Proc. of the Intl. Conf. on Advances In Engineering And Technology - ICAET-2014

ISBN: 978-1-63248-028-6 doi: 10.15224/ 978-1-63248-028-6-03-84

Tribological properties and stabilization study of surfactant modified MoS_2 nanoparticle in 15W40 engine oil

[Jamale Sonali , N.Sandhyarani and V.Sajith]

***Abstract*— One of the methods commonly employed for enhancing the lubricity of oil is the addition of solid lubricant nanoparticles, possessing lamella structure, in it. Even though higher concentration of nanoparticles will lead to better reduction in the friction and wear, stability of nanoparticle added oil has to be ensured to prevent the sedimentation of the nanoparticles, especially at higher temperatures. Present work mainly focuses on the stability of MoS_2 nanoparticles in engine oil. MoS_2 nanoparticles were synthesized by wet chemical synthesis method and were mixed in the engine oil (15W40), with the help of a standard ultrasonic shaker. Sodium dodecyl sulfate was used as surfactant to improve the stability of nanoparticle added oil. Optimum concentration of Sodium dodecyl sulfate in engine oil was determined by bubble pressure method. Stabilization study at different temperatures was done by using DLS. The properties of nanoparticle added oil such as viscosity, pour point, flash and fire point were measured as per ASTM standard methods.**

***Index Terms*—MoS_2 nanoparticles, Stability, Viscosity.**

I. Introduction

The primary function of lubricants is to control friction, wear, and surface damage of a system that contains machine elements, such as gears and bearings and the secondary function is to prevent corrosion and to scavenge heat, dirt, and wear debris. There are numerous lubricant properties that are important for the end-user applications .The most important properties, as well as the most often used for lubricant characterization is the tribological properties. Even a surface which appears to be flat, on a millimeter scale it may contain micrometer scale asperities. If two surfaces are in contact, only these asperities really touch each other. Friction is due to the interaction between the asperities of the different surfaces and the resulting energy dissipation is due to the interaction of these asperities. Wear is mainly due to relative motion between that surface and a contacting medium and is defined as damage to a solid surface that generally involves progressive loss of material. Reduction of friction and wear in various parts of automobiles such as engine components and transmission system is essential for minimizing the power loss.

Miss. Jamale Sonali(*Author*)
Dr. V. Sajith.
Dr. N. Sandhyarani
NIT Calicut
India

Various parts of automobiles are lubricated by the use of lubricating oil and grease, depending upon the operating conditions. The properties of lubricating oil are modified by the use of various types of additives. Additives are chemical compounds added to lubricating oils to impart specific properties to the oils. The additives like viscosity index improver, anti-wear additive, friction reducer, rust/corrosion inhibitors take care of friction and wear properties and the additives pour point depressant, anti-foaming agent maintains oil properties. One of the methods commonly employed for enhancing the lubricity of oil is the addition of nanoparticles in it. One of the practical problems in the addition of solid lubricant nanoparticles in oil is its long term stability. Most of the work reported in the literature mainly focuses on the enhancement of the tribological behaviour of oil, immediately on the addition of nanoparticles in it, giving less chance for the sedimentation to set in [1]. However in the practical situation the agglomeration of nanoparticles leading to the sedimentation is of much importance. Even though higher concentration of nanoparticles will lead to better reduction in the friction and wear, it has to be ensured that the nanofluid i.e. nanoparticle added lubricating oil is stable throughout the operation [2-4]. Present work mainly focuses on the synthesis of MoS_2 nanoparticles and its addition in engine oil, while giving emphasis on the stability of the nanoparticle added oil. MoS_2 nanoparticles were synthesized by means of wet chemical synthesis method and were mixed in the engine oil (15W40) with the help of a standard ultrasonic shaker. Sodium dodecyl sulfate was used as surfactant to improve the stability of nanoparticle added oil. Stabilization study at different temperatures was done by using DLS. The properties of nanoparticle added oil such as viscosity, flash and fire point were measured by means of standard ASTM methods.

I. Experimental details

This section discuss the materials used in the present work, the method of synthesis and their characterization using different techniques such as TEM, XRD, EDS etc.

A. *Synthesis and characterization of MoS_2 nanoparticles*

The additive used in the present work is $MoS_{2,}$ which was synthesized by means of wet chemical synthesis method [4]. Ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$, citric acid $C_6H_8O_7$ and ammonium sulfide $(NH_4)_2S$ were used as precursors which were supplied from Alfa Aesar. Aqueous solution of 1:3 molar ratio of ammonium molybdate

Proc. of the Intl. Conf. on Advances In Engineering And Technology - ICAET-2014

ISBN: 978-1-63248-028-6 doi: 10.15224/ 978-1-63248-028-6-03-84

tetrahydrate and citric acid was prepared by stirring and maintaining solution at 90^oC. The pH value was adjusted to 4 by addition of suitable quantity of ammonium hydroxide. After the complete dissolution of all reactants 20 – 24 wt% aqueous solution of ammonium sulfide was added drop wise while heating. The heating was continued for two hours at 90^oC and the solution showed a change in color to brown. The solution was centrifuged at 10000 rpm for 15 min and the acquired precipitant was washed by using water three times.

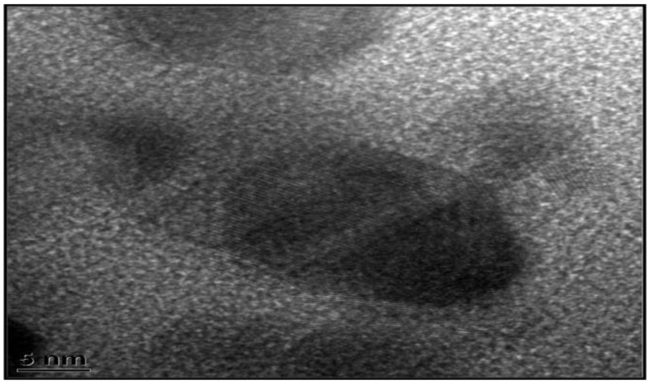

Figure 1. Lamellar structure of MoS_2 nanoparticles.

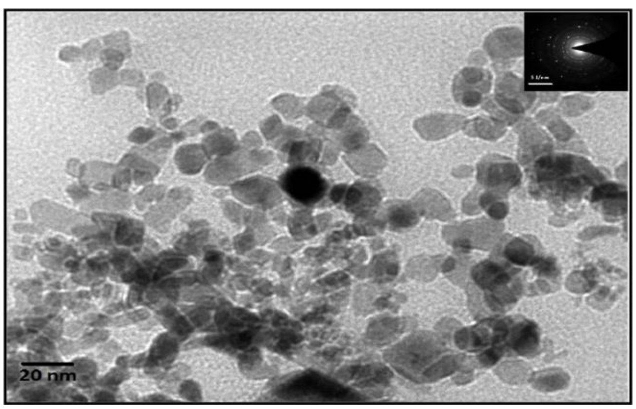

Figure 2. MoS_2 nanoparticles.

Precipitant was dried at 80 ^oC for 12hr and the black powder obtained was calcinated at 250^oC in argon gas atmosphere for 30min. The size, shape and structure of the powder were ascertained by using transmission electron microscopy (TEM). Fig. 1 shows the TEM image of lamellar structure of MoS_2 nanoparticles, which is mainly responsible for the reduction of friction coefficient as well as wear, when added in oil.Fig. 2 shows that the size of nanoparticle is less than 20 nm and shape is almost circular.

The powder was analyzed by using XRD, to validate the crystal structure. Fig. 3 shows the XRD pattern of MoS_2 nanoparticles. The XRD pattern obtained matched with the standard characteristic peak of amorphous structure. Elemental analysis of nanoparticle was done by Energy dispersive spectroscopy (EDX) and fig.4 shows the EDX pattern of MoS_2 nanoparticles. EDX spectrum of synthesized nanoparticle which revealed the weight and atomic percentage of each component present in the synthesized sample, as shown in table.1.which confirmed the presence of MoS_2 composition.

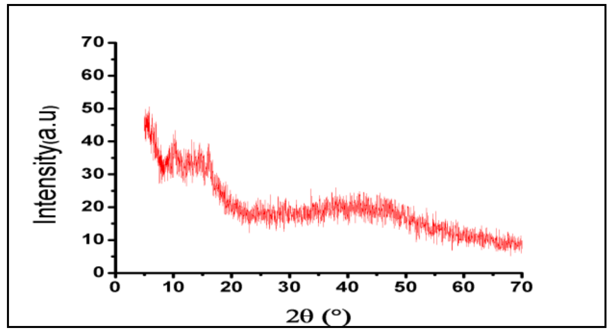

Figure 3. XRD pattern of MoS2 nanoparticles.

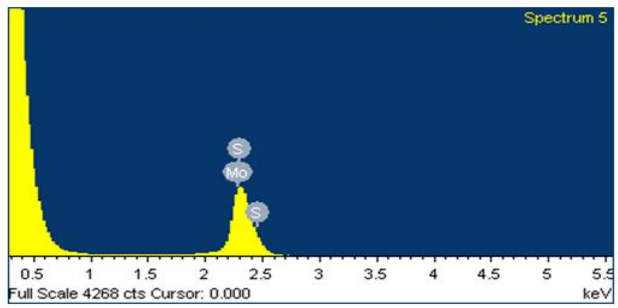

Figure 4. EDX pattern of MoS_2 nanoparticles.

TABLE I. WEIGHT AND ATOMIC PERCENTAGE OF ELEMENTS PRESENT IN SYNTHESIZED MOLYBDENUM DISULFIDE NANOPARTICLES

Element	Atomic%	Weight%
S	42.62	68.97
Mo	57.38	31.03

B. *Preparation of nanofluid*

Lubricating oil used was SAE engine oil (Mobil delvac 1300 super 15W-40, Exxon Mobil Company) was used as base oil which is typically, mineral base oil, widely used in automobile. The relative density of this oil is 874kg/m^3 at 15^oC. In present work two step method was followed for preparation of nanofluid. Required quantity of MoS_2 nanoparticles are weighed using an electronic balance and mixed with engine oil with the help of a standard ultrasonic shaker. The concentration of nanoparticle in oil was varied from 0.01 to 0.1 wt% of oil. The stabilization being a serious concern the stability of the nanoparticle added oil was improved by the addition of surfactant namely Sodium dodecyl sulfate (SDS). Sodium dodecyl sulfate was selected as surfactant as sulfur has good affinity towards the sulfur molecules present in MoS_2 nanoparticles. Bubble pressure

Proc. of the Intl. Conf. on Advances In Engineering And Technology - ICAET-2014

ISBN: 978-1-63248-028-6 doi: 10.15224/ 978-1-63248-028-6-03-84

method was used to find the optimum concentration of surfactant in oil, based on the measurement of surface tension on the addition of surfactant [5]. Addition of surfactant leads to a decrease in the surface tension initially and on the formation of micelle i.e. aggregate of surfactant molecules, a drastic change in the surface tension will be observed which corresponds to the optimum concentration. Further addition of surfactant will not lead to any reduction in the surface tension.

C. *Stability studies*

Stability studies of the nanoparticle added oil was done by the estimation of zeta potential, which is a measure of stability of nanofluid. Higher the zeta potential values higher will be the repulsive force between the nanoparticles and was measured by means of Dynamic Light Scattering system (Make: Malvern). Engine oil being highly viscous it is difficult to obtain zeta potential values accurately and hence oil was diluted by using hexane in the ratio 3.3:1, for the estimation of zeta potential. Zeta potential values were measured for the samples whose concentration was varied from 0.01 to 0.1 wt% of oil at two different temperature 25 ^{o}C and 35^{o}C.

D. *Property measurement*

Kinematic viscosity of the nanoparticle added oil was measured by means of Brookfield DVIII ultra programmable rheometer as per [ASTM-D2983]. Flash and fire point nanoparticle added oil was measured by means of Cleveland Open cup Flash and Fire point apparatus, as per ASTM[92] and was compared with that of base oil. Also pour point measured as per ASTM [D5853] and compared with base oil.

II. Results and discussion

A. *Thermal stability*

As the temperature of engine oil may reach to a range of 30 ^{o}C to 200 ^{o}C, it is essential to ensure the thermal stability of MoS_2 nanoparticle added in the oil, while in operation. The thermal stability of nanoparticle was analyzed by using Thermogravimetric Analysis (TGA) of the sample before and after calcination. Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time, as the sample specimen is subjected to a controlled temperature program, in a controlled atmosphere. Fig. 5 shows the TGA thermograph of MoS_2 nanoparticles and it was observed that nanoparticles without calcination undergo 71% weight loss at 350°C while, for nanoparticles after calcination only 12% weight loss was observed at 375°C. Thermal stability of nanoparticle after calcination improved because, all water molecules got evaporated below 200 °C. It can thus be concluded that, the particles are thermally stable enough, to be used as an additive for lubrication.

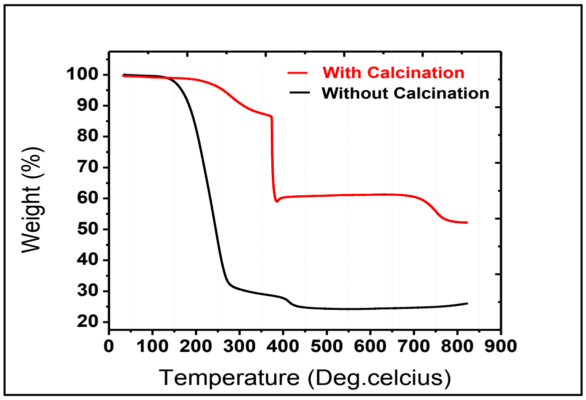

Figure 5. TGA thermograph of MoS_2 nanoparticles.

B. *Surfactant concentration optimization*

Optimum concentration of surfactant in lubricating oil was determined based on the estimation of point of formation of micelle. Once the micelle is formed in the solution on the addition of surfactant, a drastic change in the surface tension value will be observed, which can be measured. Bubble pressure method was used to determine variation in the surface tension with variation in the concentration of surfactant from 0.01 to 0.08 wt% of oil. Fig. 6 shows the deflection in tube of the bubble pressure apparatus, proportional to the surface tension with concentration of surfactant. Minimum value of deflection was observed for surfactant concentration of 0.03 wt% of oil, where as drastic change in the trend was observed.

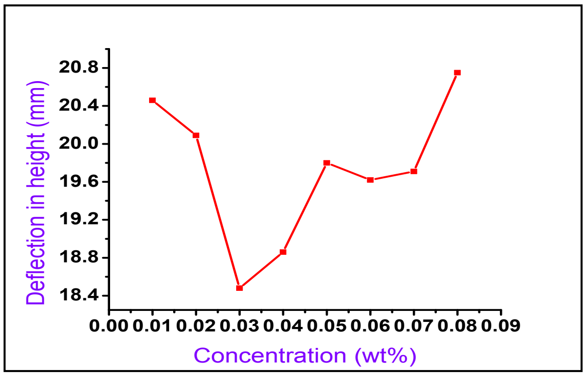

Figure 6. Deflection in pressure with concentration.

C. *Stability studies*

Stability studies of the nanoparticle added oil was done by the estimation of Zeta potential, by means of Dynamic Light Scattering system (Make: Malvern). Nanoparticle added lubrication oil was diluted by means of hexane as it is difficult to measure the Zeta potential since oil have high viscosity. The concentration of nanoparticle in oil was varied from 0.01 to 0.1 wt % of oil, while fixing the concentration of surfactant as 0.03 wt% of oil. Zeta potential of the samples was

Proc. of the Intl. Conf. on Advances In Engineering And Technology - ICAET-2014

ISBN: 978-1-63248-028-6 doi: 10.15224/ 978-1-63248-028-6-03-84

measured at two different temperatures of 25 °C and 35°C and Fig. 7 shows the variation of Zeta potential with the concentration of MoS_2 nanoparticles in lubricating oil. The maximum value of zeta potential was obtained at 0.07 wt% of oil, which corresponds to the optimum concentration of MoS_2 nanoparticles in oil having maximum stability.

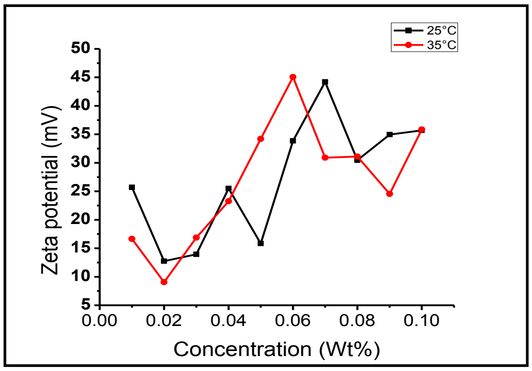

Figure 7. Variation of Zeta potential with MoS2 nanoparticle concentration.

D. *Properties study*

Viscosity – The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress and it also governs the sealing effect of oils. Effect of MoS_2 nanoparticles on viscosity of the oil was studied by means of Brookfield DVIII ultra programmable rheometer. Viscosity of base oil was determined in the temperature range 30°C to 60°C. MoS_2 nanoparticles of concentration 0.07 percentage by weight of oil, was added in oil along with the surfactant and the viscosity was measured in the same temperature range. Fig. 8 shows the variation of viscosity of nanoparticle added oil and base oil, with temperature. Viscosity of oil on addition of nanoparticle increased by 3% at 30°C and percentage change in viscosity with the addition of nanoparticles decreases with temperature as shown in Fig. 9.

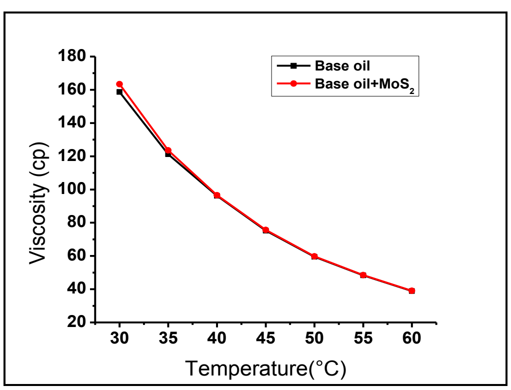

Figure 8. Variation of viscosity with temperature.

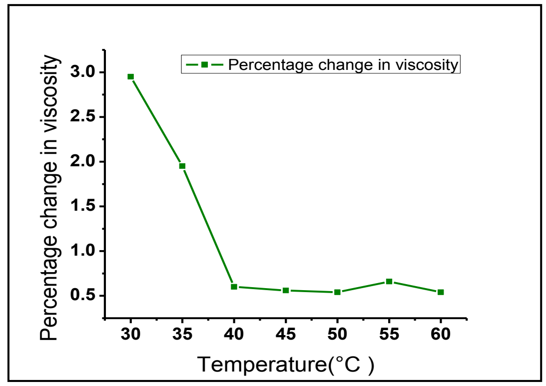

Figure 9. Variation of percentage change in viscosity with temperature.

2. Flash and fire point

Flash point is defined as a minimum temperature at which the given oil evolves just sufficient vapor to form inflammable mixture with air, as shown by the formation of a momentary flame (flash) when an external source of fire is brought in contact with the vapor. The fire point is the minimum temperature at which the oil vapor will continue to burn instead of just flashing. Flash point and fire point is important primarily from a fuel-handling standpoint. It was observed that, on the addition of MoS_2 nanoparticle in oil, flash and fire point increased by 5°C as shown in Fig. 10 and Fig. 11.

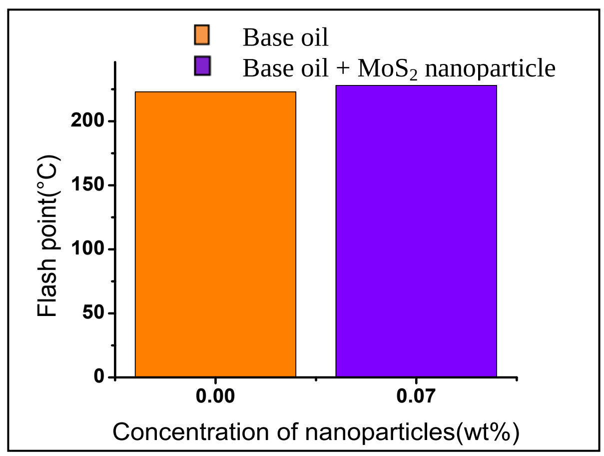

Figure 10. Comparison of Flash point.

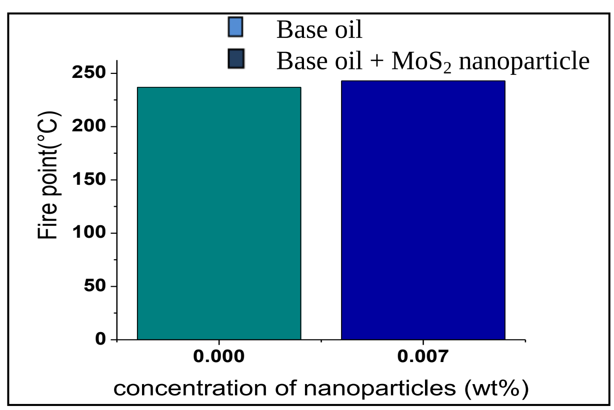

Figure 11. Comparison of Fire point.

Proc. of the Intl. Conf. on Advances In Engineering And Technology - ICAET-2014

ISBN: 978-1-63248-028-6 doi: 10.15224/ 978-1-63248-028-6-03-84

3. Pour point

The pour point of a liquid, is the temperature at which it becomes semi solid and loses its flow characteristics. Pour point plays important role in the start of vehicle and if fluid unable to flow easily can cause higher wear. It was observed that, addition of MoS_2 pour point temperature improved by 5°C as shown in fig. 12. Addition of MoS_2 nanoparticles may delay the formation of wax crystals on cooling oil and hence its Cloud point.

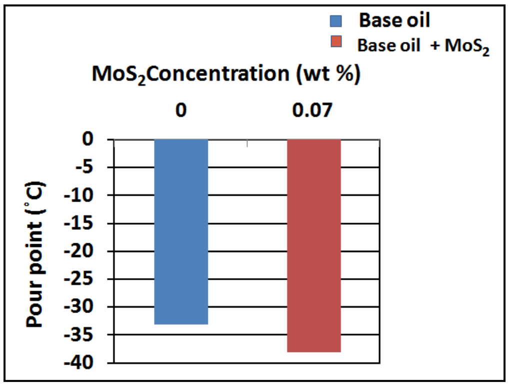

Figure 12. Comparison of Pour point.

CONCLUSION-

Present work mainly focuses on the synthesis of stable MoS_2 nanoparticles in oil suspension and its effects on various properties. MoS_2 nanoparticle of size around 20 nm were synthesized by using wet chemical synthesis. Sodium dodecyl sulfate of concentration 0.03 % by weight of oil, was used as surfactant to improve the stability of nanoparticle added oil. Stabilization studies using DLS showed an optimum concentration of MoS_2 nanoparticles as 0.07 % by weight, for maximum stability. A very slight improvement in viscosity of oil was obtained on the addition of MoS_2 nanoparticles. The flash and fire point, pour point increased by 5°C and cloud point decreased by 5°C on the addition of nanoparticles in oil.

References

[1] Chinas-Castillo,F. and Spikes,H.A., "Mechanism of action of colloidal solid dispersions," Trans. ASME 125,pp. 552-557, 2003.

[2] Zhou,J.,Yang,J.,Zhang,Z.,Kliu,W. and Xue,Q.,"Study on the structure and tribological properties ofsurface modified Cu nanoparticles," Mater. ResearchBulletin 34, pp. 1361-1367, 1999.

[3] Wu, Y.Y., Tsui W. C. and Liu, T.C., "Experimentalanalysis of tribological properties of lubricating oil withnanoparticle additives," Journal of Wear, pp. 08-021, 2006.

[4] Ye, P.,Jiang,X.,Li,S. and Li,S., "Preparation of NiMoO2S2 nanoparticle and investigation of its tribological behavior as additive in lubricating oils," Journal of Wear 253, pp. 572–575, 2002.

[5] C.D.Dushkin, Tz. Ilive ,"Dynamic surface tension micellar solution studied by maximum bubble pressure method" colliod polymer science 272,pp-1157-1165, 1994.

About Author (s):

Sonali jamale received her bachelor's in mechanical engineering from S.R.T.M university nanded. she is currently pursuing M.Tech in nanotechnology from NIT Calicut

Dr. N Sandhyraani got her MSc. from School of Chemical Sciences, M. G. University and her PhD from IIT Madras. She is post doctoral associate at Cornell University and Notre Dam University, USA. She is also a visiting researcher at Pohang University of Science and Technology, South Korea. Her research interests include Nanoscience and nanotechnology, Nanobiotechnology, Biosensors, Surface Chemistry.

Dr. V Sajith received his BTech from University of Calicut -1997. He did Diploma in management IGNOU New Delhi -2003. He received his M.Tech from I.I.T. Madras- 2005 and his PhD from NIT Calicut in 2010. He is currently assistant Professor at School of Nano Science and Technology, NIT Calicut. His research interests are Optical Measurements, Nano fluids Automobile Engineering and Heat Transfer