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Heat Transfer and Fluid Flow Analysis of Cryogen based Nanofluids in a Micro-Heat Exchanger

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Abstract: Miniaturization of equipments has lead to an increase in requirement of an effective system to transfer and dissipate heat from a working system, due to the high heat flux that possess. Because of low thermal conductivity and specific heat the heat dissipation is poor in traditional fluids. Thus these traditional fluids are replaced with nanofluids. . There are various studies regarding with their anomalous and unique thermal transport properties. Thus these studies has expanded the field of nanofluids into an unexplored field of cryogenic nanofluids.

In this work heat transfer and pressure drop analysis of different cryogen based nanofluids are analysed with different volume fractions(1%-5%). Because of the small size of micro heat exchanger, the heating is more in them. cryogenic base fluid LN2 along with CuO,Al2O3,ZnO,Fe3O4 as nanoparticles are focused on this numerical study. This work aims to investigate what's the impact on heat transfer rate and pressure drop at different volume fractions along with different combinations of cryogenic nanofluids, inorder to enhance the choices of both base fluid and nanoparticles. For this a computational investigation is carried out in 3-D geometry developed in ANSYS 17 and further analysis is done using FLUENT for steady turbulent developing flow.

Keywords: Cryogenic nanofluids, Micro-heat exchanger, Miniaturization, Traditional fluids, Volume fraction etc

I. INTRODUCTION

Heat exchangers are the devices used to transfer heat between two or more fluids. The fluids can be of single phase or two phase depending upon the heat exchanger type. The heat exchangers are classified on the basis of:

- 1) Heat transfer process
 - 2) Number of fluids
 - 3) Degree of surface compactness
 - 4) Flow arrangements
 - 5) Geometrical configuration (based on hydraulic diameters)
- a) *Geometrical Configuration:* Based on geometrical configuration again they are classified into Micro, Meso, Compact and Conventional Micro heat exchangers. In the present work Micro-heat exchangers are taken into account. Micro-heat exchangers are the heat exchangers in which the fluid flows in a confined area such as a tube or a small opening having dimensions below 10mm.

A. Different Types of Micro Heat Exchangers

They are Mainly of Four:

- 1) *One Fluid and One Passage:* In this type,there is a single fluid flow along a single passage where the heat transfer takes place.Main applications of these kind are found in Electronic devices.
- 2) *Two Fluids and Two passages:* In this type, when there has two fluids and two passages they are commonly classified by the direction of the flow between the two fluids.
- 3) *Counter Flow:* They are similar to the macro scale heat exchangers i.e, the two fluids flow in the opposite directions.The hot and cold fluids enter at the opposite ends. counter flow micro heat exchangers are more favourable than cross flow micro heat exchangers.



Figure- 1:Counter flow Micro heat exchangers

- 4) *Cross Flow*: Cross flow heat exchangers works same way as macro scale heat exchangers. In this type of heat exchanger one fluid flows right angles to the the other. They are mainly found in the applications where two-phase flow is taken into account.eg : Automobile radiators etc.



Figure -2: Cross flow Micro heat exchangers

B. Cooling challenge

In response to the ever increasing demand for the micro heat exchangers in various fields leads to its vast study along with conventional fluids and nanofluids as coolants. The major challenge regarding with the micro heat exchangers is its cooling. Due its small size, the micro heat exchanger heats quickly so the removing of the heat from them is adequate for its efficient working under optimum temperatures. So when using conventional fluids such as water, ethylene glycol, transformer oil etc the heat dissipation rate is low in them due to their low thermal conductivity and specific heat. Thus to achieve high heat transfer rate nanofluids are used. Simply nanofluids are the combinations of ordinary conventional fluids and nanoparticles having size less than 100 nm. Because of the high thermal conductivity and specific heat of these suspended solid particles on the host fluid increases the thermal transport properties of the cooling fluid. Thus there are various researches taken place with different combinations of base fluids & nanoparticles. Finally these researches has expanded the field of nanofluids into an unexplored field of cryogenic nanofluids. Here the base fluids are the cryogenic fluids itself. They have enhanced thermal transport properties at extreme temperatures as working as the coolants.

C. Objective of the study

Cryogenic nanofluids are totally a new type of nanofluids where there are no much work regarding with them. So this work aims to investigate what happens to the heat transfer rate and pressure drop when volume fraction is increased while using different combinations of cryogenic nanofluids ?

Major objectives where :

- 1) To investigate thermo-fluid behaviour enhancement of Nano particle filled flow on micro heat exchanger using ANSYS 17.
- 2) To study pressure drop variations and Nusselt number variations for different Nano particles with different volume fractions(1-5%).
- 3) To study the effect of hydrodynamic variations of Nano particle injected flow.

II. LITERATURE SURVEY

Before doing any project, there requires a complete and well-studied review about the past developments in the current project. This review is based on the relevant topics upon which the current work is based. Here are the fields in which the literature survey is explored:

A. Micro-Heat Exchanger And Applications

Zhong Qian[1] et al conducted a numerical study on the performance of microchip cooler with copper and silicon nitride compound as materials. He concluded that the better cooling capability is observed in copper cooler due to its excellent thermal conductivity. Also he observed that the reduction in cooling capacity of silicon nitride is due to its lower thermal conductivity. Mustafa[2] et al investigated the performance and efficiency of direct absorption solar collector with H₂O-Aluminium combination as the nanofluid. He summarized that while using this combination of nanofluid thermal efficiency is much more enhanced when the bottom part of solar collector is replaced with H₂O-Aluminium nanofluids.

Marcos[3] et al conducted a study on laminar counter flow parallel-plate micro-heat exchanger and arrived at a conclusion that it is confirmed that for uniform wall temperature boundary condition, nusselt number acts as lower bound for the fluid with reduced heat capacity flow rate.

Madhav[4] et al Paper describes the fabrication and test results for the cooling of high power laser diodes with Micro-heat exchanger. Here the test results indicates that the cooling system provides uniform fluid flow and heat transfer rate over an entire surface of micro-heat exchanger and at the same time maintaining low pressure drops at high flow rates.

B. Properties Of Selected Nanoparticles With Different Volume Fractions

J. Koo[5] et al Pointed that the addition of CuO nanoparticles, at low volume fractions $1 \leq \infty \leq 4\%$, to high prandtl number increases the heat transfer rate of micro-heat sinks. He also discussed that particle interactions plays a major role in high concentration suspensions. Haitao Zhu[6] et al Experimentally analysed the effect of nanoparticle clustering and alignment on thermal conductivities of aqueous Fe₃O₄ nanofluids. In this work he made a comparative study of different water based nanofluids such as Al₂O₃, CuO, TiO₂ with Fe₃O₄ nanofluid. It is found out that the thermal conductivities of Fe₃O₄ nanofluids are larger than the other nanofluids having similar volume fractions. N.T Ravikumar[7] et al Conducted an experiment on a double pipe heat exchanger to determine, heat transfer, friction factor, effectiveness, and NTU with Fe₃O₄ as nanofluid. He concluded that as the particle volume concentration and Reynolds number increases, the heat transfer increases. Bhanuteja[8] et al Reports that the overall bulk temperature of the nanofluids is higher than that of water. This is a strong indication of larger amount of heat received by the nanofluids compared with water. He used Al₂O₃, TiO₂, CuO, & SiO₂ nanoparticles mixed with water and the heat transfer rate and pressure drop are calculated along with different tube lengths. From the heat transfer analysis, SiO₂ has the higher heat transfer rate comparing with other nanofluids tested. Also analysing the pressure drop profile Ag has the least pressure drop Ayoub[9] et al Numerically studied in a micro channel heat sink with V- type inlet/outlet arrangement on the fluid flow and heat transfer characteristics based on laminar nanofluid flow. In this study he used different nanofluids such as SiO₂, Al₂O₃, ZnO, and CuO with water having different volume fractions of (0,1,1.5 & 2%) with various diameters ranging with 30,40,60 nm. He pointed out that the average nusselt number increases with decreasing the nano particle diameters. i.e the reduction in nano particle size increases the Brownian motion velocity of nanoparticles there by increasing the heat transfer rate. Azher[10] et al In his numerical study he used Al₂O₃, CuO, SiO₂, and ZnO nanoparticles With different volume fractions ranges from 0 - 4% with different types of base fluids water, glycerine and ethylene glycol. Results shows that the average nusselt number for nanofluids is higher than that of base fluid. Also increasing in volume fraction increases pressure drop also. M. Rostamani[11] et al Reported that as increasing the nanoparticle volume concentrations will increase the wall shear stress. He concluded that the nusselt number and heat transfer coefficient are mutually dependent on nanoparticles and volume concentrations of nanoparticles. Mohammad Eftekhari Yzdi[12] et al in his numerical study Brownian motion effects on natural convection of alumina-water nanofluid in a 2-D geometry reported that, as the volume fraction increases the results shows that there is a decrease in heat transfer.

C. Cryogenic Nanofluids

Rajashekhar Dondapati[13] et al Gives a computational prediction regarding with cryogen based nanofluids with different mass flow rates of 0.1 to 0.14 Kg/s. He made a strong statement about the relation of mass flow rate and pressure drop i.e, as the mass flow rate increases the pressure drop increases. Also he concluded that the enhancement in thermal conductivity is due to the Brownian motion and agglomeration of nanoparticles in base fluids.

H. Ziebland [14] et al In this paper he measured the thermal conductivity of liquid and gaseous oxygen at temperatures between 1 and 130 atm using a vertical coaxial cylinder method.

R. Span[15] et al Formulated new data sets of thermophysical properties of gaseous, liquid and supercritical nitrogen.

III. MATHEMATICAL MODELING

Multiphase mixture model is used to solve the steady, turbulent developing flow conditions. It is to be noted that mixture model is used to solve the mass, momentum and energy equations. In this numerical study an axi-symmetric model is used to describe the flow of cryogen based nanofluid through a straight circular pipe under constant heat flux boundary condition having a turbulent flow regime. The geometry of the pipe having diameter 0.0078m and length 0.873m are shown in fig;3

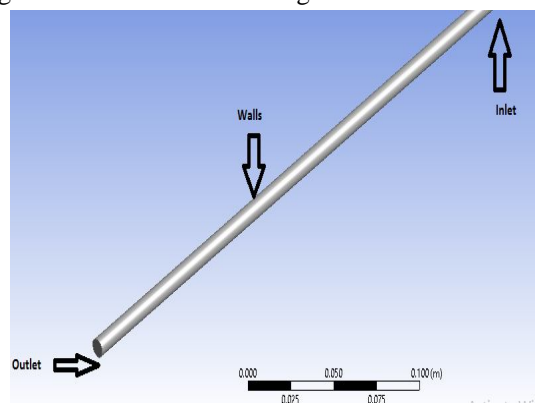


Fig- 3: Geometry of micro-heat exchanger

A. Assumptions and Boundary conditions

- 1) Constant Inlet temperature = 65K.
- 2) Heat flux at the walls are considered uniform ,91300W/m²K.
- 3) Body forces and the gravitational forces are negligible.
- 4) Multiphase Mixture model is considered, with agglomerated Nano particles assumed to be behaving as an effective fluid.
- 5) Mass flow rate is constant, 0.1 Kg/s.

B. Governing Equations

In order to understand the physical aspects regarding with fluid flow, conservation of mass, momentum, energy are solved using either analytically or computationally. Here in the present work, the equations are solved computationally with the help of Computational Fluid Dynamics(CFD) method. In order to solve the conservation equations Finite volume method(FVM) was used, thus the differential equations are transformed to discretized algebraic form. At last these discretized algebraic equations are solved with a commercial software ANSYS 17-Fluent. The conservation equations for single phase, steady, turbulent flow are shown below:[13]

C. Conservation Of Mass

$$\frac{\partial \rho_{eff}}{\partial t} + \nabla \cdot (\rho_{eff} \cdot v) = S_m \quad (1)$$

Where, ρ_{eff} = effective density of the nanofluid

S_m = source term for mass

In this work the flow is considered steady and no source of the mass, thus the Eq.(1) reduces to:

$$\nabla \cdot (\rho_{eff} \cdot v) = 0 \quad (2)$$

Whereas Eq.[2] can be written as:

$$\frac{\partial(u)}{\partial x} + \frac{\partial(v)}{\partial y} + \frac{\partial(w)}{\partial z} = 0 \quad (3)$$

Where u, v, w are the velocities in x, y and z direction respectively

I. Conservation of momentum

The equation for conservation of momentum is given below:

$$\frac{\partial(\rho_{eff} v)}{\partial t} + \nabla \cdot (\rho_{eff} \cdot v v) = -\nabla p + \nabla \cdot (\tau) + \rho_{eff} g^* + F^* \quad (4)$$

g^* and F^* are gravitational and body forces

From the assumptions it is clear that flow is steady, gravitational and body forces are assumed to be negligible due to turbulent developed flow. Thus the Eqn.[4] reduces to:

$$\nabla \cdot (\rho_{eff} \cdot v v) = -\nabla p + \nabla \cdot (\tau) \quad (5)$$

J. Conservation of energy

The equation regarding with conservation of energy is shown below:

$$\nabla \cdot (V(\rho_{eff} \cdot E)) = \nabla \cdot q \quad (6)$$

$$\nabla \cdot (V(\rho_{eff} \cdot E)) = \frac{\partial}{\partial x} \left(K_{eff} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{eff} \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{eff} \frac{\partial T}{\partial z} \right) \quad (7)$$

IV. NANOFLUIDS THERMO-PHYSICAL PROPERTIES

The thermophysical properties such as density, specific heat, thermal conductivity and viscosity of the base fluid LN2 [13] and nanoparticles Al₂O₃, CuO, Fe₃O₄ and ZnO [6], [9], [16] are taken from base journals. Also the effective thermal conductivity of the nanofluid is calculated from the Maxwell theoretical model [18].

V. COMPUTATIONAL DOMAIN

In the present problem, the flow is assumed to be unsteady incompressible, so pressure based solver is used for the numerical analysis. The SIMPLE (Semi-Implicit Method for Pressure-Linked Equations) algorithm is used as the solution method. This algorithm is essentially a guess-and-correct procedure for the calculation of pressure on the staggered grid arrangement. To initiate the SIMPLE calculation process a pressure field is guessed and the discretized momentum equations are solved using the guessed pressure field to yield the velocity components. The correct pressure is obtained by adding a pressure correction to the guessed pressure field. To avoid the divergence problem a suitable under relaxation factor is considered during the iterative process.

VI. MESH DOMAIN

Meshing is done by inputting the relevance value as 100. After meshing select the body sizing and from the grid independent study we get the suitable value of element size as 5.83e-04. Finally inflation is done so as to get fine meshing in the wall or boundary then select maximum layers for the inflation as 5 for getting 5 layers of fine mesh in the wall. Fig 4, Fig 5.

VII. GRID INDEPENDENCE STUDY

Mesh or Grid independent solution is a solution that does not vary significantly even when we make the mesh finer. When we start with a coarse mesh and solve, we may notice difference in results as make our mesh finer. But, there exists a limit, beyond which we won't observe any changes in the results even after we make it finer. Then we may state that we have achieved grid independence. At this point, the mesh will be fine enough to capture the most intricate details of the flow, which is why making it finer will not make any changes in the results. Fig 6.

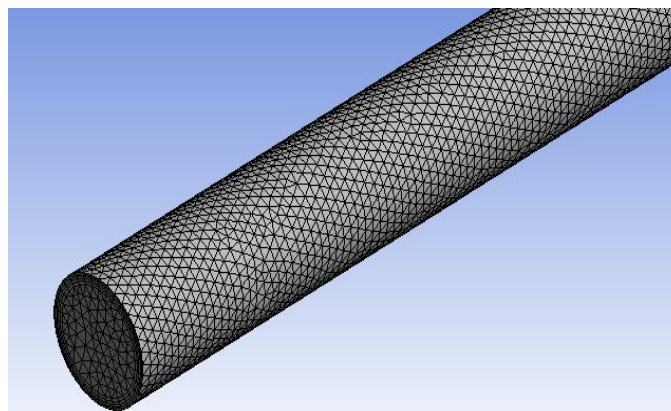


Fig -4: Meshed geometry

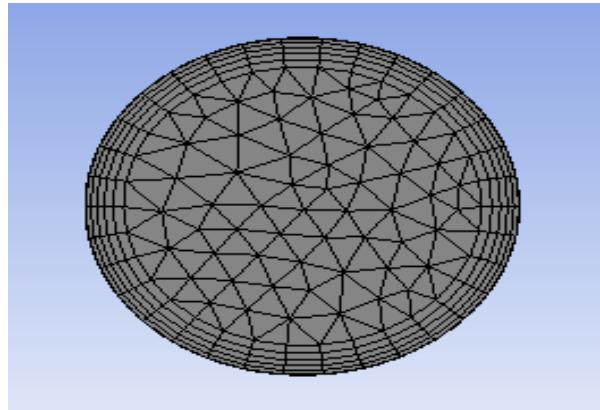


Fig-5: Front view of meshed structure

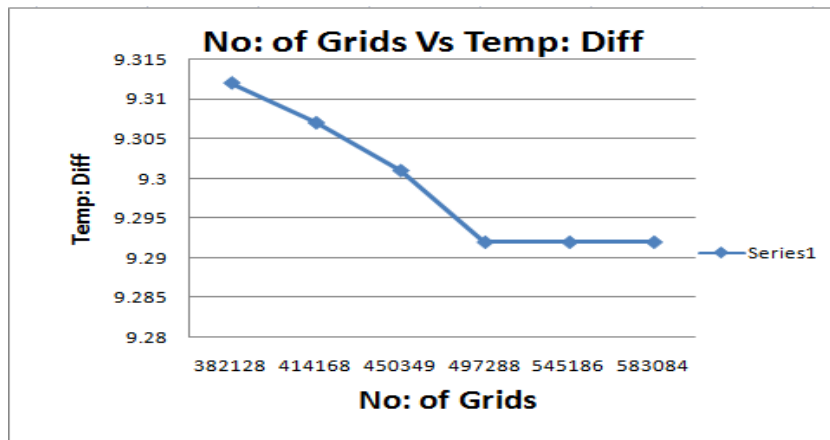


Fig -6: No: of grids Vs Temperature Difference

VIII. VALIDATION

Raja sekhar Dondapati, Vishnu saini, Kumari Neelam verma , Preeti Rao Usurumarti [1] conducted a numerical study on micro-heat exchanger with LN2 as the base fluid and Al2O3, CuO, Sic, SiO2, and TiO2 as nanoparticles. Then carried heat transfer and pressure drop analysis on micro-heat exchanger with various mass flow rates of 0.1-0.14 Kg/s having constant volume fraction of 3%. A similar model with the same dimension and boundary conditions is analysed using CFD and the resulting temperature difference Vs mass flow rate plot and pressure drop Vs mass flow rate along the solid-fluid interface is compared with the base journal shown in Fig-7 and Fig-8.

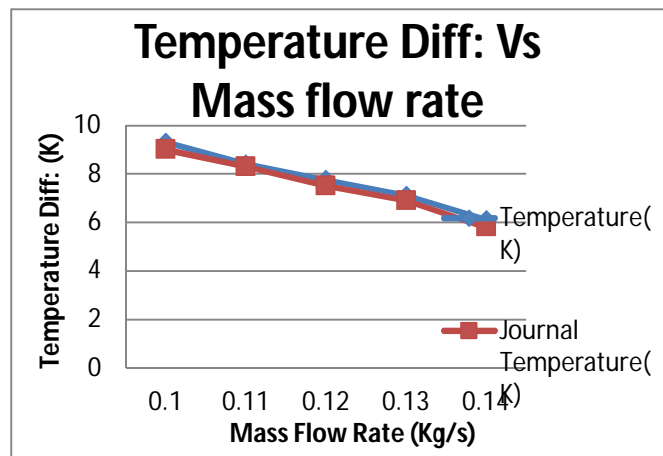


Fig-7: Temperature Vs Mass flow rate

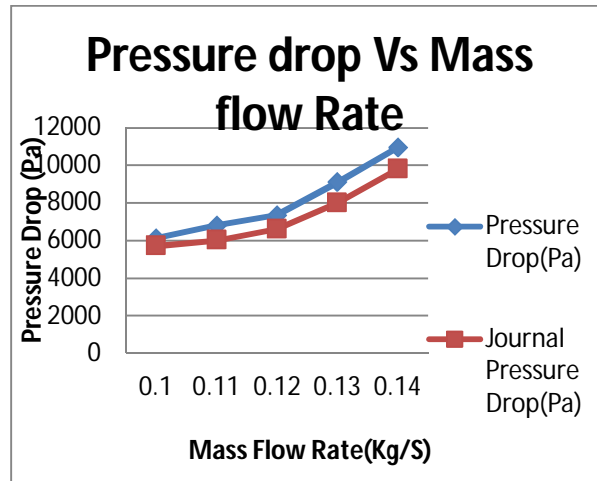


Fig-8: Variation of pressure drop with mass flow rate along the solid-fluid interface

IX. RESULTS AND DISCUSSIONS

The analysis has been carried out with LN2 and LO2 as a base fluids and nanoparticles used were Al2O3, CuO, Fe3O4. During each analysis for the same inlet conditions the temperature difference and pressure difference of both nanofluids were recorded. From that data the Thermal conductivity, heat transfer coefficient, Reynolds number, Nusselt number, Friction factor, and the pressure drop can be calculated along with different volume fractions.

A. Thermal analysis

In thermal analysis, Thermal conductivity, heat transfer coefficient, Nusselt number are analysed with different volume fractions(1-5%).

B. Thermal conductivity

In this numerical study, the effective thermal conductivity is taken into account. Effective thermal conductivity of the nanofluid is calculated from Maxwell theoretical model [18]. Because From [13] they have compared two models regarding with effective thermal conductivity. Li and Peterson experimental model[17] and Maxwell theoretical model[18]. Thus comparing two models Maxwell model shows more enhancement in the thermal conductivity than that in Li and Peterson model. From the Fig-9, it can be concluded that as the volume fraction increases the thermal conductivity increases. This is mainly due to the fact that as the volume fraction increases the solid particles in the suspension increases also the thermal conductivity of the solid particle is more than that of base fluid thus there is an increment in the effective thermal conductivity. Effective thermal conductivity is calculated from the below equation from Maxwell model:

$$\frac{K_{eff}}{K_f} = \frac{K_p + 2K_f + 2\phi(K_p - K_f)}{K_p + 2K_f - \phi(K_p - K_f)} \quad (8)$$

The table showing the effective thermal conductivities of various nanofluids with different volume fractions are shown below

Table-1: Effective thermal conductivity of different nanofluids at volume fractions(1-5%)

Volume Fraction(ϕ)	Nanofluids			
	LN2-Al2O3	LN2-CuO	LN2-Fe3O4	LN2-ZnO
1	0.17508	0.1750	0.17509	0.1749
2	0.1802	0.1801	0.1803	0.1790
3	0.18547	0.1853	0.1856	0.1851
4	0.1909	0.1906	0.1910	0.1904
5	0.19635	0.1962	0.1970	0.1957

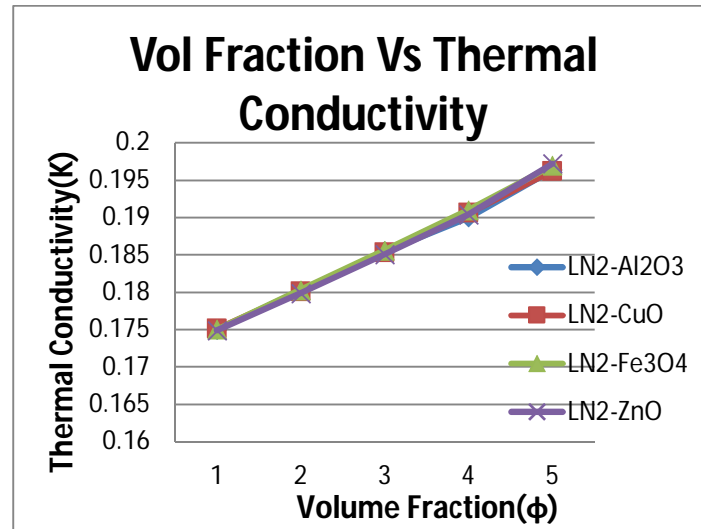


Fig-9: Volume fraction Vs Thermal conductivity

In the Fig-9 it shows that LN2- Fe₃O₄ based nanofluid has the higher thermal conductivity value followed by Al₂O₃, CuO and ZnO respectively. As stated earlier thermal conductivity of the Fe₃O₄ nanoparticle is higher comparing with the others.

C. Heat Transfer Coefficient

Heat transfer coefficient (h) is used for calculating mainly convective heat transfer. Heat transfer coefficient is the strong indication of heat transfer rate. Higher value of the h, higher will be the heat transfer. Here in this numerical study as the volume fraction increases the heat transfer coefficient decreases shown in Fig-10:

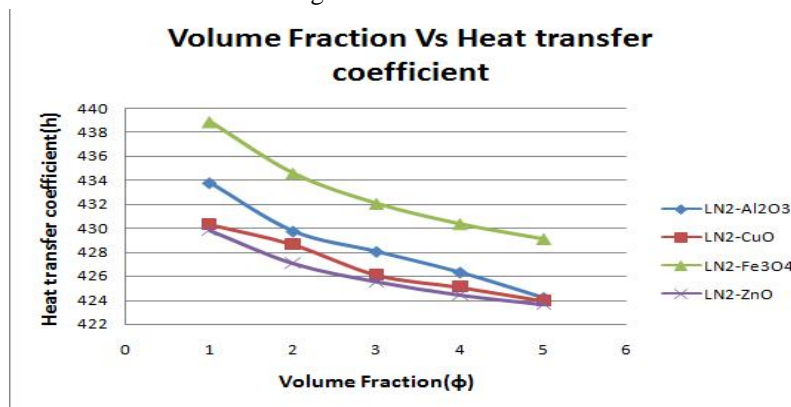


Fig-10: Volume fraction Vs h

Here in the above figure we can see that as the volume fraction increases from 1-5% the heat transfer coefficient decreases. Here the possible reason regarding with the drop of heat transfer coefficient is that as said earlier this is a developing flow thus as the boundary layer thickness increases it reduces the heat transfer coefficient, boundary layer is the region inside the flow where the fluid flow is slower than the mainstream due to the viscosity introduced by the walls. Thus as the flow became slower heat transfer by convection reduces and thus heat transfer coefficient decreases. Also it depends upon the thermal conductivity values of different nanofluids.

D. Nusselt number

Nusselt number is the ratio of convective heat transfer to the conductive heat transfer. Heat transfer rate can be explained from the nusselt number calculations. From different macro channel problems it is clear that as the volume fraction increases the nusselt number increases. But here in case of micro channel flow the aspect ratio ($\frac{D}{l}$) is small and it is about 0.00893. Nusselt number is calculated from the basic formula:

$$Nu = \frac{h l}{k} \tag{9}$$

h = Heat transfer coefficient

k = Thermal conductivity

l = characteristic length, for pipes it is considered as hydraulic diameter d. here d is taken.

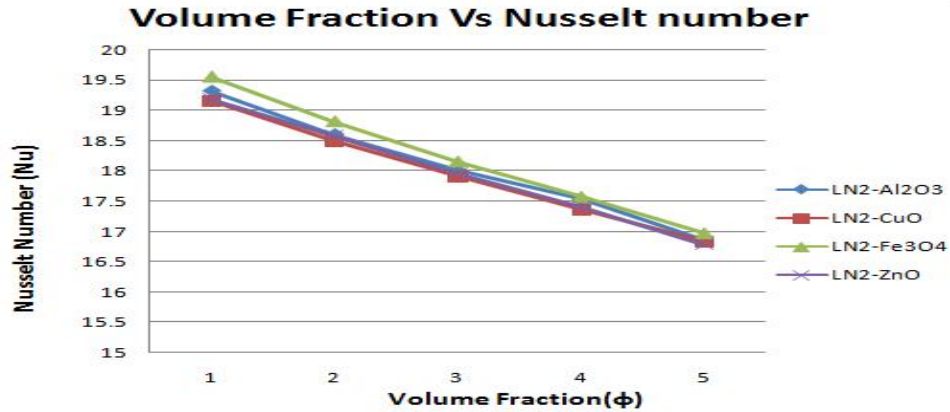


Fig-11: Volume fraction Vs Nusselt number

In Fig-11 there shows a decrease in Nusselt number as the volume fraction increases. As heat transfer coefficient h is directly proportional to nusselt number, it is clear that Fe₃O₄ has the maximum heat transfer rate as the volume fraction decreases followed by Al₂O₃, CuO and ZnO. The main reason expected for the decrease in heat transfer or the nusselt number is the slip between nanoparticle and the base fluid. Thus due to the disturbance of slip, the surface contact between nanoparticle and the base fluid does not held together. So thereby decreasing heat transfer rate.

E. Flow Analysis

This section analyses Reynolds number variations, effect of Pressure drop, friction factor etc. along with different volume fractions.

F. Reynolds Number

Reynolds number helps us to predict the fluid flow patterns, Here in this context its turbulent flow. Mainly Reynolds number depends upon the density of the nanofluids, as the density increases the Reynolds number increases. We have the equation:

$$Re = \frac{\rho v d}{\mu} \tag{10}$$

Here the density of the nanofluids is calculated from [11] and is shown below

$$\rho_{nf} = (1 - \phi)\rho_{bf} + \phi \rho_{np} \tag{11}$$

ρ_{nf} = Effective density of nanofluid

ρ_{bf} = Density of basefluid

ρ_{np} = Density of the nanoparticle

Φ = Volume fraction

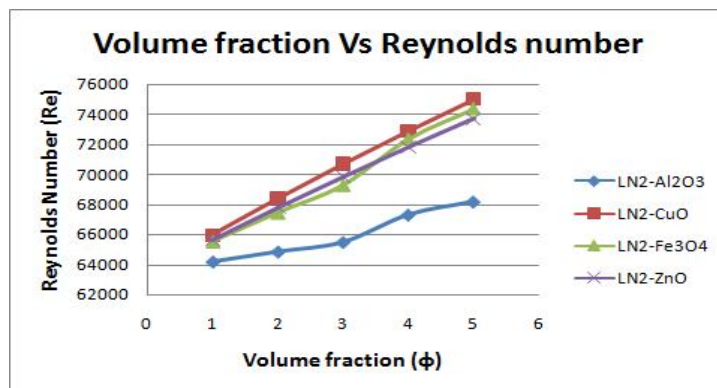


Fig-12: Volume fraction Vs Reynolds number

From the eqn-10, it is clear that as the density is directly proportional to Reynolds number. Also from eqn-11, volume fraction is also proportional to density. Thus from fig-12 it is understood that the CuO nanofluid mixed nanofluid has the highest Reynolds number around 75000, due to its higher density followed by Fe3O4, ZnO and Al2O3.

G. Friction factor

Friction factor is the measure of shear stress imparted by the turbulent flow on the walls of pipe. Friction factor depends on the roughness of the pipe and the Reynolds number. Here we can neglect the roughness of the pipe and consider the Reynolds number. Reynolds number is inversely proportional to friction factor i.e as the Reynolds number increases the friction factor reduces. Friction factor is calculated using the formula:

$$f = \frac{8 \tau_w}{\rho V^*2} \tag{12}$$

f = Friction factor

τ_w = Shear stress at walls

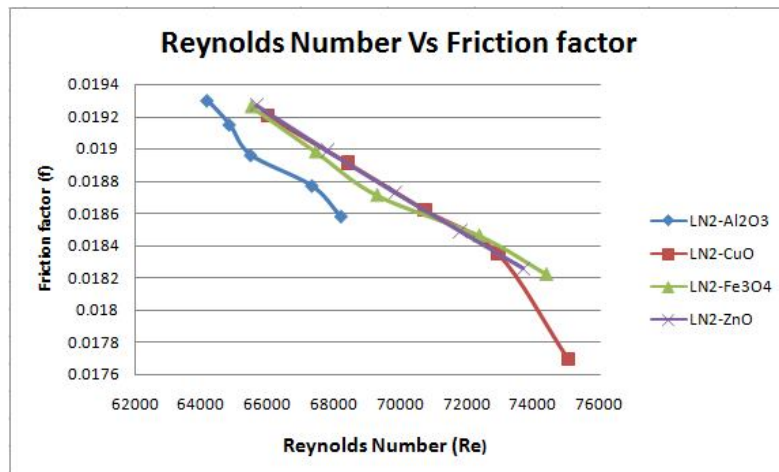


Fig-13: Reynolds number Vs Friction factor

Earlier it is shown that as the volume fraction increases it increments the Reynolds number. Therefore it can be finalized that Friction factor is a function of volume fraction also. Here from Fig-13, Friction factor is low for CuO nanofluid followed by Fe3O4, ZnO and Al2O3.

H. Pressure Drop

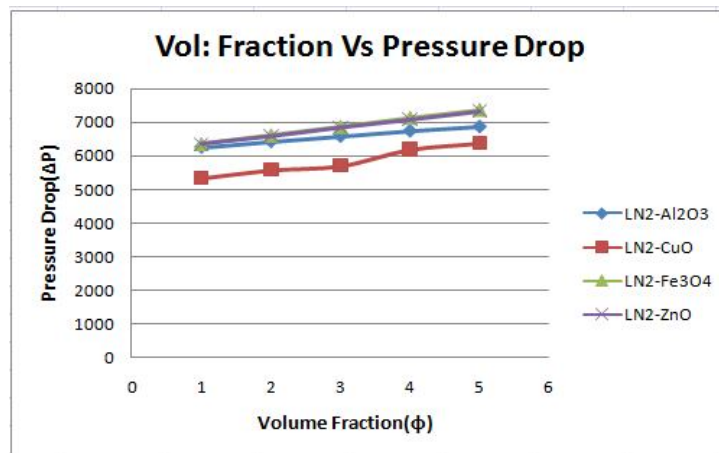


Fig-14: Volume fraction Vs Pressure drop

In this, pressure drop profiles of different nanofluids are plotted along with five volume fractions. In the above fig-14, it can be concluded that as the volume fraction increases the pressure drop increases. The pressure drop of nanofluids depend upon the

density and the diameter of the nanoparticle used. But in the fig-14 shows that CuO has the least pressure drop even though its density is high. The main reason is that here the diameter of the CuO is assumed to be 60 nm and others ranging from 38-40 nm. Thus the diameter increases it decreases the heat transfer rate due to the fact that the contact region between the nanoparticle and the base fluid reduces, on the other way increment in the diameter decreases the pressure drop and viscosity. As the diameter increases the quantity of the nanoparticles to be pumped decreases and thereby decreasing the pressure drop.

X. CONCLUSION

CFD simulations are carried out on a turbulent Mixed Convection heat transfer for LN2 mixed Al₂O₃, CuO, Fe₃O₄ and ZnO along with different volume fractions so as to perform the heat transfer and pressure drop analysis has been presented here. Influence of volume fraction on nanofluids have shown major variations in heat transfer and pressure drop analysis. Based on the results obtained from the numerical analysis the following conclusions are made:

- A. Among the nanofluids tested, Fe₃O₄ has the highest effective thermal conductivity value. Due to the higher thermal conductivity for the Fe₃O₄ nanoparticle, followed by Al₂O₃, CuO, ZnO.
- B. It can be concluded that the heat transfer coefficient decreases with increase in volume fraction. Thus from the volume fraction and heat transfer coefficient profile it is clear that the h value is higher for Fe₃O₄ based nanofluid. Here it's a developing flow so the boundary layer thickness increases reducing the heat transfer coefficient. Larger the coefficient easier the heat is transferred.
- C. Nusselt number is higher for Fe₃O₄ based nano fluid followed by Al₂O₃, ZnO and CuO. Increase in Nusselt number indicates increase in heat transfer rate. Overall as the volume fraction increases there shows decrease in heat transfer basically due to the slip between the nanoparticle and the base fluid.
- D. It is observed that friction factor decreases with increase in Reynolds number. Thus the friction factor is low for CuO based nanofluids followed by Fe₃O₄, ZnO and Al₂O₃. Friction factor depends on the roughness of pipe, diameter and density of the nanoparticle.
- E. Finally from the pressure drop profile plotted with volume fraction, shows that as the volume fraction increases the pressure drop increases. Here tested the pressure drop is low for CuO nanofluid due to the decrease in diameter of CuO nanoparticle. Also pressure drop depends on the density of the nanoparticles as the density decreases pressure drop decreases thus followed by Al₂O₃, ZnO, Fe₃O₄ respectively.

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