatment. Electrostatic stabilization provides for the expansion of ionic surfactants to the nanofluid. Several categories of surfactants, such as cationic, anionic, non-ionic, and amphoteric surfactants, are employed in nanofluid to stabilize the suspension.

Paramashivaiah et al. (2017)^[17] that homogeneous and stable graphene nanofluid of different concentrations were successfully prepared by a two-step technique with the aid of an SDS dispersant. The result showed graphene to a surfactant ratio of 1:4 gives the most stable dispersion in Simarouba oil. Finally, Ilyas et al. investigated the stability of thermal oil base nanofluid prepared by dispersed functionalized Al_2O_3 . They observed nanofluid with functionalized nanoparticles increased from a few hours to at least one month, which is longer than the nanofluid with non-functionalized nanoparticles.

2.2.3 Thermophysical of nanofluid

Nanofluid properties differ from base fluids, including thermophysical properties such as specific heat, density, viscosity, and thermal conductivity. Dispersion of nanoparticles into the based fluid changes the thermophysical properties of the based fluid.

2.2.3.1 Thermal conductivity

The thermal conductivity of the nanofluid is the most important in terms of the heat transfer performance of the nanofluid in thermal energy conversion. The thermal conductivity of nanofluid is better than base fluid due to the more excellent thermal conductivity of solid particles than liquid (demonstrated in Figure 2-3). However, several parameters affect the enhancement of the thermal conductivity of nanofluid using different nanomaterials and based fluids. For example, enhancing the thermal conductivity of nanofluid Colloidal Suspension nanomaterial size in the base fluid can improve heat transfer performance. Xuan and Li (2018)^[18] investigated the main reasons may be followed as:

1. The suspended nanoparticles increase the surface area for heat transfer and the heat capacity of the fluid.
2. The suspended nanoparticles increase the effective thermal conductivity of the fluid.
3. The interaction and collision among particles, fluid, and the flow passage of the surface are intensified.
4. The mixing fluctuation and turbulence of the fluid are intensified.
5. The dispersion of nanoparticles flattens the transverse temperature gradient of the fluid.

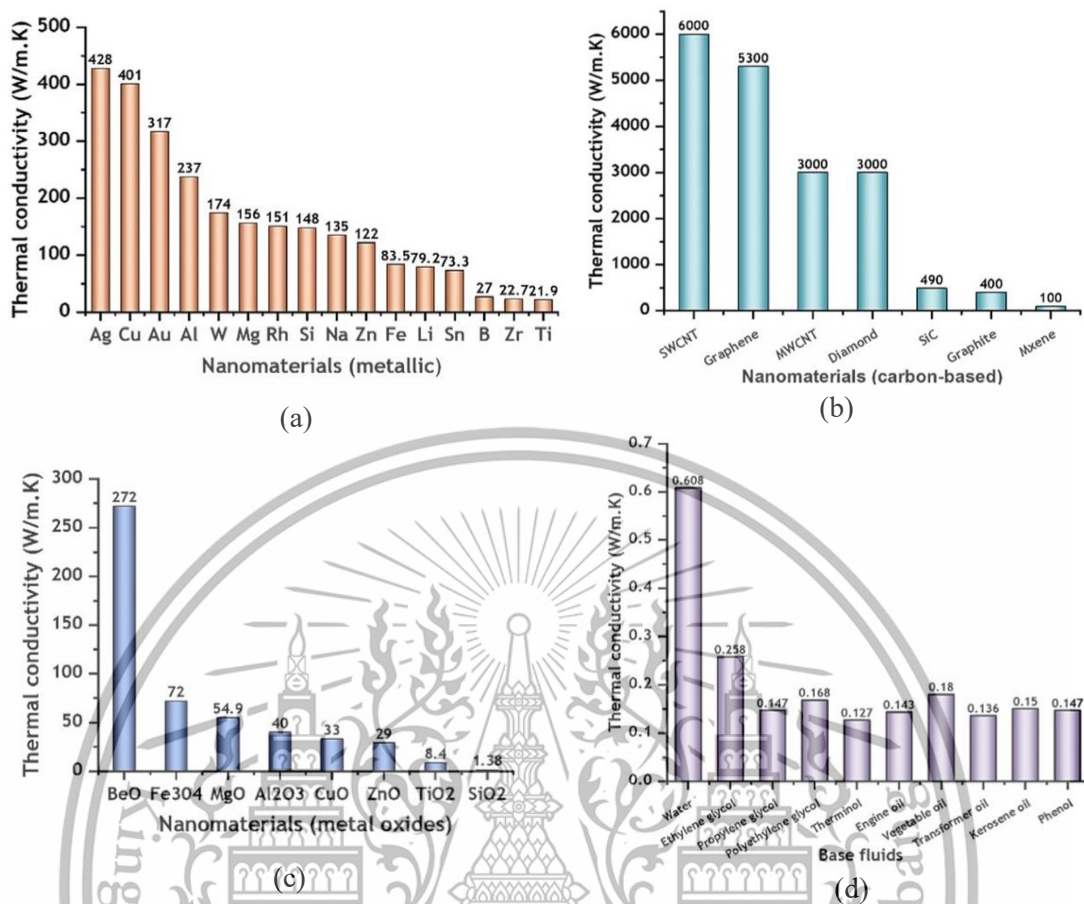


Figure 2-3. Thermal conductivity of nanomaterials (a) metallic, (b) carbon-based particle, (c) metal oxides and (d) base fluid for synthesis nanofluids.^[1]

The research identifies the effecting factor of thermal conductivity as the preparation method, size shape of nanomaterials, concentration, the thermal conductivity of the base fluid, stability of the dispersion, pH of the mixture, and operating temperature are impacting the thermal conductivity and heat transfer performance of nanofluids. The association between nanomaterials' concentration and nanofluid's thermal conductivity is well established due to the thermal conductivity of nanofluid increasing with the addition of concentration of nanomaterials up to an optimum level. Asadi et al. (2018)^[19] studied the effect of nanoparticle particle concentration and temperature on the thermal conductivity of Al₂O₃-MWCNT/thermal oil nanofluid. They found that thermal conductivity increases with increasing particle concentration and rising temperature. Colangelo et al. (2016)^[20] observed no impact of several oleic acid-based surfactants on the thermal conductivity of Therminol-66/Al₂O₃ nanofluid.

On the contrary, Timofeeva et al. (2011)^[21] noticed that adding BAC as a dispersant into Therminol-66/SiO₂ nanofluid the thermal conductivity increases until an optimum surfactant to nanoparticle ratio of 1:1 and further addition does not impact to thermal conductivity. A similar impact of surfactant on the stability of nanofluid was observed by Tiwari et al. (2020)^[22]. Qing et al. (2017)^[23] found higher thermal conductivity in the pH range of mineral oil/graphene nanofluid is 9-10, and smaller nanoparticles have higher conductivity.

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2.2.3.2 Specific Heat capacity

Specific heat capacity is one of the most critical thermos-physical properties to characterize the thermal heat storage of various thermos-fluids. While the thermal conductivity of nanofluid increases with the inclusion of nanoparticles, specific heat capacity (C_p) can increase or decrease with dispersed solid particles. This trend of respective heat capacity depends on nanomaterials type, the concentration of nanomaterials, based fluid, and temperature. This can limit the usability of nanofluids on thermal systems depending on the cost and process of heat transfer. Singh et al. (2020)^[24] evaluated C_p of Therminol-66/MWCNT (0.05-0.5) wt% at a wide range of temperatures from 25 to 300 °C. Specific heat capacity increases by adding nanoparticles. The results contributed to forming a semi-solid layer on the surface of nanoparticles and an increase in thermal conductivity, allowing nanofluid to store energy faster than based fluid. On the other hand, Ilyas et al. (2017) evaluated the C_p of Thermal oil/ Al_2O_3 (0.5-3 wt%) at 40-160 °C. The result showed a significant drop in C_p value when adding nanomaterial. Gil-Font et al. (2020)^[25] analyzed the C_p of Therminol-66/Sn nanoparticles using a cationic surfactant. C_p value slightly decreased by 2.5% due to the addition of nanoparticles, and surfactant also harmed the heat capacity of fluids. Sardinia et al. (2012)^[26] experimentally investigated the specific heat capacities of CuO-base oil nanofluids with a volume concentration of nanoparticles of 0.2–2%. They found that nanofluids showed a less specific heat capacity than that of base fluid, and it decreases with the increase in nanofluids concentration. Similar trends were found in the literature of Ilyas, Pendyala, & Narahari (2017); Teng & Hung (2014)^[6, 27]

2.2.3.3 Density

Nanofluids' density is a crucial factor in investigating heat transfer characteristics. A slight increase in the thickness of the fluid can cause adverse effects on the natural and forced convection heat transfer process. These processes mainly depend on the buoyancy-driven forces and pressure drop during flow. Ilyas, Pendyala, & Narahari (2017)^[6] investigate the influence of volume concentration of nanoparticles of MWCNT in thermal oil. The result shows that the density of MWCNT-thermal oil-based nanofluids increases with an increase in nanomaterial concentration and decreases when the temperature is raised. Similar trends were found in the literature of Teng & Hung (2014)^[27].

2.2.3.4 Viscosity

The resistance force to deformation on fluids in the opposite flow direction is defined as dynamic viscosity. It is one of the critical properties of nanofluid, which significantly affects convective heat transfer performance during the implementation of thermal energy conversion systems due to its direct association to pressure drop and pumping power. The viscosity of the nanofluid is affected by several vital parameters depicted in Figure 2-4. Various research groups used different types of oil base fluids and nanoparticles to study the change in the thermophysical properties and viscosity of nanofluid are reviewed in Table 2-2.

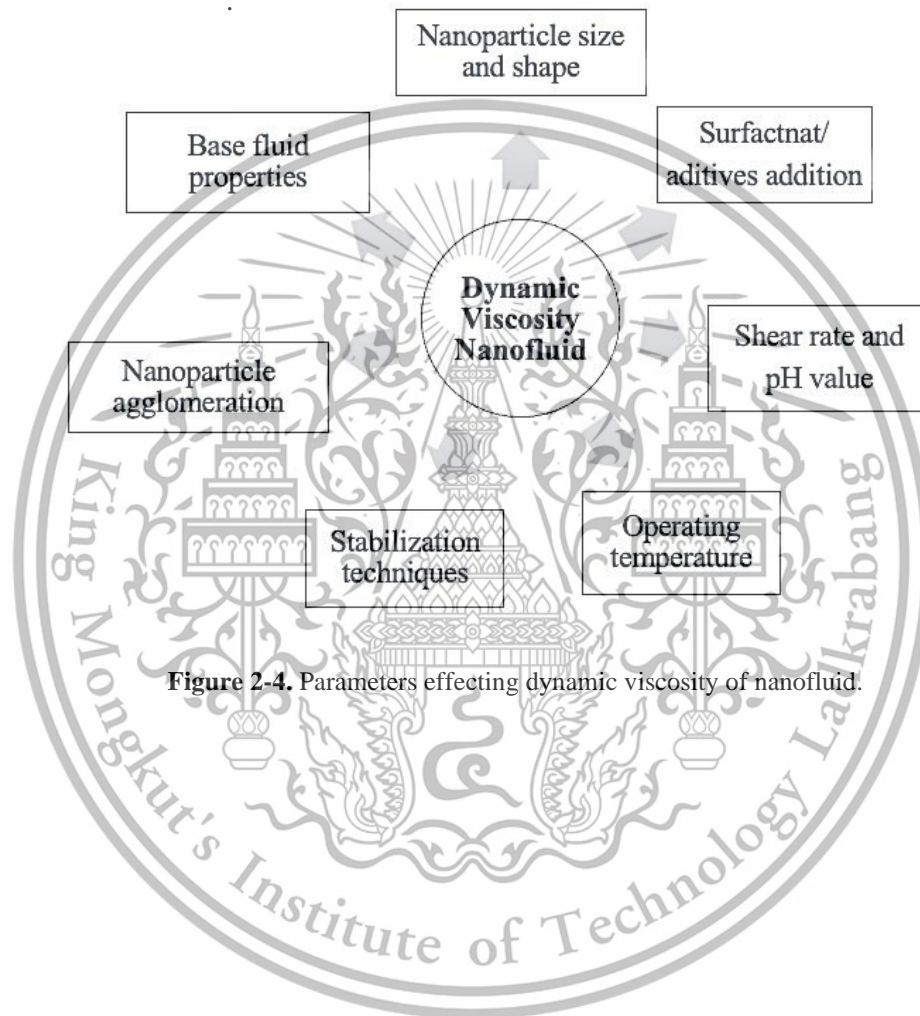


Figure 2-4. Parameters effecting dynamic viscosity of nanofluid.

Table 2-2. Summary of reviewed experimental studies on thermal-physical properties and viscosity of oil-based nanofluid.

Author	Base fluid	Particle material	Particle size	Surfactant	Loading	Results and remarks
Hussein et al., (2018) ^[28]	Palm oil	TiO ₂	30 nm	-	0.01-0.09 vol.%	<ul style="list-style-type: none"> -Viscosity of the nanofluid increase with increased particle volume concentration, with a deviation of 0.2-4% compared with pure palm oil. -Thermal conductivity of nanofluid, with an increase of 0.1-2% compared with pure palm oil due to increased volume concentration. -Friction factor and heat transfer coefficient increase when increasing nanoparticle volume fraction.
Javed et al. (2018) ^[8]	Waste palm oil	CuO	25 nm	-	0.1%-0.9% wt.	<ul style="list-style-type: none"> -The thermal conductivity of nanofluid increases with increased nanoparticle concentration. -When adding 0.7% wt. of nanoparticle, show maximum thermal conductivity enhancement of 190% compared to pure palm oil. - This nanofluid shows a more significant stability enhancement without particle aggregation (6 months) due to CuO nanoparticle adsorption of oleic acid groups in palm oil on the surface.
Timofeeva et al., (2011) ^[21]	Synthetic oil (Therminol 66)	SiO ₂	15 nm	Cationic surfactant	0.12, 3.6, 5.0, and 7.0 vol.%	<ul style="list-style-type: none"> -This research uses a cationic surfactant (Benzalkonium chloride) and interesting nanoparticle and surfactant concentration effects. -The results show a linear increase in thermal conductivity with particle concentration increase predicted by the practical medium theory (ETM). - Viscosity of nanofluid increases with particle concentration increase and depending on the effect of surfactant to nanoparticle ratio. -The heat transfer efficiency of nanofluid shows higher benefits when nanofluid is used in a laminar flow regime or at high temperatures in a turbulent flow.
Tong et al., (2022) ^[29]	Palm oil	Al ₂ O ₃	20 nm	-	0.5,1.0, and 1.5 vol%	<ul style="list-style-type: none"> -The nanofluid with 1.0 vol% of nanoparticle shows the best heat transfer performance.

Table 2-2. Summary of reviewed experimental studies on thermal-physical properties and viscosity of oil-based nanofluid. (Continuous)

Chen & Xie, (2009) ^[30]	Silicone oil	Multiwalled carbon nanotubes (CNTs)	L: 20 μ m D: 30-50 nm	Hexamethyldisilazane	0.002, 0.0054, 0.2 and 1.0vol%	<p>-This research prepared a silicon oil-based nanofluid containing CNTs using hexamethyldisilazane as a dispersant and studied the effects of CNTs' loading and temperature on the thermal conductivity. Furthermore, the viscosity of the nanofluid was studied.</p> <p>- The thermal conductivity enhancement ratio $(k_{nf}-k_0)/k_0$ (k_0 is the thermal conductivity of based fluid and k_{nf} is CNTs nanofluid) increases with temperature and CNTs loading.</p> <p>-The viscosity of CNTs nanofluid increases with increasing CNTs volume fraction and decreases with increasing temperature.</p> <p>-The dispersant added in silicone oil decreased the silicone oil viscosity.</p>
Suhaimi et al., (2020) ^[31]	Mineral oil and ester oil MIDEL7131 (Synthetic oil)	SiO ₂ , TiO ₂ , CuO, and ZnO	30nm \pm 5nm	-	0.1, 0.3, 0.5, 0.7, and 1.0 vol%	<p>-The nanofluid prepared using SiO₂ was only found to be suitable due to no agglomerations in any of the volume fractions in the base oil.</p> <p>-The density of SiO₂ nanofluid remains constant with increasing volume fraction of SiO₂ nanoparticle. This is advantageous because there will be no rise in pressure drop or pumping power when the dispersion of nanoparticles.</p> <p>-The viscosity of mineral oil base nanofluid is constant while synthetic ester oil-based nanofluid increases with increased volume fraction.</p>
Huaqing Xie (2002) ^[32]	Palm oil	Al ₂ O ₃	60.4 nm	-	0.018, 0.035, and 0.05vol%	<p>-The enhanced thermal conductivity increases with the volume fraction of the nanoparticle and reduces with an increase in the specific surface area.</p> <p>-The enhancement of the thermal conductivity is depended on the specific surface area and size of the nanoparticle</p>
Ilyas, et al. (2017) ^[33]	Thermal oil	Al ₂ O ₃	40 nm	Oleic acid	0.5-3 wt%	<p>-Viscosity increased with increasing nanoparticle loading. A significant decrease is noted with increasing temperature.</p> <p>-Thermogravimetric analysis improve life and degradation temperature of nanofluid increase with increasing nanoparticle.</p> <p>-The specific heat capacity of nanofluid decrease with increasing nanoparticle.</p>

Table 2-2. Summary of reviewed experimental studies on thermal-physical properties and viscosity of oil-based nanofluid. (Continuous)

Taha-Tijerina, et al. (2014) ^[34]	Mineral oil	Nano-diamond	6 nm	-	0.01-1 wt%	- It shows that the increment of viscosity of nanofluid is significantly less (< 6%) with the addition of 0.1 wt% of Nano-diamond particles into the oil.
Asadi, et al. (2018) ^[35]	Engine oil	MWCNT-Mg(OH) ₂	L: 30 μ m D: 1-4nm	-	0.25-2 vol%	-Maximum viscosity of nanofluid rises 50% at 60 °C when adding two vol% of nanoparticles. -It observed that minimum viscosity increases by 5% when adding 0.25 vol% of nanoparticle
Vignesh, et al. (2020) ^[36]	Mustard oil	MWCNT	20 nm	-	0.2-1 wt%	-The viscosity enhances with the rise of MWCNT weight. Similar to the temperature increase, the viscosity decrease. -The viscosity index of pure mustard oil is lower than the addition of MWCNT, and one wt% of MWCNT showed maximum viscosity index value.
Gholamreza, et al. (2011) ^[37]	Synthesis oil	SWCNTs	L: 15 μ m D: 2nm	-	0.01-0.2 wt%	-The result showed that the maximum enhancement of the viscosity index of nanofluids concerning the pure lube oil is 32.94% with 0.2wt% of SWCNTs.

2.3 Application of nanofluid

Nanofluids have shown great potential as new generation coolant, antibacterial activity, and medical and power generation. Leong et al. (2010)^[38] studies on the heat transfer characteristics of an automotive car radiator using ethylene glycol-based copper nanofluids as coolants. The result found that the heat transfer rate increase when the volume concentration of the nanoparticle is increased. Nguyen et al.(2007)^[39] experimentally investigated heat transfer enhancement of an Al₂O₃/water nanofluid flowing inside a closed system used to cool micro-electronic components. The results showed that the inclusion of nanoparticles into distilled water enhanced the cooling block convective heat transfer coefficient. A 6.8 vol.% concentration found that the heat transfer coefficient increases as much as 40% compared to the base fluid. Zhong et al. (2008)^[40] studies on the antibacterial activities of the ZnO nanofluids. The result shows that ZnO nanofluid had the best antibacterial behavior against E. coli DH5 α bacteria due to the photocatalytic properties of ZnO nanoparticles. Nanofluids could also be used for safer surgery by producing effective cooling around the surgical region, enhancing the patient's chance of survival and reducing the risk of organ damage. Sheikhpour et al. (2020)^[41] collected information about applying magnetic nanofluid systems is an essential route for targeted drug delivery, hyperthermia, and differential diagnosis. Also, nanofluids could be used as a potential antibacterial agent to overcome antibiotic resistance. The efficiency of the direct absorption solar collector (DAC) using nanofluid as the working fluid is up to 10% higher than that of a flat-plate collector. Khullar et al. (2012)^[42] found that nanofluids-based concentration parabolic solar collectors have the potential to harness solar radiant energy more efficiently in comparison to conventional parabolic troughs.

CHAPTER 3

MATERIAL AND METHODS

3.1 Material

1. Sodium metasilicate pentahydrate commercial grade from KemAus, Australia
2. Sodium aluminate general propose grade from Fisher scientific corporation, UK
3. Sodium hydroxide 10% w/w analytical reagent grade from Fisher scientific corporation, India
4. Deionized water
5. Pure palm oil

3.2 Equipment

1. Beaker
2. Round bottom flask
3. Magnetic string bar
4. Hot plate
5. Thermocouple
6. Condenser
7. Litmus paper
8. Spatula stainless
9. Buchner
10. Pump (Unit of INDEX corporation, USA)
11. Filter paper
12. Oil bath
13. Condenser clamp
14. Oven (BINDER Model ED56)
15. Aluminum foil
16. X-ray diffractometer (Rikaku SmartLab, Japan)
17. Ultrasonic Bath
18. Viscosity at 40 °C (ASTM D445) using viscometer (Cannon Instrument, USA)
19. Density (ASTM D6304) using density meter (Anton Paar, Thailand)
20. Specific heat capacity (E1269) using differential scanning calorimeter (TA discovery DSC25, USA)
21. Planetary Ball Milling (MTI Corporation TMAX-XQM, USA)
22. Particle Analyzer (Beckman Coulter delsa Nano C, USA)
23. Thermogravimetric analysis (Shimadzu DTG-60H Japan)

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3.3 Method

3.3.1 Preparation of nanoparticle (Zeolite NaA)

Zeolite NaA was synthesized by crystallization process using sodium metasilicate pentahydrate and sodium aluminate as a precursor material. Initially, dissolve 13.89 g of sodium metasilicate pentahydrate with 37.17g of deionized water using a magnetic stirrer to the homogenous liquid mixture. Later, dissolve 3.4 g of sodium hydroxide in 34 g of deionized water and add 6 g of sodium aluminate. Then, stir the solution using a magnetic stirrer until the solution is clear. Next, gradually drop sodium metasilicate solution into sodium aluminate solution and mix the solution for 1 hour using a magnetic stirrer until the solution is in gel form. After solution is gel form, put the solution into round bottom flask and reflux at 110 °C for 1 hr. Finally, separate obtained zeolite NaA and solution using Buchner repeat this step until pH < 9. After separation, put zeolite NaA into oven at 110 °C for 24 hr. Zeolite NaA particle were obtained and ground to reduce particle size by planetary ball milling at 500 rpm for 30 min, 60 min and 180 min.



Figure 3-1. Image of the setup of the experiment equipment for reflux.

3.3.2 Characteristic of Zeolite NaA

Characterization was carried out of the synthesized zeolite NaA to analyze their properties. The experimental XRD pattern of the target product has been compared with the database of zeolite NaA structure determined by X-ray powder diffractometer Rigaku (Smart Lab) from Rigaku, USA, using a Bragg–Brentano geometry. The powder patterns were collected in the continuous mode with scan speed duration time at 10 min. Cu K- α 1 radiation was used with the tube voltage operated at 40 kV and tube current performed at 30 mA in the two thetas (2θ) range 5 deg - 80 deg. The size of the particles was examined by the particle analyzer to assess their extent.

3.3.3 Preparation of nanofluid

A two-step method was used for the preparation of nanofluid. First, zeolite NaA 632 nm was dispersed into 100g of pure palm oil at 0.5, 0.25, 0.75, and 1% wt and then mixed by the magnetic bar for 20 min. After that, the nanofluid was homogenized using an ultrasonic bath (400 watts of power) for 45 minutes to stabilize the nanofluid and reduce the accumulation of particles. After sonicating, all samples were kept for at least 48 hr. to explore particle precipitation.

3.3.4 Nanofluid analysis

The viscosity of the nanofluids (μ) and viscosity index were measured at 40°C and 100°C using a viscometer Cannon Instrument, USA. In addition, the nanofluid's density (ρ) was measured using a density meter Anton Paar, Thailand.

The specific heat capacity (C_p) was measured using a differential scanning calorimeter TA discovery DSC25, USA. Measurements were performed in aluminum pans using ~20 mg of a nanofluid sample with temperature scans between 40 and 100°C with a 5 °C per minute heating/cooling rate.

The thermal stability measured by thermogravimetric analysis (TGA) is performed at temperature range from 20 to 600 °C and heating rate of 20°C per minute to examine the effect of nanoparticles on the degradation of palm oil.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the obtained results were discussed, including (4.1) Characteristics of zeolite NaA particle to confirm by using an X-ray diffractometer (XRD) and reduce the size by Planetary Ball Milling. Study properties of nanofluid that consist of (4.2) Kinematic viscosity (μ) and viscosity index of nanofluid, (4.3) Density of nanofluid (ρ), (4.4) Specific heat capacity (C_p), (4.5) Thermogravimetric Analysis (TGA) and (4.6) Dispersion behavior of nanofluid.

4.1 Characteristic of Zeolite NaA particle

4.1.1 X-ray diffractometer (XRD)

Figure 4-1 shows the XRD pattern of zeolite NaA records in the 2θ range of 15° to 50° . The six peaks correspond to the (420), (600), (622), (642), (644), and (664) planes of typical zeolite LTA. The result indicates that the synthesized zeolite is NaA zeolite which was realized by using diffraction pattern files provided by Joint Committee on Powder Diffraction Standards (JCPDS). [43]

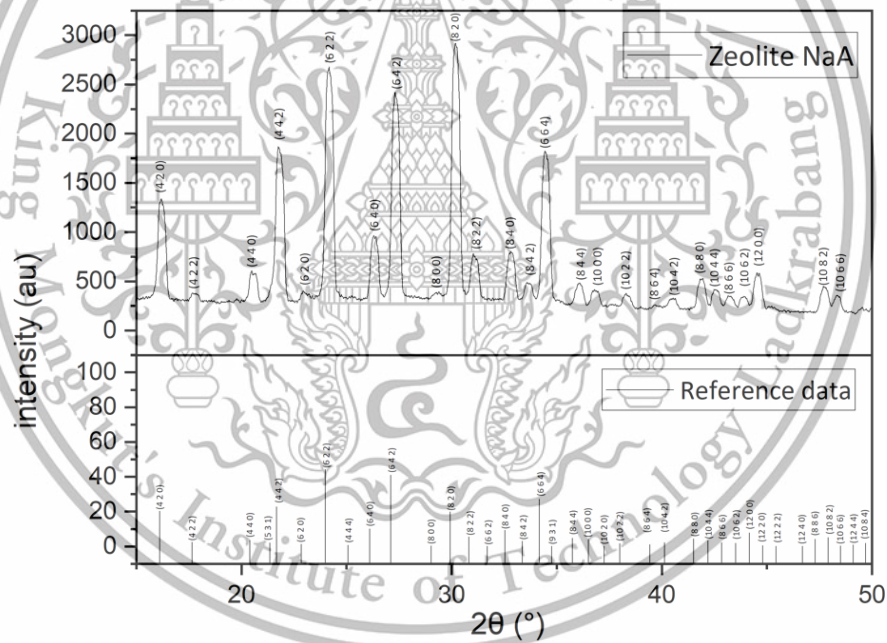


Figure 4-1. XRD patterns of the synthesized zeolite NaA sample.

4.1.2 Size of particle

The milling process was performed using a planetary ball Beckman Coulter delsa Nano C, USA. Grinding time varied from 30, 60 and 180 min. The rotational speeds were constant at 500 rpm for each experiment. The investigation was carried out in a 50 mL zirconium jar with a protective jacket of zirconium oxide balls used for this milling process. The grinding jar was set up and arranged eccentrically on the sun wheel of the planetary ball mill. The direction of movement of the sun wheel, being opposite to that of grinding jars was selected with the ratio of zeolite NaA to zirconium ball is 1: 5. The influence of time on the size of zeolite NaA is presented in Figure 4-2. Size of zeolite NaA indicated that increasing of milling time, size of zeolite NaA decrease. This Study shows that the average particle size of NaA zeolite particles decreased from 4 μm to less than one μm after 30 minutes of milling.

Further extension of the ball milling duration to 60 min, the average particle size decreased to 700 nm. After 180 min of ball milling, the average particle size was about 632 nm. So, we choose zeolite NaA whose smallest size is 632 nm, for dispersion into palm oil.

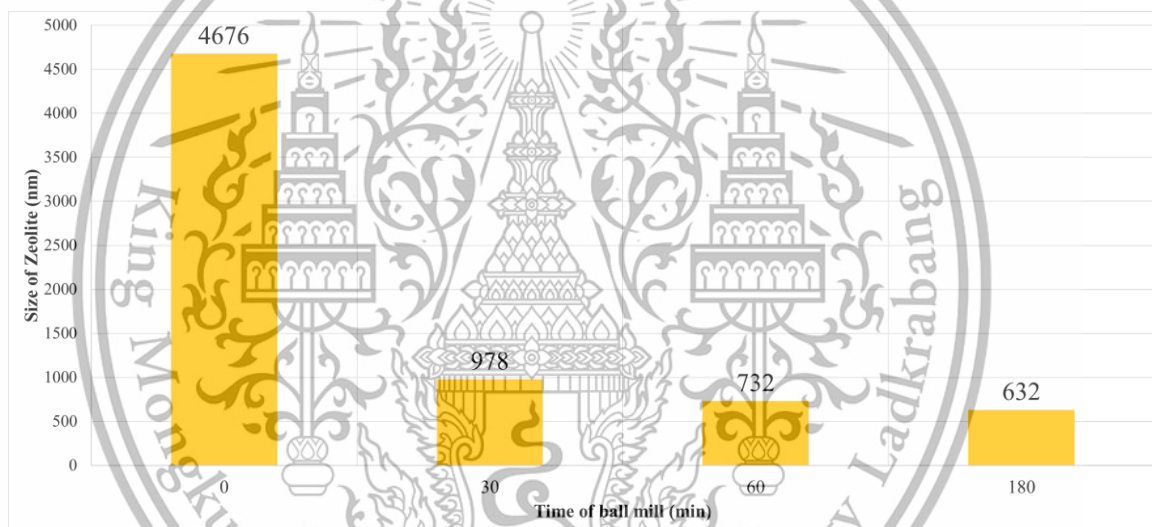


Figure 4-2. The influence of grinding time on size of zeolite NaA particle.

4.2 Kinematic viscosity (μ) and viscosity index of nanofluid

4.2.1 Kinematic viscosity (μ)

The viscosity of zeolite NaA-palm oil-based nanofluids is experimentally measured using viscometer, Cannon Instrument, USA. The influence of the additive zeolite NaA nanoparticle concentration, which is 632 nm, on the kinematic viscosity of palm oil, at 40 °C and 100 °C is presented in Figure 4-3. The viscosity of nanofluids with 0.25%, 0.5%, 0.75%, and 1.0 wt% nanoparticles in 40 °C has increased by 0.81%, 0.91%, 2.47%, and 4.06%, respectively. At 100 °C, increased values of 30.75%, 31.06%, 31.37%, and 31.52% in viscosity were observed for 0.25%, 0.5%, 0.75%, and 1.0 wt% nanoparticles, respectively. It also indicates that as temperature increases, viscosity decreases rapidly, resulting in the impact of temperature on liquid viscosity that weakens the intermolecular forces. Mousavi et al. (2019) ^[44] studied the viscosity

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of dispersion MoS₂ in diesel engine oil. They found that the viscosity of the prepared nanofluids increases at both 40 °C and 100 °C by incrementing the concentration of the nanoparticles. This increased viscosity by nanoparticles is caused by nanoparticles placed between oil layers. With increased concentration, nanoparticles become agglomerated, creating more oversized and asymmetric particles; collisions will be increased. Therefore, the fluid layers would not move on each other compared to the base fluid, leading to increased viscosity.

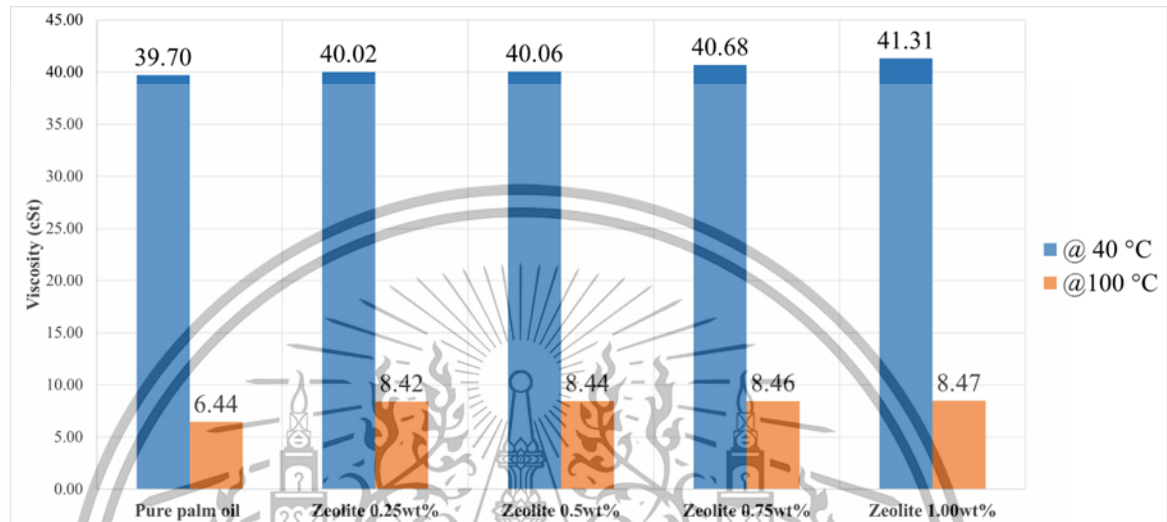


Figure 4-3. Comparison of kinematic viscosity at 40 °C and 100 °C.

4.2.2 Viscosity Index

The influence of the additive nanoparticle concentration on the viscosity index of palm oil is presented in Figure 4-4. The viscosity index of nanofluids with 0.25%, 0.5%, 0.75% and 1.00 wt% nanoparticles has increased 71.68% ,72.57%, 69.03% and 66.37% respectively. Viscosity index increases when increase concentration of nanoparticles because nanoparticles have a high surface area and can form stable network or structure within fluid, leading to improved viscosity-temperature behavior. The network created by nanoparticle helps maintain the fluid's viscosity at different temperature, resulting in a higher viscosity index. At 0.75% and 1.0 wt% is slightly lower than the other concentration due to adding too many particles results in agglomeration. The agglomeration of particles results in a higher viscosity and a greater change in viscosity results in a decrease in viscosity index. The grading of heat transfer oil for different applications depends on the viscosity index of oil. A slight change in viscosity of the oil can make it unsuitable for the desired application.

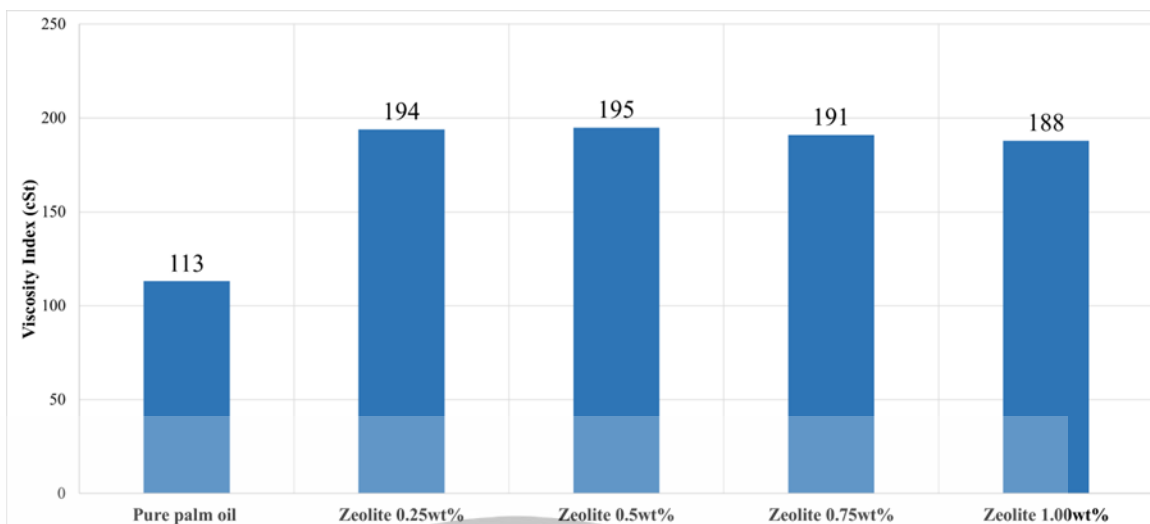


Figure 4-4. Comparison of viscosity index.

4.3 Density of nanofluid (ρ)

The density of zeolite NaA-palm oil-based nanofluids is experimentally measured using density meter, Anton Paar. The influence of the additive nanoparticle concentration on the density of palm oil at 25 °C (ASTM D6304) is presented in Figure 4-5. The density of nanofluids with 0.25%, 0.5%, 0.75%, and 1.0 wt% nanoparticles in 25 °C has increased by 0.11%, 0.22%, 0.33%, and 0.54%, respectively. This is because the mass of the substance is directly proportional to the number of particles in it. When more particles are added to a substance, the total mass of the substance also increases. If the volume of the substance remains constant, then the density of the substance will increase since there is more mass per unit volume. Vajjha et al., 2009^[45] found that the cause of increasing in density is the added nanomaterials are of higher density than the base fluid. This similarity tends to increase density found in the literature of Pendyala & Narahari (2017)^[6] and Teng & Hung (2014)^[27]

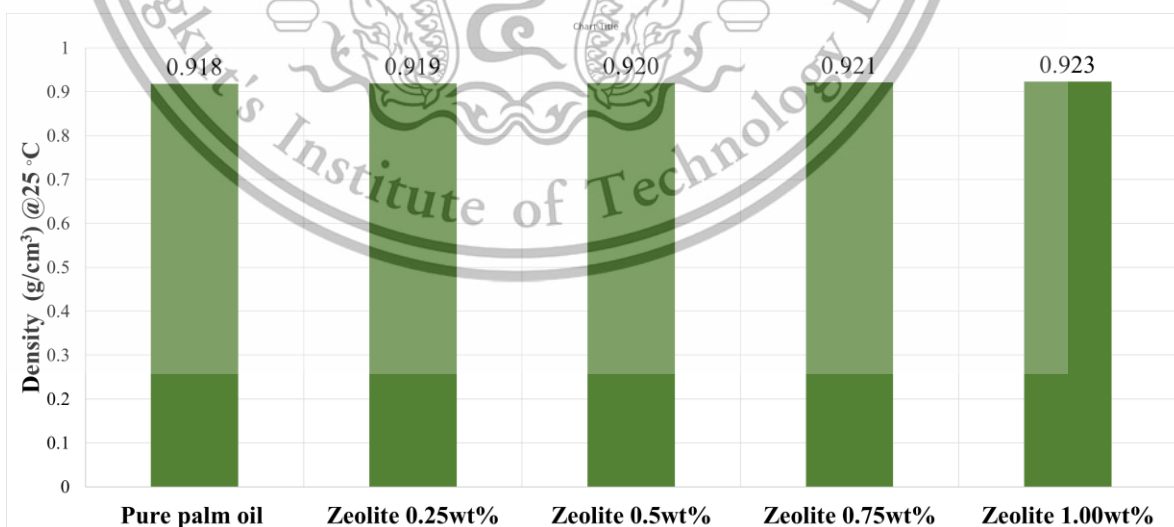


Figure 4-5. Density of nanofluid at different concentration of nanoparticles.

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4.4 Specific Heat capacity (c_p)

The specific heat capacity of the nanofluid was measured using a differential scanning calorimetry (DSC), TA Discovery DSC25 USA. The temperature ranged from 40 to 100 °C, and a heating rate of 5 °C/min was applied to pure palm oil, as well as 0.5wt% and 1wt% nanofluid samples. The results from the measurements are shown in Figure 4-6, where it can be observed that the specific heat capacity of palm oil increases with the increase in zeolite NaA concentration. This is attributed to the formation of a compressed layer at the interface between the solid particles and liquid molecules, which amplifies the capability of thermal energy storage in the nanofluid. The reason mentioned above is study from reported studies on carbon nanotube in distilled water by Byeongnam Jo (2014) [46]. In the same way, when the temperature increases, the specific heat of all nanofluid samples also increases because the specific heat is influenced by the vibration, rotation, and movement of molecules. Therefore, as the temperature rises, the specific heat will increase.

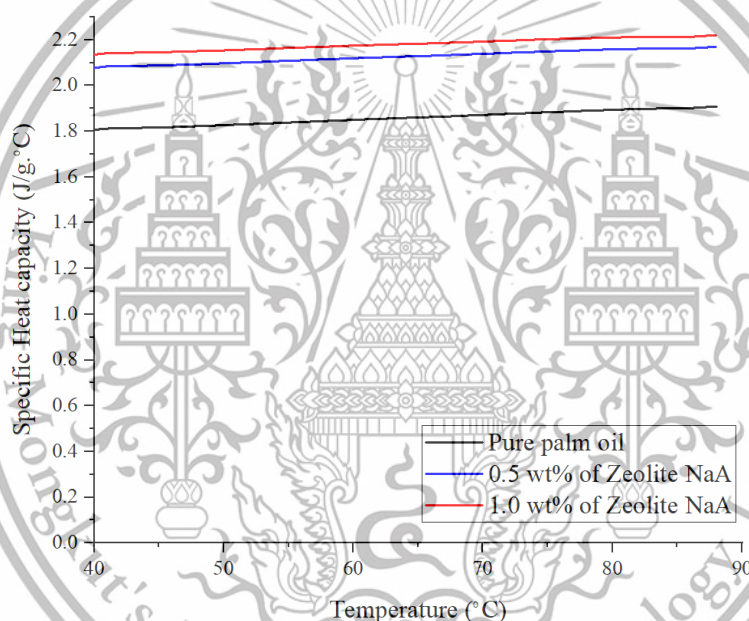


Figure 4-6. The specific heat capacity of nanofluid at different concentration of nanoparticles.

4.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed to investigate the effect of nanoparticle concentration on the degradation of palm oil. All samples were tested from 20 to 600 °C at a constant heating rate of 20 °C/min, and the weight was estimated with respect to temperature. The results are shown in Figure 4-7 revealing that palm oil starts to degrade at 263°C, while the addition of 1wt% zeolite NaA particles in palm oil shows a start of degradation at 350°C. The shift in the degradation curve demonstrates that the nanofluids can withstand high temperatures. Among the different concentrations tested, the nanofluid with a concentration of 1 wt.% shows the highest shift in the degradation temperature compared to pure palm oil. This finding is consistent with the results reported in the literature by Ilyas (2017).

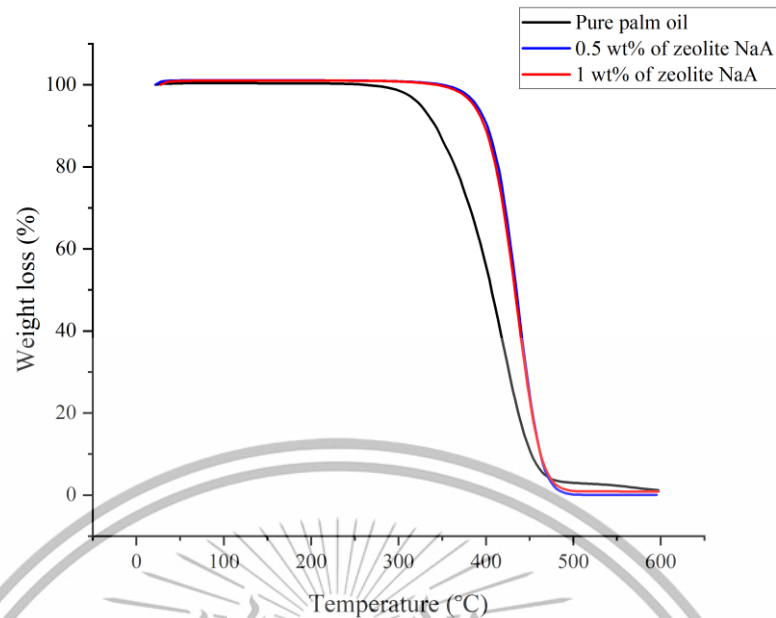
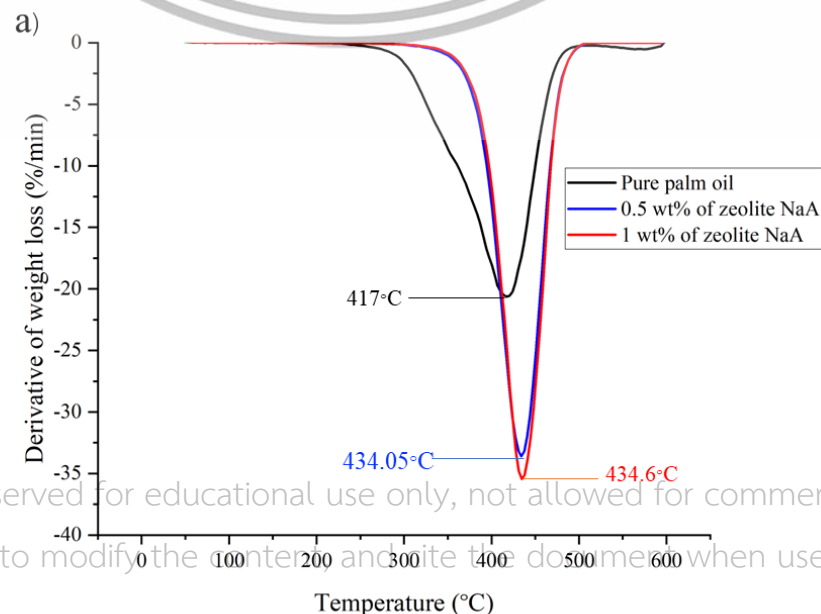


Figure 4-7. Thermogravimetric analysis (TGA) of nanofluid at different concentration of nanoparticles with respect to temperature.

The derivative of thermogravimetric analysis (DTGA) was determined for all nanofluid samples to gain a comprehensive understanding of the degradation phenomenon and the significance of nanoparticle concentrations on the lifespan of palm oil. The peak positions are shown in Figure 4-8 (a), where it was found that the maximum change in weight loss for pure palm oil occurred at 417°C. However, with the addition of 1wt% zeolite NaA particles, the peak shifted to 434.6°C. These results clearly suggest a change in the degradation temperature due to the presence of nanoparticles. The change in weight loss was observed over time, as shown in Figure 4-8 (b). A slight shift in time was observed with an increase in zeolite NaA particle concentration. The maximum weight loss was observed for pure palm oil at 1230 seconds, while the addition of 1wt% zeolite NaA showed the peak at 1280 seconds. These results clearly indicate the potential of palm oil to withstand higher temperatures and increase its lifespan when zeolite NaA particles are added.



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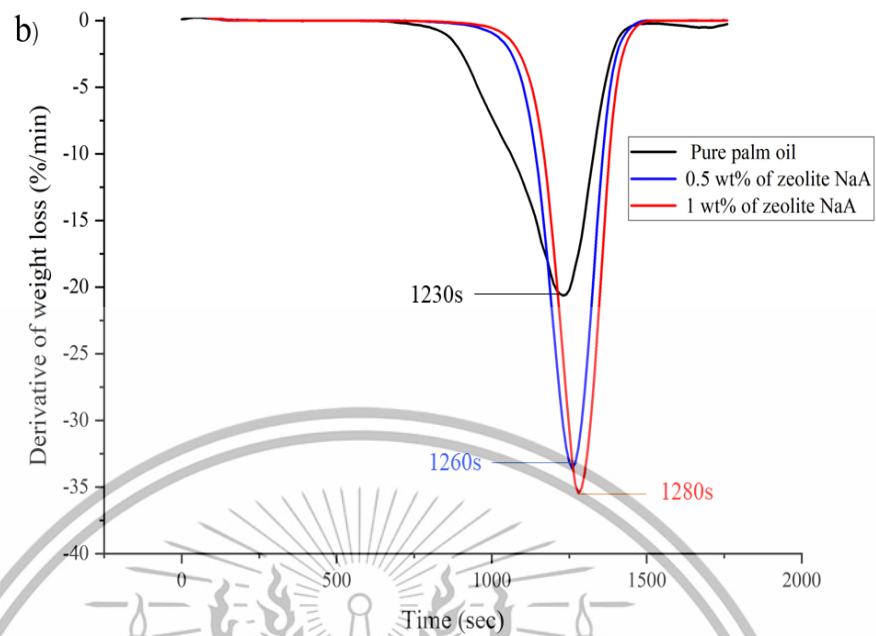


Figure 4-8. Derivative thermogravimetric analysis (DTGA) of nanofluid at different concentration of nanoparticles with respect to a) Temperature b) Time.

CHAPTER 5

CONCLUSION

5.1 Conclusion

This research focuses on improving the quality of heating oil with zeolite NaA. Palm oil was selected for heating oil due to its high flash point and environmentally friendly when compared with synthetic oil and mineral oil. The aim of this investigation was to examine the effect of the concentration of zeolite NaA suspension in palm oil on the specific heat capacity, thermogravimetric analysis (TGA), viscosity, viscosity index, and density. The zeolite NaA was successfully synthesized with sodium metasilicate and sodium aluminate using the crystallization method. After milling for 180 minutes, the results showed that the minimum size of zeolite NaA was 632 nm. An increase in zeolite NaA concentration led to an increase in the density of palm oil, which is due to the mass of the substance is directly proportional to the number of particles in it. When more particles are added to a substance, the total mass of the substance also increases. Density is a crucial parameter in nanofluids and plays a vital role in various applications, particularly in thermal applications. A higher density indicates that particles are packed more closely, resulting in a greater number of molecules available for heat transfer and, consequently, an increase in heat transfer properties. Likewise, an increase in zeolite NaA concentration resulted in higher viscosity due to enhanced interactions between nanoparticles and the base liquid's molecules. At a concentration of 1 wt% zeolite NaA, the viscosity of palm oil increased by 4% compared to pure palm oil. Furthermore, as the temperature rises, the viscosity of a nanofluid decreases due to the weakening of intermolecular forces between nanoparticles. An increase in the viscosity of palm oil after being suspended with zeolite NaA may have a negative impact on pumping power, causing a severe pressure drop and a decrease in heat transfer properties. The viscosity index at 0.5 wt% of zeolite NaA showed a maximum viscosity of 195. This viscosity index is slightly higher than that of pure palm oil after adding zeolite NaA particles due to the increasingly non-uniform distribution. The deposition of nanoparticles with increasing temperature demonstrates that the rate of change in viscosity of palm oil is less affected by temperature. A high viscosity index indicates good performance of the heating oil. The specific heat capacity of palm oil increases when zeolite NaA particles are added. This high specific heat capacity indicates that it has enhanced heat storage and heat transfer capabilities. Thermogravimetric analysis, conducted by increasing the amount of zeolite NaA particles, indicated that it can withstand heat better than pure palm oil and has a longer service life.

5.2 Recommendations

5.2.1 Study effect of another parameter on heat transfer properties such as thermal conductivity of palm oil to confirm palm oil is a potential heat transfer fluid.

5.2.2 The primary issue of concern is the stability of nanofluid, which leads to decreased efficiency in industrial applications and maintenance problems.

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APPENDIX

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APPENDIX A

A.1 Synthesis zeolite NaA



Figure A-1. Dissolve 13.89 g of sodium metasilicate pentahydrate with 37.17 g of deionized water using a magnetic stir to the homogenous liquid mixture.

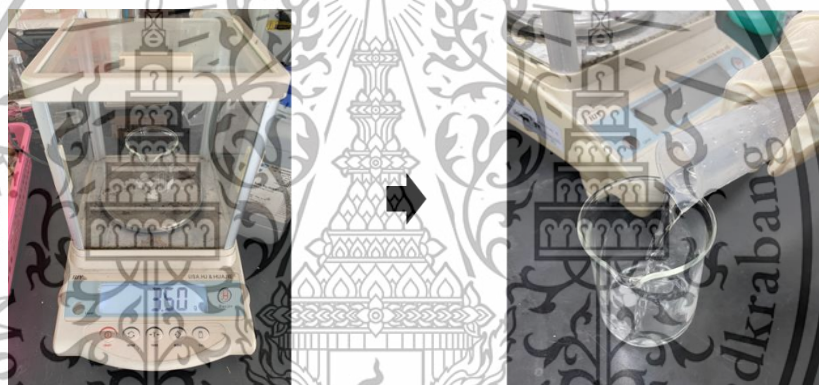


Figure A-2. Dissolve 3.4 g of sodium hydroxide in 34 g of deionized water using a magnetic stir to clear liquid.

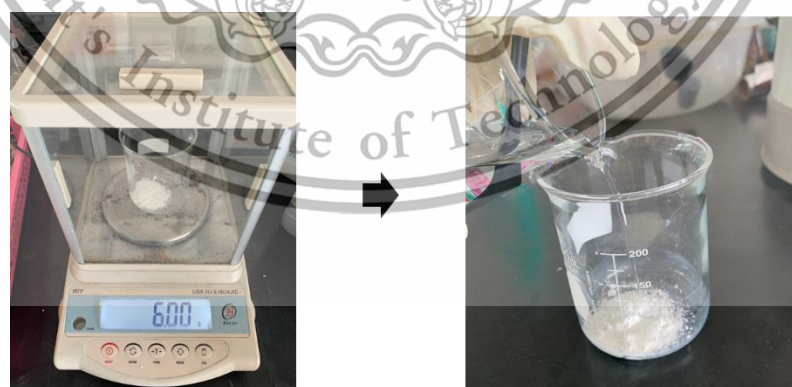


Figure A-3. Add 6 g of sodium aluminate to the sodium hydroxide solution.

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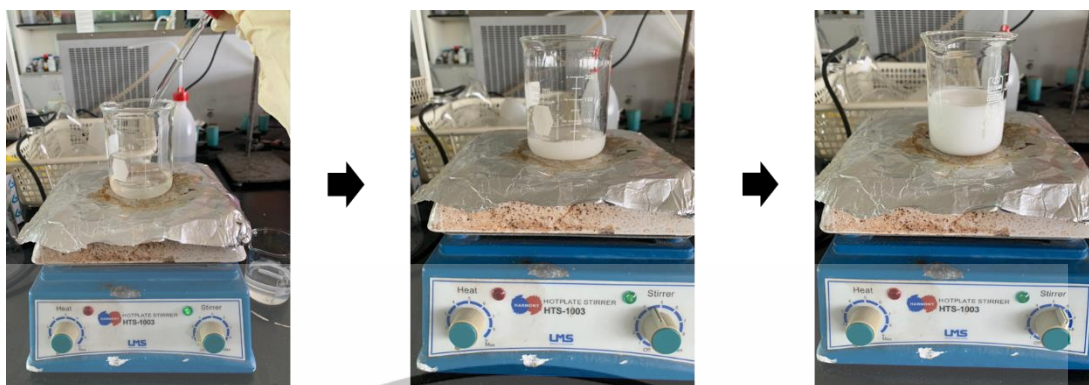


Figure A-4. Gradually drop sodium metasilicate pentahydrate solution into sodium aluminate solution and mix the solution for 1 hour using a magnetic stirrer until the solution is in gel form.

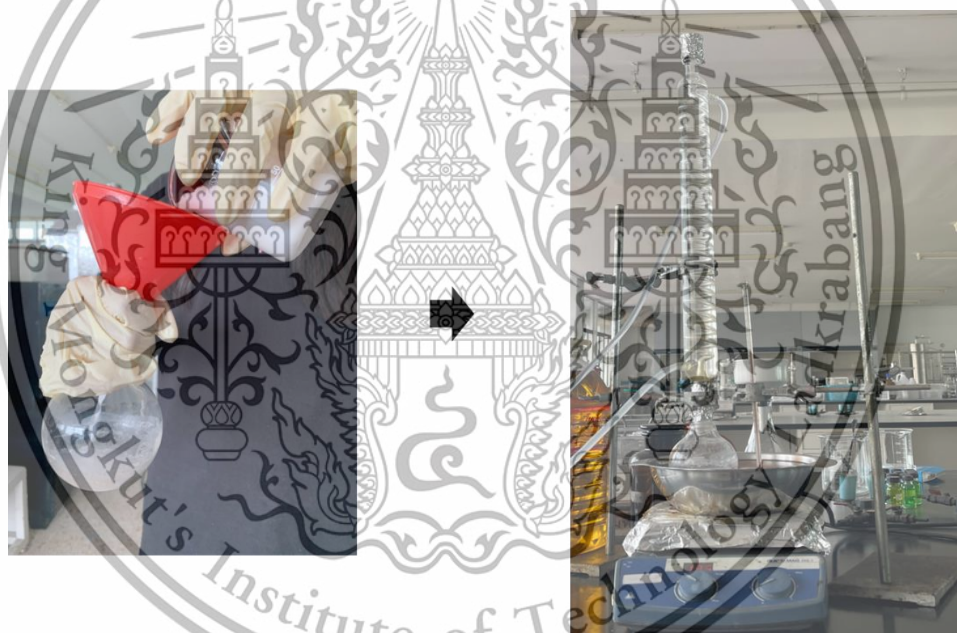


Figure A-5. Put the solution into round bottom flask and reflux at 110°C for 1 hr.



Figure A-6. Separate obtained zeolite NaA and solution using Buchner repeat this step until pH < 9. After separation, put Zeolite NaA into oven at 110 °C for 24 hr.

A.2 Preparation palm oil with zeolite NaA



Figure A-7. Zeolite NaA disperse into palm oil base fluid at difference particle loading (0.25%, 0.5%, 0.75% and 1.00 wt%) by stir in magnetic bar. After that, put into sonicate bath to stability zeolite NaA.

APPENDIX B

Size distribution of zeolite NaA

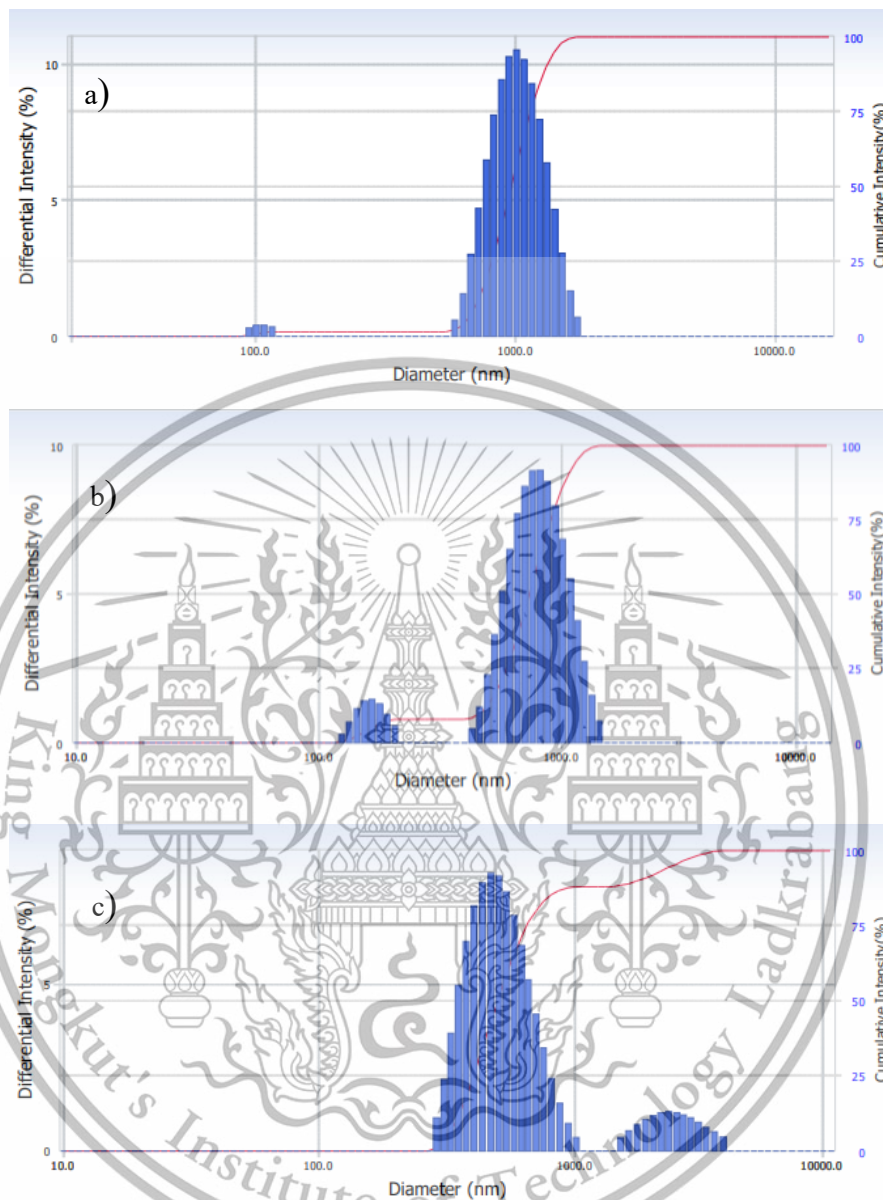


Figure B-1. Comparison of grinding time on size of zeolite NaA particle a) 30 min b) 1 hr c) 3 hr.

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APPENDIX C

Stability of nanofluid

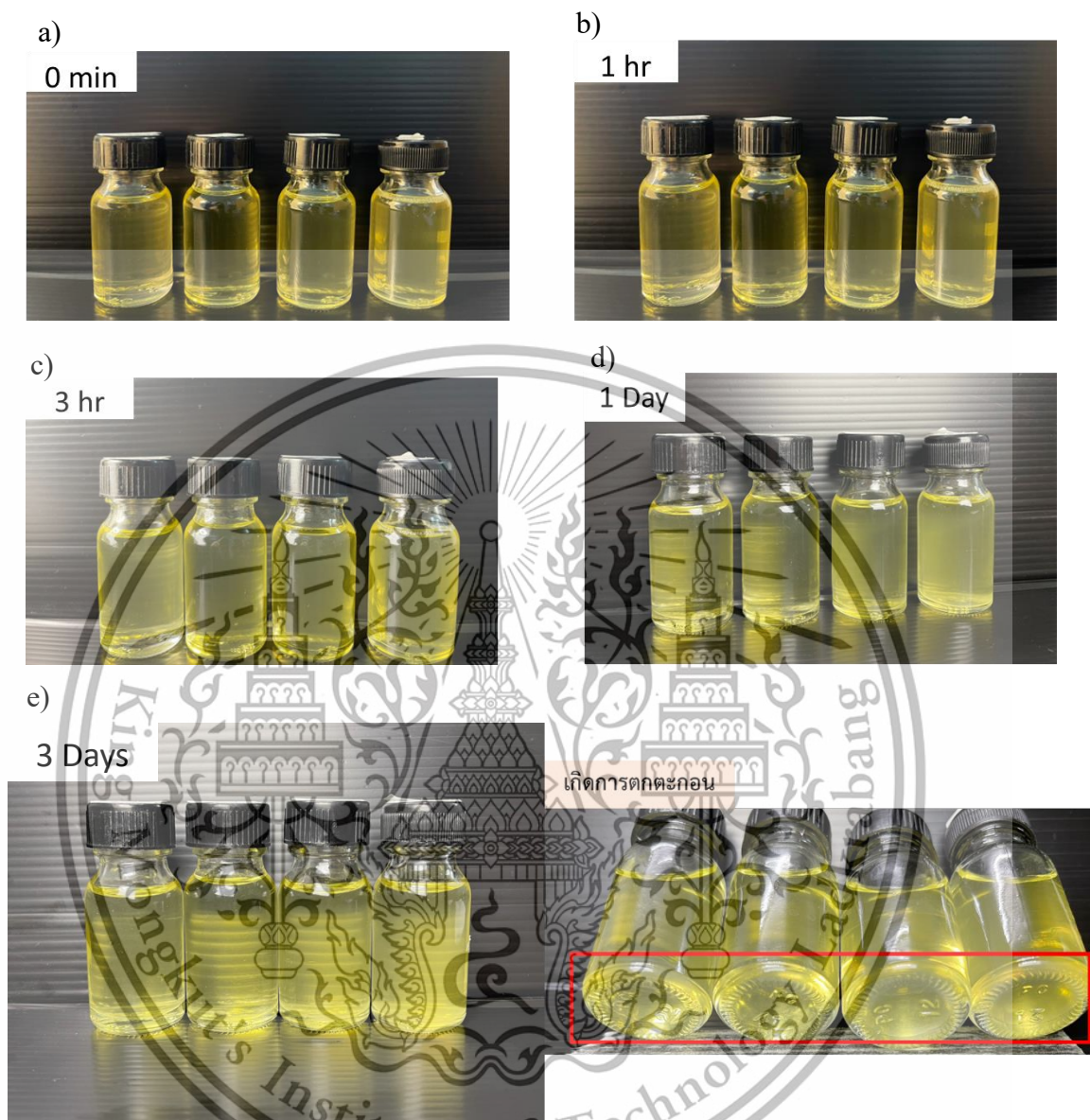
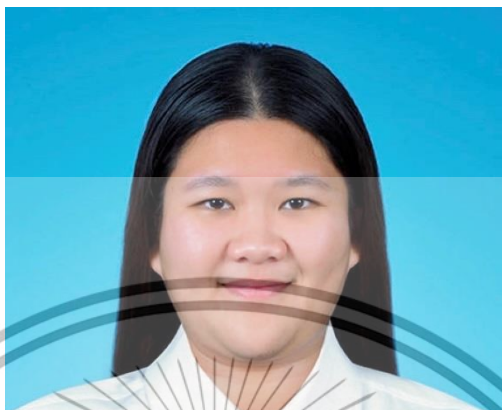


Figure C-1. Settling characteristic a) 30 min b) 1 hr. c) 3 hr. d) 1 day and e) 3 Days.

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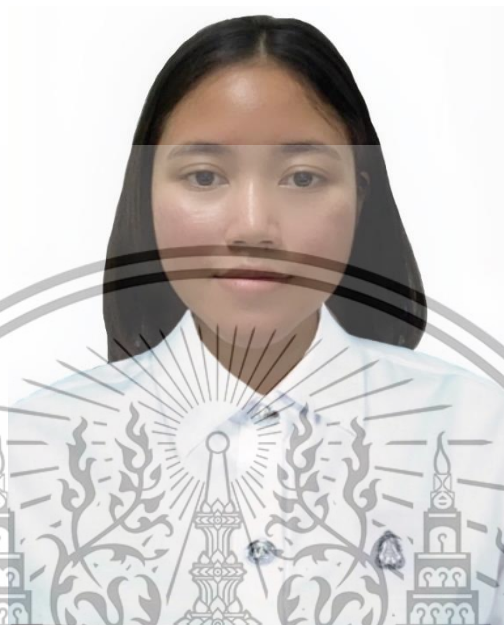
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