

41 State-of-the-art review on water-based nanofluids for low temperature  
42 solar thermal collector application

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55 **Abstract**

56 In the last decade, nanofluids have set significant milestones as efficient working fluids in the  
57 field of solar energy conversion to meet rising energy demand. Research on thermophysical  
58 properties, long-term stability, and rheology is progressing to achieve effective practical  
59 deployment of nanofluids in renewable solar photo-thermal energy conversion sectors (i.e.,  
60 solar collectors). Nonetheless, researchers and engineers are having a difficult time coping with  
61 nearly infinite culpable variables influencing the output of various types of nanofluids. This  
62 paper aims to provide an up-to-date analysis of the developments and challenges of widely  
63 used water-based nanofluids, with a focus on formulation methods, main properties  
64 (thermophysical, stability, and rheological), and effective implementation in low temperature  
65 solar collector systems. Previous experimental and numerical studies on the subject have been  
66 compiled and thoroughly scrutinized, providing crucial phenomena, mechanisms, flaws, and  
67 responsible parameters for achieving stable and optimized thermal properties that integrate  
68 with heat transfer performance. It has been discovered that optimizing the critical factors leads  
69 to superior behavior of the nanofluids, which results in improved thermal efficiency of the solar  
70 collectors. Finally, emerging concerns are identified, as are potential recommendations to  
71 resolve existing problems in the field for future advancement that would mobilize rapid  
72 progress and practical engineering use of water based nanofluids on solar collectors.

73 **Keywords:** Nanofluids, Thermophysical Properties, Stability, Rheology, Solar Collectors.

## Nomenclature

### Abbreviations

NF	Nanofluid	DSC	Dynamic Scanning Calorimetry
NP	Nanoparticle	DLVO	Derjaguin Landau Vewey and Overbeek
BF	Base Fluid	ZP	Zeta potential (mV)
HTF	Heat Transfer Fluid	EDL	Electrical double layer
SC	Solar Collector	IEP	Isoelectric Point
TC	Thermal conductivity	FPSC	Flat plate solar collector
$d_p$	Particle diameter (nm)	ETSC	Evacuated tube solar collector
ECS	Energy Conversion System	DASC	Direct absorber solar collector
CNT	Carbon Nanotube	PV/T	Photovoltaic/thermal solar collector
SWCNT	Single-walled carbon nanotube	UV-Vis	Ultraviolet–visible spectroscopy
MWCNT	Multi-walled carbon nanotube	MDS	Molecular dynamic simulation
EG	Ethylene glycol		
SDS	Sodium Dodecyl Sulphate		
SDBS	Sodium Dodecyl Benzene Sulphonate	$\mu$	Dynamic viscosity (Pa.s)
CTAB	Cetyl Trimethyl Ammonium Bromide	$\varphi$	Particle concentration (%)
CTAC	Cetrimonium chloride	$\zeta$	Zeta potential (mV)
GA	Gum Arabic	$\alpha$	Absorptivity
PVP	Polyvinylpyrrolidone	$\varepsilon$	Dielectric Constant
DDC	Distearyl Dimethylammonium Chloride		
PLS	Potassium Lauryl Sulphate		
k	Thermal conductivity (W/m.K)	nf	Nanofluid
$c_p$	Specific heat capacity (Kj/kg.K)	bf	Base Fluid
T	Temperature (K)	np	Nanoparticle

### Greek Letters

### Subscripts

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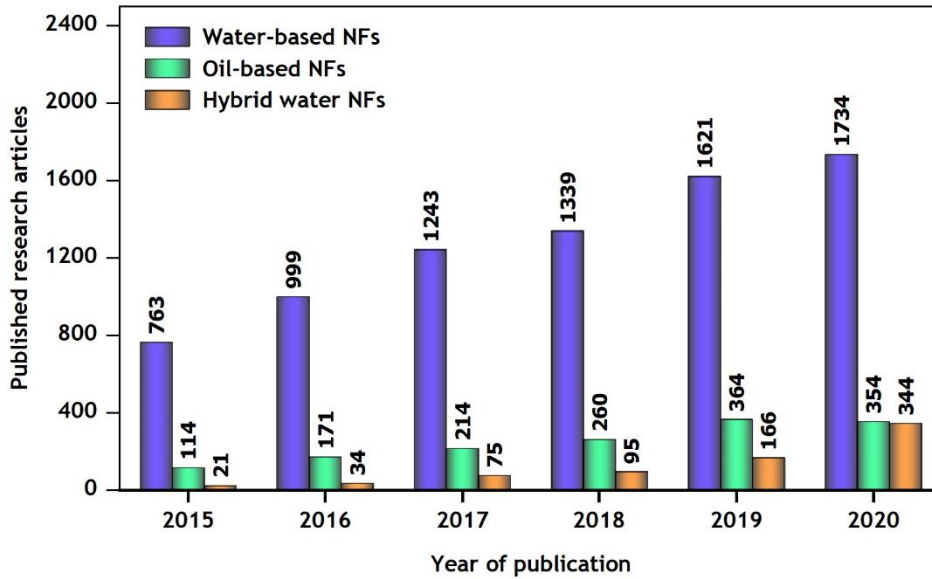
## 75 1. Introduction

### 76 1.1. Overview on nanofluid

77 Nanofluids (NFs) are superior colloids formed by dispersing nanoscale (1-100 nm) materials  
78 in pure base fluid (BF), which is usually a liquid. Masuda, et al. [1] synthesized nanoscale  
79 suspensions for the first time experimentally in 1993, and Choi and Eastman [2] named them  
80 as ‘nanofluid’ in 1995. Due to remarkably extra-large surface area and dominant characteristics  
81 of dispersed solid particles of nanomaterials relative to BFs, NFs convey superior heat transfer  
82 properties [3]. The surfaces of nanoparticles (NPs) regulate their properties rather than their  
83 volume, providing efficient and flexible thermal, optical, mechanical, and electrical properties

84 [4]. The addition of very low weight concentration of these NPs into conventional heat transfer  
85 fluids (HTFs) remarkably enriches essential thermo-physical, optical, and chemical features of  
86 the fluids. The important thermo-physical properties of HTFs, such as conductive heat transport  
87 and specific heat capacity, have a significant impact on the thermal energy efficiency of cooling  
88 fluid-based thermal energy storage and energy conversion systems. Numerous studies have  
89 confirmed a considerable escalation in thermal conductivity, specific heat capacity and heat  
90 transfer characteristics of nanofluids in comparison with their BFs [5-7]. Beyond all the  
91 promising NF characteristics, colloidal stability of suspended NPs in main fluid emerges as the  
92 most difficult barrier to overcome, as particles appear to congregate over time. The primary  
93 factor in the sustainable use of NFs in various heating and cooling applications is the  
94 maintenance of a long suspension period [8]. Furthermore, the excellent properties and  
95 suspension stability of NFs are dependent on key parameters such as suspension stability, as  
96 well as types of BFs, NPs, particle concentration ( $\varphi$ ) and morphology that can cause significant  
97 divergence in thermal characteristics.

98 Water based nanosuspensions are the most researched and used class of nanosuspensions due  
99 to the numerous advantages of water as a BF, including higher thermal conductivity and heat  
100 capacity than other BFs (i.e., oils and glycols), extreme availability, simplicity, and commercial  
101 prospects. Water-based NFs are suitable for low-temperature thermal applications up to 90°C,  
102 and they are particularly well-suited for use as HTF in solar energy harvesting due to their  
103 advanced photo-thermal properties, relatively good thermal stability, and sustainable nature as  
104 compared to other traditional toxic liquids such as ethylene glycol, ionic liquids, and so on.  
105 Aside from regular NF (i.e., dispersion of a single distinct nanomaterial in the BF), the hybrid  
106 category of NF (i.e., dispersion of two distinct nanomaterials) has piqued the interest of  
107 researchers for further advancement [9]. Extensive research articles have been published in  
108 recent years that investigate the properties, factors, and future potential of water-adopted NFs  
109 in practical fields such as solar thermal collectors. **Fig. 1** represents previous publications  
110 reported on water-based NF, which considerably outnumbers other variants of NF in recent  
111 years (2015-2020), indicating huge interest in water-based due to its unique properties.



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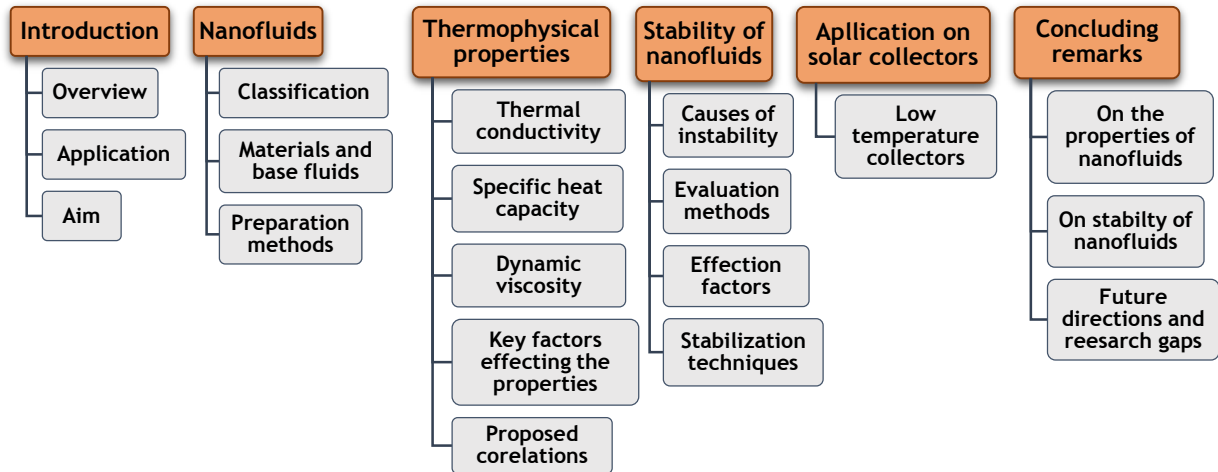
113 **Fig. 1.** Published research articles on water, oil and hybrid based nanofluids from year 2015  
 114 to 2020 (Source of data: Scopus, using keywords: Water nanofluids, Oil nanofluids and  
 115 Hybrid water nanofluids).

116 **1.2. Application of nanofluids on solar thermal collectors**

117 Various water based NFs are commonly applied in thermal and thermo-electric heating-cooling  
 118 systems, including but not limited to heat exchangers [10], automobile cooling [11],  
 119 photovoltaic cooling [12], building heating [13], industrial process heating, thermo-electric  
 120 cooling [14], refrigeration systems [15].

121 However, the dearth of sustainable energy resources has become a sophisticated challenge to  
 122 meet the ever-growing global energy demand alongside depletion of carbon-based fossil energy  
 123 resources and their constant threat to the environment. In this context, experts are focusing on  
 124 the search for alternative renewable energy sources that will be adequate to meet the massive  
 125 energy demand in the future. Since the energy demand will keep escalating in the future, one  
 126 way to compensate for the energy scarcity is by utilizing sustainable renewable energy sources.  
 127 Solar energy is one of the most convenient, pollutant-free, sustainable, renewable and  
 128 abundantly available energy resources to harvest clean thermal energy [16]. A plethora of  
 129 research is being conducted on solar energy systems by substituting traditional HTFs with NFs  
 130 to advance the thermal energy conversion efficiency [17-19]. Solar collector (SC) systems are  
 131 one of the emerging renewable energy sectors that is rapidly expanding due to the development  
 132 of NFs as advanced working fluids [20, 21]. SCs are engineered systems to harness solar  
 133 radiation and produce sustainable energy that can be utilized in different domestic and

134 industrial heating and cooling processes [22]. Mahian, et al. [23] recently published a review  
 135 on the advancement of NF-based renewable energy conversion systems (i.e., solar thermal  
 136 collectors) and their environmental effects. Over the last few years, research and development  
 137 have resulted in a significant increase in the energy efficiency of various SC systems operated  
 138 with NFs replacing traditional BFs [17].



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**Fig. 2.** Overview of layout of this review paper.

141 ***1.3. Aim of this review***

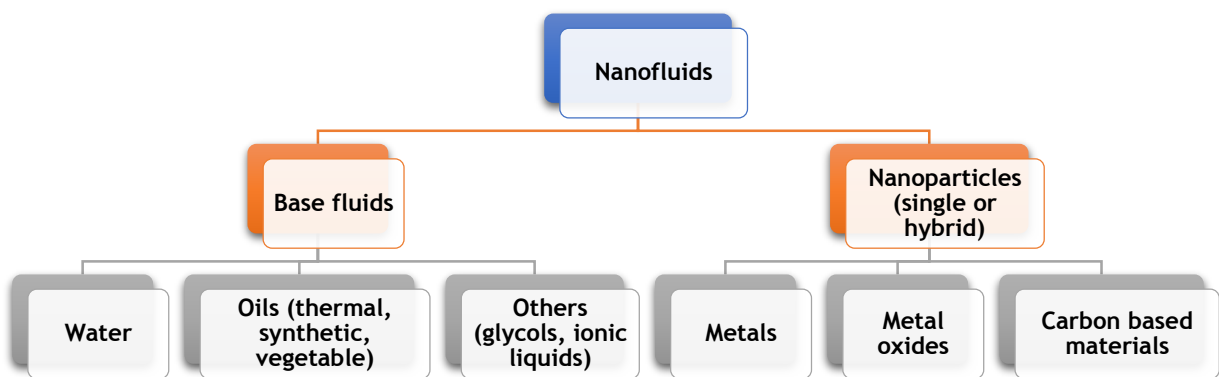
142 The aim of this paper is to provide a detailed state-of-the-art analysis on research developments  
 143 in thermo-physical properties of water-based NFs, as well as suspension stability, and potential  
 144 implementation in low temperature SC technologies. A few articles [24, 25], attempted to  
 145 provide a general overview of different properties (thermal and optical) and applications of  
 146 NFs on SCs, while others while others [8, 26] endeavored to address NF stability issues. Yet,  
 147 there are no comprehensive review that particularly intends to articulate overall advances on  
 148 most frequently applied water-based NFs characteristics, stability mechanisms, limitations, and  
 149 applications on SCs. Therefore, the authors are inspired to provide a much needed, detailed,  
 150 and up-to-date analysis of the thermo-physical properties (thermal conductivity, cp, and  
 151 rheology), stability behavior (mechanism, critical parameter, and evaluation techniques), and  
 152 implementation of the NFs on low temperature thermal SCs to assess their effectiveness. Since  
 153 water-based NFs are best suited for low-temperature solar collectors, the detailed NF  
 154 characterization is thoroughly analyzed and compiled from preparation to implementation on  
 155 SCs to provide a clear understanding of the topic based on extensive previous research.  
 156 Furthermore, potential properties of NFs are comprehensively discussed, providing causes and  
 157 effects of several critical parameters and insights of suspension stability are reported. The

158 application section critically examines the performance of several water-based NF-operated  
 159 SCs, scrutinizing influential factors to assess the overall impact of the NFs on system  
 160 performance. Based on the review of extensive experimental and numerical studies,  
 161 challenging issues and research gaps are identified, important conclusions are drawn based on  
 162 present developments and recommendations are rendered for further advancement in the field.  
 163 This study offers an essential step towards robust development and understanding of water-  
 164 based NFs for implementation in photothermal ECS i.e., SCs. The layout of the article is  
 165 demonstrated in **Fig. 2**.

166 **2. Nanofluids**

167 **2.1. Base fluid and nanomaterials**

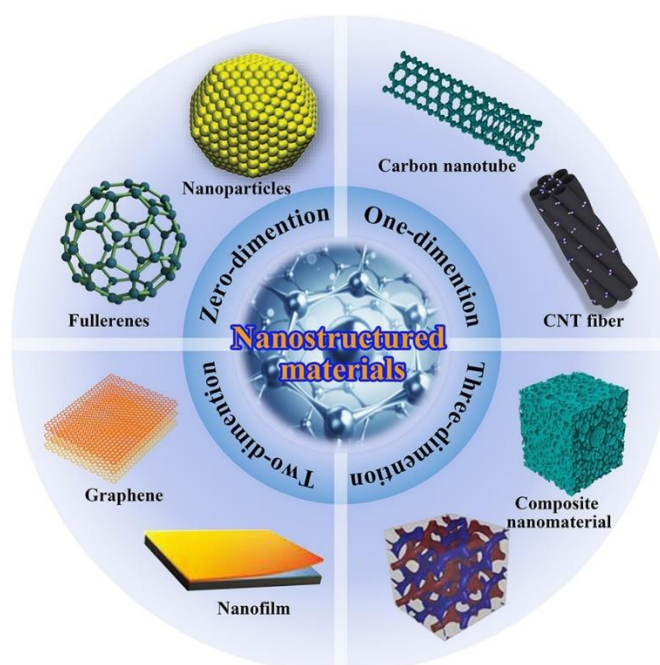
168 NFs are developed diffusing nanostructured materials at nanoscale range into pure  
 169 conventional working fluids. The NF classification based on extensively used BFs and  
 170 nanomaterials is depicted in **Fig. 3**. Water, oils (thermal, synthetic, and vegetable), glycols  
 171 (ethylene and propylene), and ionic liquids have all been used as dispersion medium in the  
 172 formulation of NFs based on thermal systems and working temperature ranges. Each of the  
 173 fluids has some advantages and drawbacks on their own while implemented on thermal  
 174 systems. Water-based NFs are superior to other BFs in low temperature applications due to  
 175 their superior thermo-physical properties, low cost, and availability. In contrast, for medium to  
 176 high temperature thermal systems, other fluids (oils, glycols, and liquid salts) are generally  
 177 utilized.



178  
 179 **Fig. 3.** Classification of nanofluids in terms of base fluids and nanoparticles.

180 Suspended nanomaterials are the most distinctive feature of NFs as these particles possess  
 181 unique thermal and optical properties and significantly impact the characteristics of BFs.  
 182 Nanomaterials have at least one dimension in the nanometer range with high conductive surface

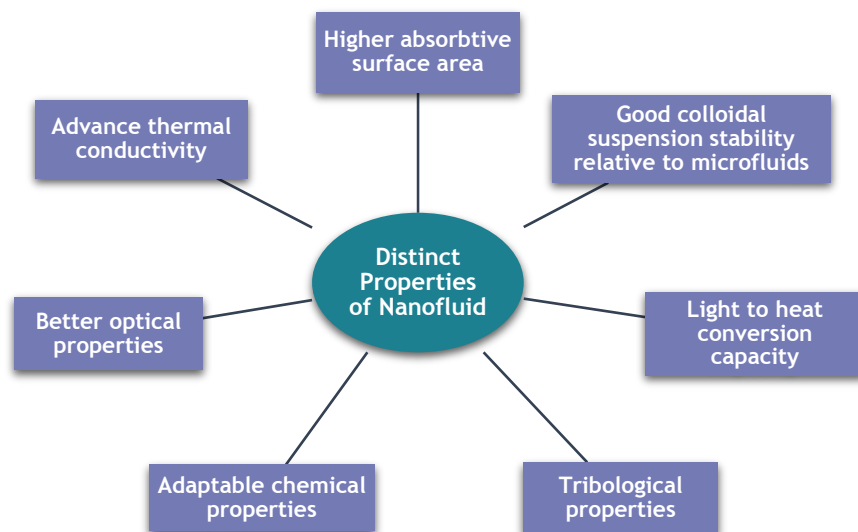
183 to volume ratio, superior physical, chemical, and mechanical properties relative to their bulk  
 184 form. Nanomaterials can be metallic (e.g., Ag, Cu, Ti, Fe, Al), polymers, ceramics, non-  
 185 metallic (CuO, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) and carbon-based (SWCNT, MWCNT, graphene, MXene)  
 186 materials which are formed in various geometrical shapes such as spherical, cylindrical, rod-  
 187 like, and plate-like. In terms of their dimensions at the nanoscale, nanostructured materials can  
 188 be divided into four categories: (a) zero-dimensional (0-D) nanomaterials with no dimensions,  
 189 such as nanoparticles and graphene/carbon quantum dots; (b) one-dimensional (1-D)  
 190 nanomaterials with one dimension at the nanoscale range, such as nanotubes and nanowires;  
 191 (c) Two-dimensional (2-D) nanomaterials with layered nanofilms such as graphene and MXene  
 192 nanoflakes; (d) Bulk three-dimensional (3-D) nanomaterials that are confined at nanoscale  
 193 dimensions such as bulk powder, composite nanomaterials and multi-nanolayers. **Fig. 4**  
 194 represents an illustration of nanostructured materials based on their dimensions at nanoscale  
 195 length. Colloidal suspension comprises of a BF and one of those types of particles defined as  
 196 NF. If the suspension is made up of more than one type of dispersed particle in fluid, it is  
 197 referred to as hybrid NF [27]. Many studies have been published in the literature in which  
 198 various types of nanomaterials are combined with water to characterize their potency in  
 199 practical applications. The specifics of the NFs formulation and characterization will be  
 200 covered in subsequent parts of this study.



201  
 202 **Fig. 4.** Demonstration of nanomaterials with unique dimensions at the nanoscale range [4].

203 **2.2. Formulation of nanofluids**

204 NFs are considered advanced thermo-fluids due to their enhanced thermophysical properties,  
205 including conductive heat transfer coefficient, thermal conductivity, thermal diffusivity, and  
206 heat storage capability, as compared to conventional working fluids such as water and oils.  
207 Exceptional properties of NFs are depicted in **Fig. 5**, which are considered necessary in various  
208 applications and to perform efficiently according to their advantages over microfluids. The  
209 formulation of NF suspension is an important step because it can influence a few main  
210 parameters, including suspension stability and thermo-optical properties. The first stage of NF  
211 formulation includes the synthesis of nanostructured materials, which are later combined with  
212 BF to produce a solid-liquid suspension. In nanotechnology, many physical, chemical, and  
213 physiochemical techniques are frequently used to synthesize NPs. Furthermore, during the  
214 synthesis process, NPs are assessed using various systematic approaches such as transmission  
215 microscopy, infrared spectroscopy, X-ray diffraction, and Raman spectroscopy.  
216 To prepare stable NFs, two standard methods are used: the single-step method, which  
217 incorporates two separate procedures of nanoparticle fabrication and dispersion into BF  
218 concurrently, and the two-step method, which integrates two separate processes of particle  
219 fabrication followed by dispersion using several stabilization techniques for uniform dispersion  
220 of solid particles. Both fundamental approaches possess several advantages and drawbacks in  
221 terms of flexibility, thermophysical characterization, and economics. The major challenge in  
222 nano powder dispersion technology is NP sedimentation over time. Although the single-step  
223 technique is stated to generate stable NFs, it is discovered that thermal properties are more  
224 predominant when fluids are fabricated in two steps [28]. The following sections address these  
225 methods in greater detail.



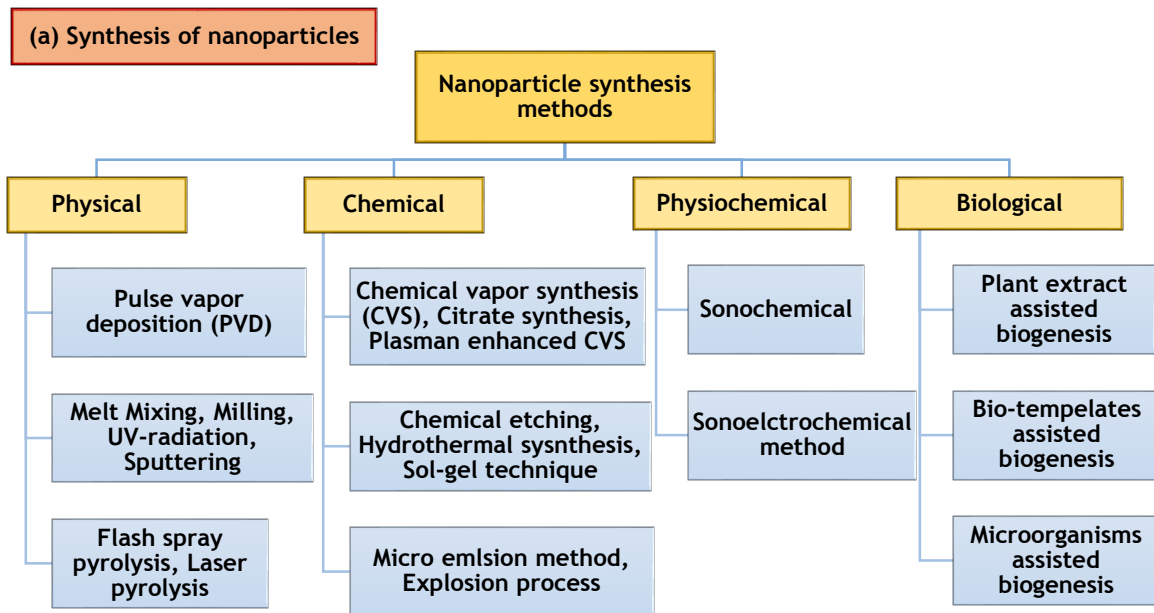
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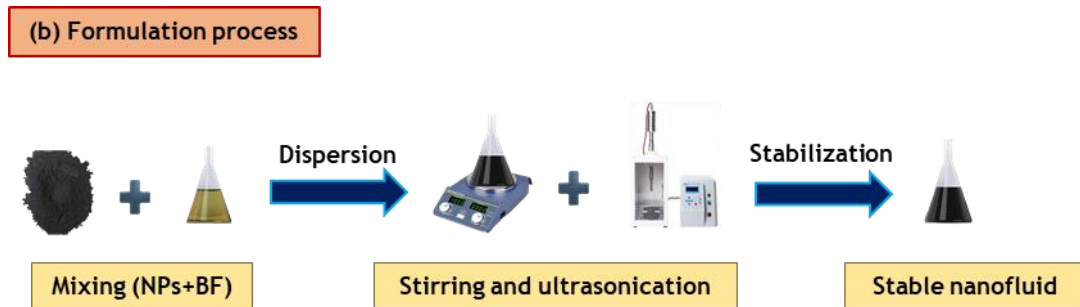
227 **Fig. 5.** Distinct advanced properties of nanofluids relative to microfluids.

228 **2.2.1. Two-step technique**

229 The two-step (also recognized as top-down/dispersion) method is the simplest, cost-effective,  
230 and scalable technique where solid nanomaterials are independently synthesized and  
231 subsequently suspended into a pure fluid and stabilized using chemical dispersants and/or  
232 mechanical, physical treatments to formulate stable NF. In the first step, bulk materials are  
233 broken down into suitable nano range using several approaches, such as wet-chemical etching  
234 and/or physical procedures. The synthesis step also includes a few intermediate processes such  
235 as drying of the particles, storage, and the dispersion of the particles. **Fig. 6(a)** categorizes  
236 various nanomaterial synthesis techniques. The stabilization step comprises multifarious  
237 techniques, for instance, chemical (electrostatic, steric, and electro-steric), and/or physical  
238 (ultrasonication, high pressure homogenization and ball milling) treatments. **Fig. 6(b)**  
239 construes formulation of NF using the two-step method. Clustering of dry NPs is, however,  
240 unavoidable during the drying phase, storage time, and dispersion into BF in this system of NF  
241 formulation [29]. The primary drawback of the two-step technique is that the high surface  
242 energy of the NPs results in nonhomogeneous particle dispersion, which results in short-term  
243 suspension stability and unpredictable thermophysical properties. This shortcoming can be  
244 compensated for by repeated physical or chemical treatments that break down the aggregation  
245 and maintain the consistency of the mixture over a longer period of time. Sarsam, et al. [30]  
246 formulated water-based graphene NFs employing several surfactants (SDBS, SDS and, CTAB)  
247 along with ultrasonication as a physical stabilization technique. The study revealed that pristine  
248 GNPs are not consistently dispersed in water without dispersants. Inclusion of various  
249 surfactants and then performing the ultrasonication for 60 minutes delivered considerably  
250 stable suspension for over two months. The addition of different surfactants, followed by  
251 ultrasonication for 60 minutes, resulted in a significantly stable suspension for more than two  
252 months. Two-step methods are the predominant techniques to formulate NFs due to their  
253 simple production procedures, flexibility with parameters and scalable production for industrial  
254 usage. This technique is frequently used to formulate carbon-based, metallic, and oxide-based  
255 NFs in various base fluids including water. In essence, the two-step method is the suitable  
256 technique to formulate and obtain thermo-physical, chemical, and optically enriched NFs at  
257 large scale production.



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**Fig. 6.** Formulation of nanofluid in two-step method (a) Synthesis techniques of nanoparticles, (b) dispersion and stabilization of nanomaterials into base fluid.

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### 2.2.2. Single-step technique

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The single-step (also familiar as one-step or bottom-up) synthesis technique uses wet-chemistry procedures wherein fabrication of nanomaterials and dispersion into base fluid are performed concurrently to formulate NFs. Several chemical vapor decomposition methods such as plasma arc [31], spraying or sputtering [32], laser ablation [33] and electric explosion [34] techniques are employed to formulate stable nanofluid in this method. These methods eliminate the clustering issues encountered by the two-step process and produce stable suspension of NPs into base fluid. Lo, et al. [35] synthesized CuO/water NF in a single step using Cu wire as the electrode. They revealed that the technique is capable of producing a stable and uniformly distributed suspension without agglomeration of particles. Zhu, et al. [36] introduced an efficient single-step synthesis technique to formulate Cu/ethylene glycol NFs by reducing copper sulfate pentahydrate with sodium hypophosphite solution under microwave radiation. They found this method to be useful for preparing well-dispersed suspensions, and

275 the reaction rate is stated to be significantly higher when using microwave radiation than  
276 conventional heating. Mohammadpoor, et al. [28] developed Cu-based NFs using both single-  
277 step and two-step methods and investigated the fluids' thermal properties and stability. They  
278 reported that NFs prepared in a single step method were found to be more stable than samples  
279 prepared in a two-step technique, whereas the two-step method produced NFs with better heat  
280 transfer properties. Nonetheless, large-scale fabrication of NFs is unfeasible using the bottom-  
281 up approach due to the procedure's complexity and extremely high production cost.  
282 Additionally, a few critical parameters, such as particle size and concentration, are difficult to  
283 monitor in this fabrication process, as it is based on batch production with limited control over  
284 the conditions. The formulation of NFs in single and two-step methods, as well as the  
285 stabilization techniques and stability indicator used, are outlined in **Table. 1**.

**Table 1.** Summary of recent studies on NF formulation using standard single step and two-step method along with deployed stabilization

techniques.

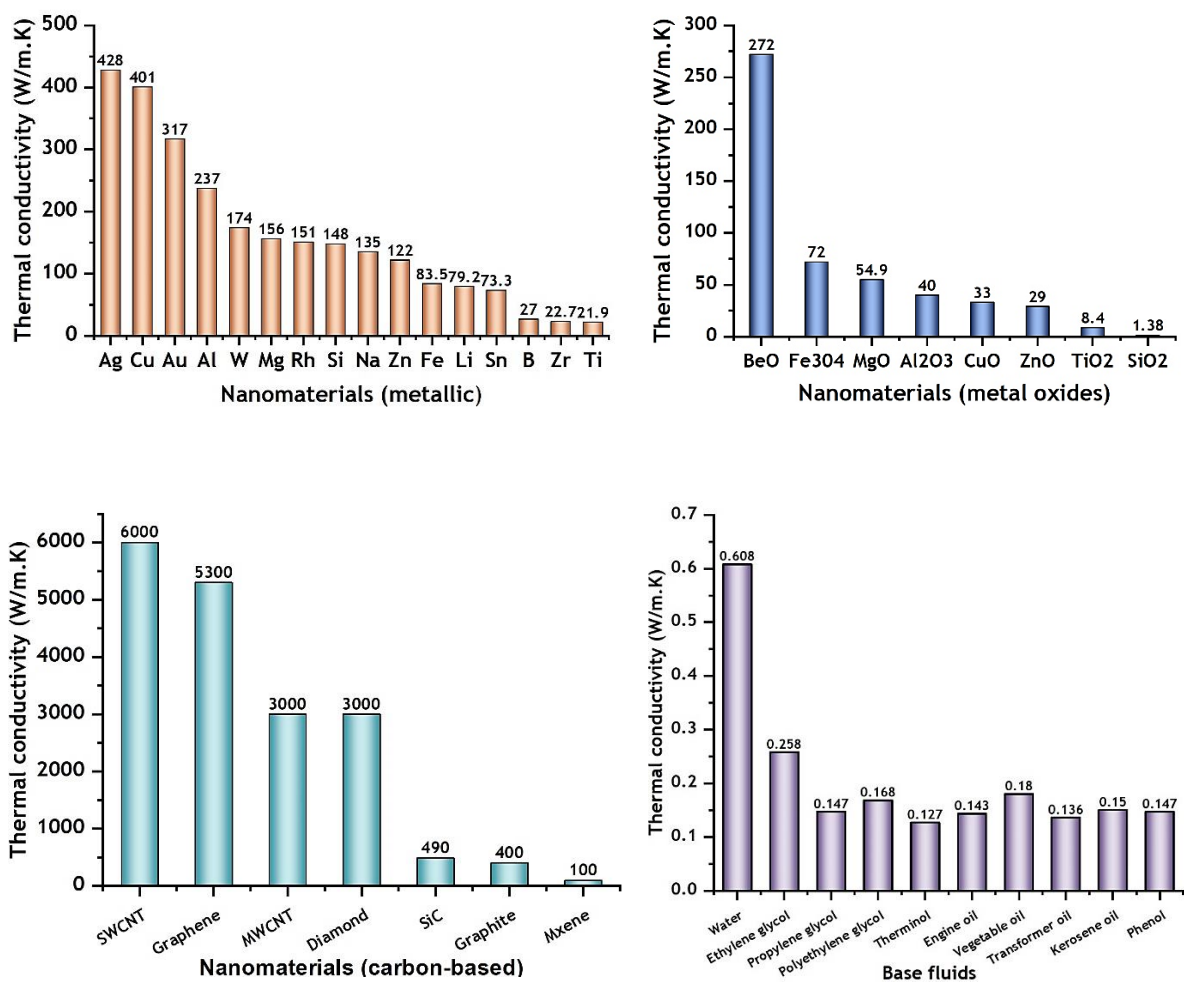
Nanofluid(s)	Particle size and concentration ( $\Phi$ )	Surfactants/ Stabilization techniques	Formulation method	Stability indicator(s)	Reference
<b>Metallic nanofluid</b>					
DI water/Al /Cu	Al (80 nm), Cu (40 nm) $\Phi = 0.3$ vol.%	Sodium dodecyl sulphate (SDS)/ ultrasonication, magnetic stirring.	Two-step	$\zeta = -41.2$ and $-38.4$ mV respectively	Akash, et al. [11]
DI water/Cu /Fe /Ag	Cu, Fe and Ag (30-50 nm) $\Phi = 0.1$ wt.%	--/Sonication	Single step	7,2 and 5 days, respectively.	Khoshvaght- Aliabadi, et al. [37]
<b>Metal-oxide nanofluids</b>					
Distilled water/ZnO /TiO <sub>2</sub>	ZnO (15-30 nm) TiO <sub>2</sub> (21 nm) $\Phi = 0.15$ wt.%	No surfactant used/magnetic stirring, ultrasonication.	Two-Step	$\zeta = 32$ mV $\zeta = 38.1$ mV	Zare, et al. [38]
Water/Al <sub>2</sub> O <sub>3</sub>	45 nm $\Phi = 1-3$ vol.%	Sodium dodecyl benzene sulfonate (SDBS)/ magnetic stirring, ultrasonic processing.	Two-step	$\zeta = -38.6$ mV	Elminshawy, et al. [39]
Water/TiO <sub>2</sub>	25 nm $\Phi = 0.1$ wt.%	SDS/ultrasonic bath, ultrasonication.	Two-step	$\zeta = -47.9$ mV	Ghadimi and Metselaar [40]
<b>Carbon nanotube based nanofluids</b>					
Water/SWCNT	Length: 20-50 nm, Height: 0.1 nm $\Phi = 0.1-20$ mg/mL	SDBS/ultrasonication.	Two-step	Two months	Islam, et al. [41]
DI water/MWCNT	Length: 6 $\mu$ m, Diameter: 5 nm $\Phi = 0.3$ vol.%	SDS/ultrasonication, magnetic stirring.	Two-step	$\zeta = 42.3$ mV	Akash, et al. [11]
Distilled water/MWCNT	MWCNT (10-20 nm) $\Phi = 0.15$ wt.%	Functionalized by -COOH group, magnetic stirring, ultrasonication.	Two-Step	$\zeta = 41.4$ mV	Zare, et al. [38]
Water/CNT	Length: 10-30 $\mu$ m, Diameter: 10-20 nm $\Phi = 0.1-1$ wt.%	GA, SDS, PVP/magnetic stirring and ultrasonication.	Two-Step	$\zeta = -63.2$ mV	Almanassra, et al. [42]

<b>Two-dimensional nanomaterial based nanofluids</b>					
DI water/rGO-Ag	Crystalline, 325 mesh, 99% purity $\Phi = 0.0005-0.05$ wt. %	SDBS /ultrasonication.	Two-step	> two weeks	Abdelrazik, et al. [43]
Water/Ti <sub>3</sub> C <sub>2</sub>	Lateral size = 1-10 $\mu$ m Thickness = 1 nm $\Phi = 0.0005$ to 0.05 wt. %	CTAB, SDBS/magnetic stirring, ultrasonication.	Two-step	$\zeta =$ maximum 62.64 and -124.71 for CTAB and SDBS, respectively.	Abdelrazik, et al. [44]
Water/GNPs	Lateral size = 2 $\mu$ m Thickness = 2 nm $\Phi = 0.1$ wt. %	BS, SDS, CTAB, and GA/water bath, ultrasonication.	Two-step	> two months	Sarsam, et al. [30]
Water-EG (60:40)/ Graphene	Length = 3 $\mu$ m Thickness = 123-424 nm $\Phi = 0.1-0.3$ wt. %	NPE 400, HCL + NaOH solution/stirring, sonication.	Two-step	Three weeks.	Sarafraz, et al. [45]
<b>Hybrid nanofluids</b>					
Water/MWCNT-CeO <sub>2</sub>	1-20 $\mu$ m $\times$ 20 nm and < 30 nm respectively $\Phi = 0.25-1.5$ vol. %	SDBS, SDS, CTAB, DDC, GA and PVP/ultrasonication	Two-step	> one month	Tiwari, et al. [46]
Water/G-BN	Graphite (40 $\mu$ m), BN (20 $\mu$ m) $\Phi = 0.05-5$ vol. %	Covalent functionalization of G/BN composite/ultrasonication.	Two-step	Several months $\zeta = -48$ to -31 mV	Zhao, et al. [47]
Water/Cu-Zn-Al LHD	Length = 49 nm, thickness = 9 nm $\Phi = 40-240$ ppm	--/magnetic stirring, sonication.	Single step	$\zeta = 34.6$ to 38.6 mV	Chakraborty, et al. [48]

289 **3. Thermophysical properties of nanofluids**

290 **3.1. Thermal conductivity (k)**

291 The thermal conductivity (TC) of NFs is the most critical property for determining their heat  
292 transfer performance (HTP) in thermal energy conversion and storage systems. TC of NFs is  
293 superior compared to BF due to greater thermal conductivity of solid particles compared to  
294 liquids (demonstrated in **Fig. 7**). Numerous studies have shown a significant increase in TC  
295 when NPs are added to the typical BF. Several parameters, however, have both positive and  
296 negative impact on the enhancement of TC using various groups of nanomaterials and BFs.



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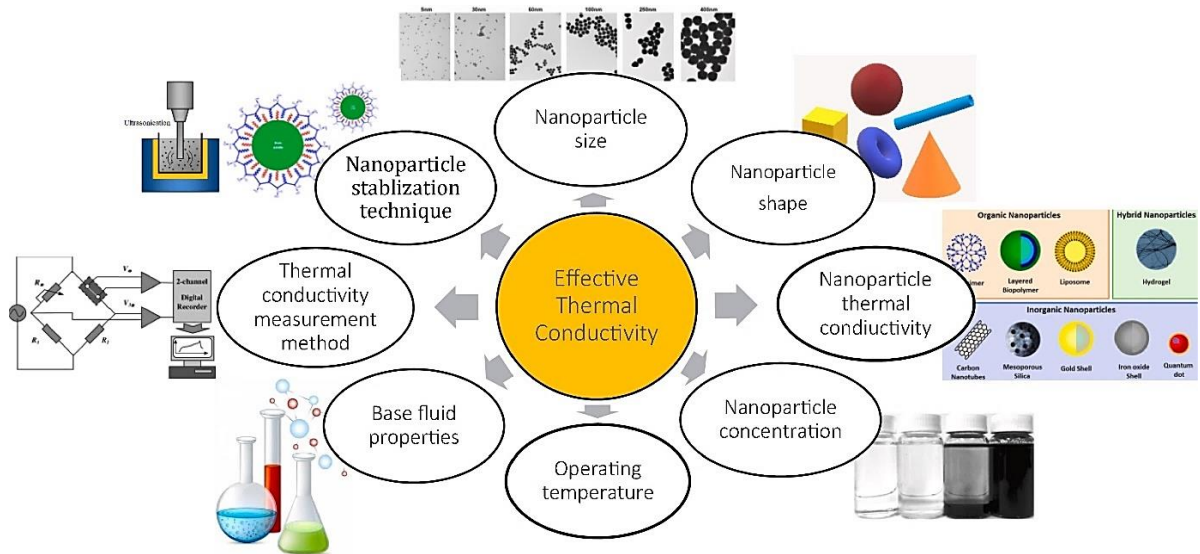
298 **Fig. 7.** Thermal conductivity (at 25°C) of frequently used nanomaterials (metallic, metal  
299 oxides and carbon-based nanomaterials) and base fluids for synthesis of NFs.

### 300 *3.1.1. Influential factors effecting TC of NF*

301 TC has been rigorously studied for the last few decades as being one of the key properties of  
302 advanced NFs as heat transfer fluids. The studies of NFs show that the presence of solid  
303 particles in BF impacts TC significantly. Crucial factors affecting the effective TC and HTP of  
304 NFs have been established, such as preparation methods, dispersion stability, concentration  
305 ( $\phi$ ), size and shape of NPs, TC of BF, addition of chemical additives, pH of mixture, TC  
306 evaluation techniques and operating temperature variation (represented in **Fig. 8**). Gupta, et al.  
307 [49] comprehensively reviewed the effect of several parameters on thermophysical properties  
308 of NFs including TC, using various types of NPs and dispersed mediums. In addition, several  
309 mechanisms related to TC and heat convection using NFs such as: Brownian motion, particle  
310 agglomeration, dispersion stability, intermolecular forces between particles and liquid layers  
311 of BF were critically investigated by several researchers in the field [50, 51]. Milanese, et al.  
312 [52] observed layering phenomena in water/Cu NF as they attempt to find the causes for  
313 experimentally evaluated higher TC of water/Cu NF over water/CuO. The numerical MDS  
314 study clarified that the formation of double shell-like layers of water molecules on the surface  
315 of Cu NP leads to the improved TC of water/Cu NF, while no significant layering is noticed in  
316 water/CuO suspension. Iacobazzi, et al. [53] studied the effect of several mechanisms on TC  
317 of micrometric and nanometric Al<sub>2</sub>O<sub>3</sub> based suspensions using a set of BFs (water, frozen-  
318 water, and oil). In comparison to Brownian motion, layering, thermal boundary resistance,  
319 clustering, and ballistic phonon motion mechanisms, the effect of mass difference scattering  
320 phenomena based on phonon theory was found to be the most efficient in predicting a decrease  
321 in the TC of microfluid-nanofluid.

322 The association of  $\phi$  and TC of NF is well established as it intensifies for corresponding  
323 addition of  $\phi$  up to an optimum level and subsequently deteriorates due to aggregation of  
324 excess particles. In terms of temperature, TC amplification is favorable at elevated  
325 temperatures due to the enhanced Brownian motion and kinetic energy of the NPs. These  
326 augmentation trends of TC established the effectiveness of NFs in temperature dependent  
327 thermal operations e.g., energy storage, solar collectors, heat exchangers and heating/cooling  
328 devices [54]. NPs synthesized in different sizes and shapes depending on the used synthesis  
329 techniques and structure of the nanomaterials are observed to cause variation in outcomes of  
330 TC. Research explored that greater surface to volume ratio of NPs yields more growth in TC,  
331 which is exactly why CNT and two-dimensional NP based NFs are generally recognized as  
332 more efficient [55]. In addition, formulation of NF at optimized preconditions and stabilization

333 criteria e.g., sonication time, chemical additives, pH of dispersed mixture, suspension  
 334 homogeneous and evaluation approach have substantial impact on TC. TC can be  
 335 measured using different techniques, e.g., transient hot-wire method, optical measurement  
 336 method, temperature oscillation method and 3- $\omega$  method. The transient-hot-wire (THW)  
 337 method is the most convenient technique to examine TC of NFs due to its simplicity and good  
 338 precision. Theoretical correlations developed by researchers are also used to evaluate the TC  
 339 of various categories of NFs. Numerous experimental and analytical studies on NF have  
 340 established the linear growth of NFs TC in response to the addition of a wide range of NPs in  
 341 BF and increasing temperatures. Afrand, et al. [56] investigated TC of water/Fe<sub>3</sub>O<sub>4</sub> (20-30 nm)  
 342 NF at  $\phi$  of 0.1-0.3 vol.% varying the temperature from 25-55 °C. The measured TC results  
 343 using THW-based KD2-pro showed addition of NPs has a dominant impact on improving  
 344 effective TC ( $k_{nf}/k_{bf}$ ) relative to escalating temperatures as 90% enhancement is obtained at  
 345 3 vol.% and 55°C. The results are consistent with other metal oxides-based NFs e.g., water-  
 346 based TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CuO, SiO<sub>2</sub>, MgO and so on (see **Table. 2**).

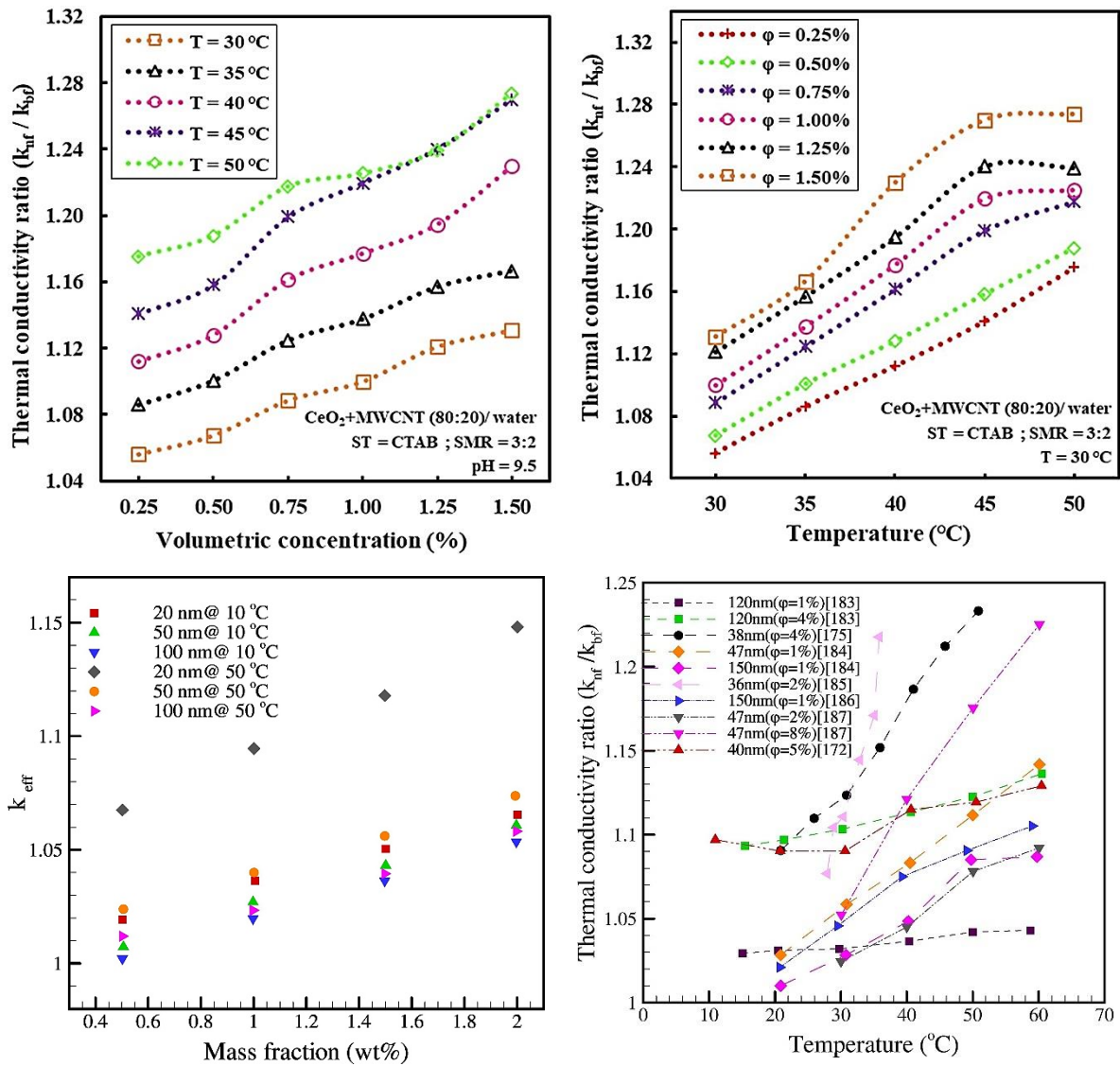


347  
 348 **Fig. 8.** Influential parameters affecting thermal conductivity of NFs [57].

349 As mentioned earlier, recent development in manufacturing of carbon-based nanomaterials  
 350 (e.g., CNT, MWCNT, SWCNT, and two-dimensional Graphene) has received unprecedented  
 351 attention in nanotechnology due to advanced thermo-physical and electro-chemical properties.  
 352 Hence, carbon-based nanomaterials are being utilized frequently in traditional liquids to  
 353 develop innovative NF suspension with advanced TC. Tiwari, et al. [46] studied the effect of  
 354 solid particles addition and temperature on TC amplification using water/MWCNT-CeO<sub>2</sub> NF.  
 355 They revealed that the TC ratio increases at rising  $\phi$  and temperatures. They noticed that TC  
 356 of the NFs adequately influenced concurrently against temperature and particle loading, the



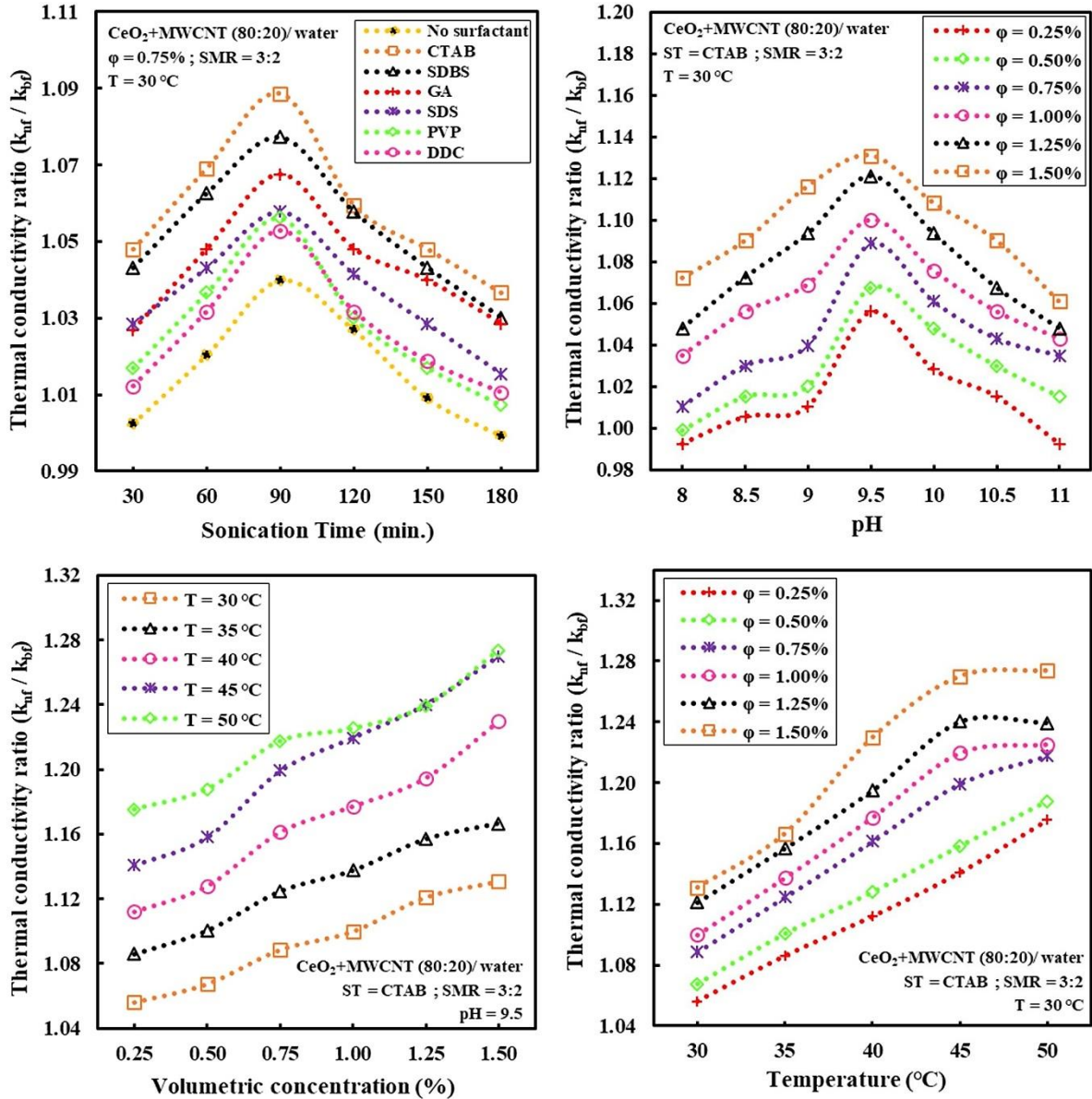
357 highest 27.38% augmentation is obtained at 1.5 vol.% and 50°C (**Fig. 9**). Similar trends in TC  
 358 augmentation against intensifying  $\varphi$  and temperature using graphene NPs is reported by [58].



359 **Fig. 9.** Effect of particles addition and temperature on thermal conductivity (a, c) variation of  
 360 TC against increasing particles concentration (b, c, d) TC increment with respect to  
 361 temperature and particle size variation (for details see [46],[59]).

362 In an extensive study, Tiwari, et al. [46] investigated effects of sonication time, several  
 363 surfactants as stabilizers, surfactant to NF ratio (SNF), pH values,  $\varphi$ , and temperature on  
 364 effective TC ( $(k_{nr}/k_{bf})$ ) of hybrid water/MWCNT+CeO<sub>2</sub> NF (**Fig. 10**). At optimized  
 365 conditions (90 min sonication time, CTAB as dispersant, SNF3:2, pH9.5, 1.50 vol.%, and  
 366 50°C), the highest increment of 27.38% is obtained. Keklikcioglu Cakmak [60] demonstrated  
 367 that surfactants have a negative impact on the TC of water/GO NF by examining three separate  
 368 surfactants (CTAB, SDS, and TX-100) used to stabilize the suspension. Regardless of variation

369 in  $\varphi$ , NFs elucidated less TC and poor stability relative to BF using the stabilizers. On the  
 370 contrary, Almanassra, et al. [42] reported that surfactants (GA, SDS and PVP) have no effect  
 371 on  $k_{nf}/k_{bf}$  studying water/CNT (0.1-1wt.%) NF from 20-45°C at an optimum ratio (particle:  
 372 surfactant) of 1:0.5.



373 **Fig. 10.** Effect of different surfactants, sonication time and pH value on TC enhancement of  
 374 water/MWCNT+CeO<sub>2</sub> nanofluid [46].

375 Iacobazzi, et al. [61] critically examined the effect of clustering mechanism on TC of  
 376 water/Al<sub>2</sub>O<sub>3</sub> NF. The analysis showed that, within the considered cluster dimension range of  
 377 168-20933 nm, the TC ratio deteriorates at smaller clusters (up to 3820 nm), but notably  
 378 increases at larger dimensions up to 20933 nm. Further assessments on stability and  
 379 backscattered light revealed that the sedimentation mechanism (i.e., larger clusters) results in

380 a higher TC ratio due to the convective motion of NPs around the hot wire caused by the  
381 gravitational force effect. Teng, et al. [62] observed variation of TC using varying NP size (20,  
382 50 and 100 nm) on water/Al<sub>2</sub>O<sub>3</sub> (0.5-2wt.%) at 10-50°C and concluded that smaller NP sizes  
383 can provide a substantial increase in TC than larger particles. Smaller NPs was found to be  
384 more temperature sensitive due to higher collision rates relative to larger particles resulting in  
385 more augmentation in TC at higher temperatures. Timofeeva, et al. [63] considered different  
386 shapes of Al<sub>2</sub>O<sub>3</sub> particles at nanoscale range (< 100 nm) to experimentally study shape-effect  
387 on TC of water-EG/Al<sub>2</sub>O<sub>3</sub> NF at concentration of 1-9 vol.% and 21±0.5°C. As the NP loading  
388 increases,  $k_{nf}/k_{bf}$  enhances in the order of cylinder > brick > blade > platelet shaped particles.  
389 In addition, experimental data confirms that sphericity of less than 0.6 results in deterioration  
390 of  $k_{nf}/k_{bf}$  as negative interfacial effects dominate. Despite this, researchers concluded that  
391 the impact of NP sizes and shapes is subject to major disagreements in the published literature  
392 due to a variety of operating conditions, including diverse synthesis/fabrication techniques, TC  
393 evaluation methods, a restricted range of NP sizes, temperature, pH value, and NP morphology,  
394 and inadequate information on operating conditions and chemicals [57, 64].  
395 Zhang, et al. [65] observed a drastic impact of pH value variation on TC for water/TiO<sub>2</sub> (20nm)  
396 NF in the range of 2-12. Their experiment revealed that TC fluctuates severely within an  
397 unstable range of pH (5-8) near the isoelectric value of 6.5 whereas smaller (2-4) and higher  
398 (9-12) range of pH results. Optimized effective TC ( $k_{nf}/k_{bf}$ ) is achieved with good  
399 suspension stability at pH 10, 0.25 vol.% and 25°C. TC augmentation is attributed to optimum  
400 aggregation formed by the NPs and optimized size rather than optimum stability of the  
401 particles. In addition, prominent increment is evaluated against raising particle fractions (0.08-  
402 2 vol.%) and elevated temperatures (25-60 °C), the findings are supported by [66].  
403 Garoosi [67] proposed empirical correlations considering key parameters (temperature, particle  
404 loading and size) for several combinations of NPs and BFs. The studied model is found to be  
405 more reliable than classical models, with a standard deviation of only 4.7%. The correlations  
406 are recommended for further analysis of TC in NF-based thermal engineering devices. Cui, et  
407 al. [68] performed a MDS study to analyze consequences of NP properties (materials, sizes,  
408 shapes and  $\varphi$ ) on TC using Cu, Ag, Au and Fe nanomaterials. The proposed model predicts  
409 TC of the NFs and concludes that TC improves with raising  $\varphi$  and smaller NP size. Ag NPs  
410 had the highest TC of all, while higher fraction of  $\varphi > 3vol. \%$  showed a reducing trend for  
411 TC. In a recent study established on experimental data by [69], revealed an ANN-based model  
412 to predict TC of several metal oxide/water NFs. The model can accurately (uncertainty < 2%)

413 predict TC data for NP loading of 0.02-2 wt.% at 20-90°C. Zendejboudi, et al. [70] reviewed  
414 widely used and effective data-driven numerical approaches to predict TC of a broad range of  
415 NFs. Studies on TC of widely utilized water-based mono and hybrid NFs and the mechanism  
416 of TC augmentation, impacts of influential parameters along with numerical or molecular  
417 dynamics correlations to estimate the TC, are reviewed in **Table. 2**.

**Table. 2.** Summary of recent experimental studies on TC of water-based NF with details information and important outcomes.

Reference	Nanofluids	Concentration ( $\Phi$ )	Surfactants/ Dispersants	Temperature range	Key findings
Sarsam, et al. [30]	Water/GNPs	2 nm $\times$ 2 $\mu$ m $\Phi$ = 0.1 wt.%	DBS, GA, CTAB, and SDS	20-40 °C	<ul style="list-style-type: none"> <li>• Highest augmentation in TC relative to water, 10.80% with GA surfactant. 60 minutes of ultrasonication time provided the most stable NF and the 2<sup>nd</sup> highest growth of TC.</li> </ul>
Chakraborty, et al. [71]	Water/TiO <sub>2</sub>	< 100 nm $\Phi$ = 0-100 ppm	Polyvinylpyrrolidone and Tween 20	30-50 °C	<ul style="list-style-type: none"> <li>• Maximum 8.3% increment is obtained at 40 ppm at 30°C. However, beyond 40 ppm results in a negative outcome due to aggregation.</li> </ul>
Das, et al. [72]	Water-[MMIM][DMP]/ MXene	1–10 $\mu$ m $\times$ 1 nm $\Phi$ = 0.05-0.2 wt.%	--	25-60 °C	<ul style="list-style-type: none"> <li>• TC was augmented by 47% at 0.2wt.% using 2D MXene particles and exhibited linear growth with increasing temperature.</li> </ul>
Alshayji, et al. [73]	DI water/Diamond	3-10 nm $\Phi$ = 0.125-1.25 vol.%	none	20-60 °C	<ul style="list-style-type: none"> <li>• 25% growth in TC relative to water is observed at 0.125 vol.% and 60°C, attributed to higher conductivity of diamond particles.</li> </ul>
Amiri, et al. [74]	Water/GNP-COOH /GNP-SDBS	0.5-3 $\mu$ m $\times$ 0.55-3.74 nm $\Phi$ = 0.025-0.1 wt.%	SDBS and solvents (H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> )	20-80 °C	<ul style="list-style-type: none"> <li>• Functionalized GNP-COOH NFs attained intensified TC relative to water and better than GNP-SDBS functionalized NFs as well.</li> <li>• 68% heat transfer enhancement obtained with GNP-COOH NF, which is 33% higher than GNP-SDBS NFs.</li> </ul>
Sadri, et al. [75]	Water/GAGNPs	n/a $\Phi$ = 0.05 vol.%	--	20-45 °C	<ul style="list-style-type: none"> <li>• 24.18% TC increment is found by adding acid functionalized GNPs at 45°C and 0.05 vol.%.</li> </ul>
Singh, et al. [76]	Water/Al <sub>2</sub> O <sub>3</sub> /rGO- Al <sub>2</sub> O <sub>3</sub>	4-5 nm $\Phi$ = 0.01-0.1 vol.%	--	32-45 °C	<ul style="list-style-type: none"> <li>• While the TC of Al<sub>2</sub>O<sub>3</sub> based NF deteriorated above 0.02 vol.%, hybrid NF showed excellent TC, at 45°C and 0.1 vol.%, obtained 2.0766 W/m.K, much higher than 0.608 W/m.K of water .</li> </ul>
Sundar, et al. [77]	Water/ND-CO <sub>3</sub> O <sub>4</sub> Water-EG/ND-CO <sub>3</sub> O <sub>4</sub>	ND (4-5 nm), ND-CO <sub>3</sub> O <sub>4</sub> (16.95 nm) $\Phi$ = 0.05-0.15 wt.%	--	20-60 °C	<ul style="list-style-type: none"> <li>• Water-based NF outperforms other base fluids in terms of TC improvement. Maximum increments are 15.7, 8.71, and 13.34 % at 0.15 wt.% and 60°C</li> </ul>

					for water, EG, and water-EG based hybrid NF, respectively.
Huminic, et al. [78]	Water/Fe-Si	1-20 nm $\Phi = 0.25-1$ wt.%	CMCNa	20-50 °C	<ul style="list-style-type: none"> <li>The TC is found to be increasing with temperature and inclusion of hybrid nanocomposite.</li> </ul>
Moldoveanu, et al. [79]	Water/Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	43 and 20 nm respectively $\Phi = 1-3$ vol.%	--	20-50 °C	<ul style="list-style-type: none"> <li>TC intensifies linearly with inclusion of NPs and increasing temperature. 23.61% higher TC is achieved at 3 vol.% and 50 °C.</li> </ul>
Maheshwary, et al. [64]	Water/TiO <sub>2</sub> (spherical, cubic and rod)	16 to 32 nm $\Phi = 0.5-2.5$ wt.%	--	303-353 K	<ul style="list-style-type: none"> <li>TC augmented with longer sonication time and reduced particles sizes and it also varies based on shapes of dispersed particles. Contributions of particle concentration, size and shape are 69.43, 24.95 and 5.62% respectively.</li> </ul>
Sabiha, et al. [80]	Water/SWCNT	500 nm × 1-2 nm $\Phi = 0.05-0.25$ vol.%	SDS	20-60 °C	<ul style="list-style-type: none"> <li>At 0.2 vol.% and 60 °C, TC increased by 36.76%. TC is less at lower temperatures due to less Brownian motion.</li> </ul>
Kumar and Sonawane [81]	Water/CuO /TiO <sub>2</sub>	26 and 9 nm respectively $\Phi = 0.02-0.06$ vol.%	--	30-50 °C	<ul style="list-style-type: none"> <li>CuO NP exhibited higher TC increment for the NFs in comparison with TiO<sub>2</sub> particles, augmentation is 25 and 16% respectively.</li> </ul>
Hussein, et al. [82]	Water/CF-MWCNT + CF-GNP + h-BN	5 μm × 15 nm and 2 μm respectively $\Phi = 0.05-0.1$ wt.%	Tween-80	20-60 °C	<ul style="list-style-type: none"> <li>64% intensified TC is achieved for the hybrid NF at 60 °C and 0.1 wt.%. Advance properties of the functionalized particles are attributed as reasoning aspects of TC enhancement.</li> </ul>
Hemmat Esfe and Saedodin [83]	Water/MgO	20 to 60 nm $\Phi = 0.5-2$ vol.%	--	--	<ul style="list-style-type: none"> <li>The effect of particle concentration and size is examined. The highest vol.% and smallest size of NP are observed to be the best combination for TC enhancement.</li> </ul>
Sundar, et al. [84]	Water/Nano-diamond	10-15 nm $\Phi = 0.2-1$ vol.%	H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub>	293-333 K	<ul style="list-style-type: none"> <li>A 22.86% increment is obtained due to effective micro-convection at higher temperature and <math>\phi</math> of NPs in base fluid.</li> </ul>
Chen, et al. [85]	Saline water/SiC	30 nm $\Phi = 0.04-1$ vol.%	Polyvinylpyrrolidone and NaOH	10-50 °C	<ul style="list-style-type: none"> <li>TC of saline-water based NF was improved by 5.2% with respect to BF, SiC has a good impact to</li> </ul>

					increase above 6% relative to water at 0.4 vol.% loading.
Zhang, et al. [86]	Water/CRGO	Thickness (~4.3 nm) $\Phi = 0.2-1$ mg/ml	--	20-60 °C	<ul style="list-style-type: none"> <li>● TC improvement is 32.19% at 60°C for 1 mg/ml CRGO particles. TC advancement is attributed to ultrathin layered structure and extra-large surface area of graphene nanomaterial.</li> </ul>
Shalkevich, et al. [87]	Water/Au	2-45 nm $\Phi = 0.00025-1$ vol.%	EGMUDE	25-40 °C	<ul style="list-style-type: none"> <li>● A highest of 1.4% TC augmentation was recorded for H<sub>2</sub>O/Au NF dispersing 40 nm gold particles at 0.11 vol.% and 37 °C.</li> </ul>
Srinivas, et al. [88]	Carboxylated water/MWCNT	1-25 $\mu\text{m} \times$ 20-40 nm $\Phi = 0.025-1$ wt.%	Sebacic Acid and 2-ethylhexanoic Acid	30-50 °C	<ul style="list-style-type: none"> <li>● 17.85% growth in TC is achieved at 1 wt.% and 50°C for CNTs dispersed in functionalized carboxylate water.</li> </ul>
Wu, et al. [89]	Water/SWCNT /MWCNT	1-2 and 8 nm respectively, length < 30 $\mu\text{m}$ $\Phi = 0.0962-0.3846$ vol.%	Humic acid	30-80 °C	<ul style="list-style-type: none"> <li>● SWCNT-based exhibited superior TC than MWCNT-based suspension. The maximum augmentation found is 40.5% at 0.3846 vol.% of SWCNT nanomaterials.</li> </ul>
Wusiman, et al. [90]	Water/MWCNT	5 $\mu\text{m} \times$ 5-20 nm $\Phi = 0.1-1$ wt.%	SDBS and SDS	20-45 °C	<ul style="list-style-type: none"> <li>● TC dropped with increasing <math>\phi</math> of surfactants. However, SDBS performed better than SDS as surfactant.</li> </ul>
Wang, et al. [66]	Water/Cu /Al <sub>2</sub> O <sub>3</sub>	25 nm $\Phi = 0.02-0.8$ Wt.%	SDBS	25 °C	<ul style="list-style-type: none"> <li>● Maximum 15 and 18% increments are attained at 0.8 wt.% for Cu and Al<sub>2</sub>O<sub>3</sub> based NFs, respectively. pH and <math>\phi</math> of SDBS had a substantial effect on TC of the NFs.</li> </ul>
Sahooli, et al. [91]	Water/CuO	4 nm $\Phi = 1-6$ vol.%	Polyvinylpyrrolidone	10-50 °C	<ul style="list-style-type: none"> <li>● 31% TC enhancement is obtained for the NF at 50°C using PVP as surfactant. pH 8 and PVP <math>\phi</math> of 0.095 wt.% caused optimized TC.</li> </ul>
Ghadimi and Metselaar [40]	Water/TiO <sub>2</sub>	25 nm $\Phi = 0.1$ wt.%	SDS	25 °C	<ul style="list-style-type: none"> <li>● Variation in sonication time and surfactant <math>\phi</math> leads to improvement in TC. 3 h sonication and 0.1wt.% of SDS showed improved TC of the studied NFs.</li> </ul>

Song, et al. [92]	Water/stainless steel	70 nm $\Phi = 0.017$ wt.%	SDBS	25 °C	<ul style="list-style-type: none"> <li>● TC improved 8.3% at pH 11 with 0.017 wt.% of the steel particles. In addition, sonication time of 60 min was observed to be optimum for the NF.</li> </ul>
Shahsavari, et al. [93]	Water/CNT-Fe <sub>3</sub> O <sub>4</sub>	10 $\mu\text{m} \times 10\text{-}30$ nm and 13 nm respectively $\Phi = 0.9$ to 2.25 vol.%	Gum Arabic and Tetramethylammonium hydroxide	25-35 °C	<ul style="list-style-type: none"> <li>● At a field strength of 470 mT, the highest augmentation of TC observed was 151.31% for 0.9% FF+1.35% CNT. However, temperature had a negative effect on TC due to the presence of the magnetic field.</li> </ul>
Garg, et al. [94]	Water/MWCNT	0.5-40 $\mu\text{m} \times 10\text{-}20$ nm $\Phi = 1$ wt.%	Gum Arabic	15-35 °C	<ul style="list-style-type: none"> <li>● TC increased by 20% at 1 wt.% and an optimum ultrasonication period of 40 minutes. The heat transfer coefficient was also augmented by 32% relative to water.</li> </ul>
Xing, et al. [95]	Water/SWCNT	5-30 $\mu\text{m} \times 1\text{-}2$ nm $\Phi = 0.1\text{-}1$ wt.%	CTAB	10-60 °C	<ul style="list-style-type: none"> <li>● 16.1% improved TC is attained by dispersing 1 wt.% of SWCNT nanomaterials and CTAB dispersant at 60 °C.</li> </ul>
Taherialekouhi, et al. [96]	Water/Graphene oxide-Al <sub>2</sub> O <sub>3</sub>	3.4-7 and 20 nm respectively $\Phi = 0.1\text{-}1$ vol.%	--	25-50 °C	<ul style="list-style-type: none"> <li>● TC intensified 33.9% at 1 vol.% and 50°C with the dominant effect of temperature relative to solid concentrations.</li> </ul>
Mousavi, et al. [97]	Water/MgO-TiO <sub>2</sub>	25-45 and 18-23 nm respectively $\Phi = 0.1\text{-}0.5$ vol%	SDS	15-60 °C	<ul style="list-style-type: none"> <li>● The highest enhancement of TC was obtained to be 21.8% for MgO-TiO<sub>2</sub> (80:20) at 60°C.</li> </ul>
Okonkwo, et al. [98]	Water/Al <sub>2</sub> O <sub>3</sub> -Fe	29 and 46 nm $\Phi = 0.05\text{-}0.2$ vol.%	--	25-65 °C	<ul style="list-style-type: none"> <li>● The hybrid NF showed a 14% enhancement in TC at 0.2 vol.% while it was 7.5% for mono water/Al<sub>2</sub>O<sub>3</sub> NF.</li> </ul>
Hussein, et al. [99]	Water/CF-GNPs	2 $\mu\text{m}$ $\Phi = 0.02\text{-}0.1$ wt.%	SDS, CTAB, Tween-80 and TX-100	20-60 °C	<ul style="list-style-type: none"> <li>● TC augmented 29.2% at 0.1 wt.% of CF-GNPs using an optimum sonication time of 60 minutes. Covalent functionalization of particles leads to higher effective TC.</li> </ul>

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**Table 3.** Summary of proposed empirical correlations to estimate thermal conductivity of water-based NFs.

Reference	Nanofluids	Correlation	Applicability	Accuracy
-----------	------------	-------------	---------------	----------



Water-based nanofluids				
Tiwari, et al. [46]	Water/MWCNT-CeO <sub>2</sub>	$\frac{k_{nf}}{k_{bf}} = 1 + 0.580453 \times \left(\frac{T}{T_0}\right)^{1.54358} \times \varphi^{0.356853}$	0.25 ≤ φ ≤ 1.5 vol. % T = 30-50 °C	Max. error = 0.881%
Garooosi [67]	Water/Ag, Cu, Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , CuO, SiO <sub>2</sub> , ZnO, MgO, Fe, Fe <sub>3</sub> O <sub>4</sub> , Al, AlN, CaCO <sub>3</sub>	$\frac{k_{nf}}{k_{bf}} = \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\varphi}{k_p + 2k_{bf} - (k_p - k_{bf})\omega\varphi} + 3.762 \times \left(\frac{T}{T_0}\right)^{8.661} \left(\frac{d_p}{d_{bf}}\right)^{8.661} \left(\frac{k_p}{k_{bf}}\right)^{8.661} \varphi^{0.64} e^{(-5.742\varphi)}$	0 ≤ φ ≤ 12 vol. % 10 nm ≤ d <sub>p</sub> ≤ 12 μm	Standard deviation = 4.7%
Alawi, et al. [100]	Water/Al <sub>2</sub> O <sub>3</sub> /CuO /SiO <sub>2</sub> /ZnO	$\frac{k_{nf}}{k_{bf}} = \left[ \frac{k_p + 2k_{bf} - 2\varphi(k_{bf} - k_p)}{k_s + 2k_{bf} - \varphi(k_{bf} - k_s)} \right] + 5 \times 10^4 \beta \varphi \rho_f C_p \sqrt{\frac{k_B T}{d_p \rho_p}} f(T, \varphi)$	Φ = 1-5 vol. % d <sub>p</sub> = 20-100 nm T = 300-320 K	n/a
Hemmat Esfe, et al. [101]	Water-EG/SWCNT-ZnO	$\frac{k_{nf}}{k_{bf}} = 0.8707 + 0.179\varphi^{0.179} e^{0.09642\varphi^2} + \varphi T \times 8.883 \times 10^{-4} + \varphi^{0.252} T \times 4.435 \times 10^{-3}$	Φ = 0.15 to 1.92 vol. % T = 25-50 °C	R <sup>2</sup> =0.9918
Rostamian, et al. [102]	Water-EG/SWCNT-CuO	$\frac{k_{nf}}{k_{bf}} = 1 + (0.04056 \times \varphi T) - 0.003252 \times (\varphi T)^2 + 0.0001181 \times (\varphi T)^3 - 0.000001431 \times (\varphi T)^4$	Φ = 0.02 to 0.75 vol. % T = 20-50 °C	Max. error < 4%
Timofeeva, et al. [63]	Water-EG/Al <sub>2</sub> O <sub>3</sub>	$\frac{k_{nf}}{k_{bf}} = 1 + (C_k^{shape} + C_k^{surface})\varphi$ where, $C_k^{surface} = -f \cdot l_k$	Φ = 5 vol. % Shapes = platelets (9 nm), blades (60×10 nm), cylinders (80×10 nm), and bricks (40 nm)	n/a

Pare and Ghosh [69]	Water/Al <sub>2</sub> O <sub>3</sub> /CuO /ZnO	$\frac{k_{nf}}{k_{bf}} = a + bT + c\varphi + dT^2 + e\varphi^2 + fT\varphi$	$\Phi = 0.02-2 \text{ wt.}\%$ $T = 20-90 \text{ }^\circ\text{C}$ $d_p = 40 \text{ nm}$	Max. error < 2%
Beck, et al. [103]	Water/Al <sub>2</sub> O <sub>3</sub>	$k_{nf} = [4.4134\varphi (1 - e^{-0.025d_p})]k_{bf} + k_{bf}$	$2 \leq \varphi \leq 4 \text{ vol.}\%$ $8 \leq d_p \leq 282 \text{ nm}$ $T = 298 \text{ K}$	n/a
Sun, et al. [104]	Water/SiO <sub>2</sub>	$\frac{k_e - k_0}{k_\infty - k_0} = 1 - \exp \left[ \frac{-6.3 \left( \frac{r - r_0}{r_0} \right)^{1.4}}{\varphi^{-0.3} \left( \frac{d_p}{G_p} \right)^{-0.2}} \right]$	$1.96 \leq \varphi \leq 12.85 \text{ vol.}\%$ $d_p = 10-60 \text{ nm}$	Max. error = $\pm 20\%$
Hemmat Esfe, et al. [105]	Water/Fe	$\frac{k_{nf}}{k_{bf}} = 1 + (0.26876 \times \varphi^{0.99288} \times d_p^{-0.35106})$	$0.000313 \leq \varphi \leq 0.01 \text{ vol.}\%$ $d_p = 37, 71, 98 \text{ nm}$	R <sup>2</sup> =0.9988
Hemmat Esfe, et al. [106]	Water/CNT- Al <sub>2</sub> O <sub>3</sub>	$\frac{k_{nf}}{k_{bf}} = \frac{A + T}{B + C\varphi} + \frac{D}{T}$	$\Phi = 0-1 \text{ vol.}\%$ $T = 303 \text{ to } 332 \text{ K}$	Max. error = 2%

421

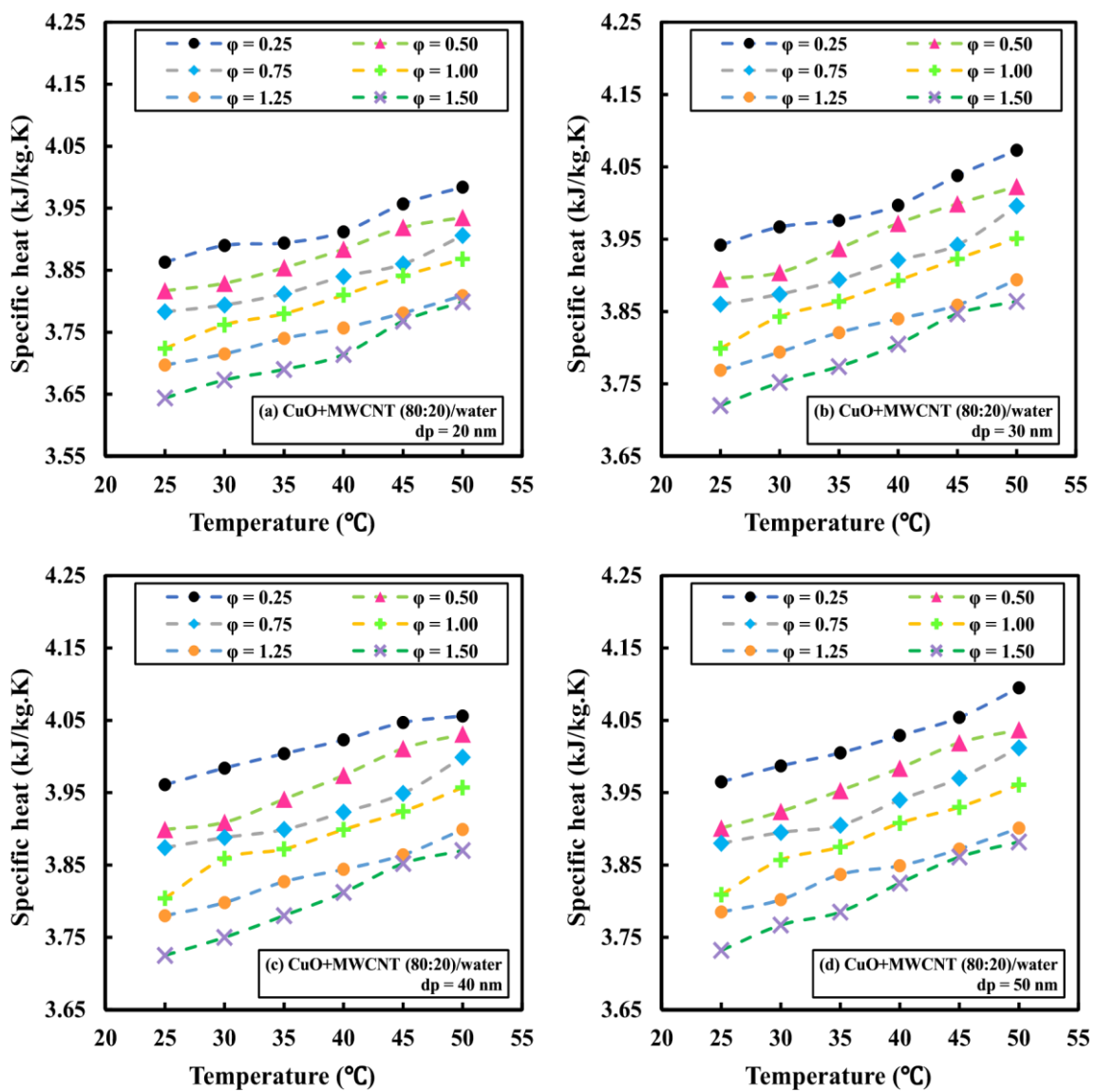
### 422 3.2. Specific heat capacity ( $c_p$ )

423 Specific heat ( $c_p$ ) is one of the most essential thermo-physical properties to characterize thermal  
424 heat storage merit of various advanced thermo-fluids. Although TC of NF is generally  
425 enhanced by the addition of NPs,  $c_p$  may either increase or decrease with the presence of  
426 scattered solid particles relative to the fluid. This trend of  $c_p$  depends on nanomaterial type,  $\varphi$ ,  
427 base fluid and temperature. Working fluids must have sufficient heat capacity to provide  
428 adequate energy efficiency when used in a thermal heat transfer or storage device. Hence, it is  
429 essential to establish an explicit concept of interaction between  $c_p$  and the influential factors to  
430 characterize potential NFs. Generally, various types of thermal DSC devices are employed to  
431 experimentally measure  $c_p$  of NFs due to its convenience and technical simplicity [107-109].  
432 Wole-Osho, et al. [110] experimentally studied  $c_p$  of water-based mono ( $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$ ) and  
433 hybrid ( $\text{Al}_2\text{O}_3$ -  $\text{ZnO}$ ) NFs at 0.33-1.67vol.% and 25-65°C. The presence of solid particles  
434 resulted in a linear decrement of up to 30.12%. Starace, et al. [111] evaluated  $c_p$  of 13 different  
435 NFs considering various BFs (including water and oils), NPs, surfactant,  $\varphi$ , particle size and  
436 temperature. They concluded no notable augmentation is caused by the addition of NPs as  $\frac{c_{p_{nf}}}{c_{p_{bf}}}$   
437 is found to be below 1 for the majority of the samples. Moldoveanu and Minea [112] analyzed  
438  $c_p$  of regular and hybrid NFs using metal oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$ ). The obtained data  
439 indicate that the relative  $c_p$  of the NFs is below one for all samples, indicating a decrease in  
440 heat capacity due to the addition of solid NPs (0-3vol.%). The authors proposed the following  
441 correlation based on the observed data (applicable for the reported NFs at  $\varphi$  of 0-5vol.% and  
442 ambient temperature with an uncertainty of 11%).

$$443 \quad (C_p)_{nf} = \left(\frac{\rho_p}{\rho_{bf}}\right)^{0.2} \left(1 + \frac{d_p}{50}\right)^{0.4167} \left(1 - \frac{\varphi}{100}\right)^{2.272} (C_p)_{bf} \quad (1)$$

444 In contrast, some published works claim opposite characteristics of heat capacity by analyzing  
445 different NFs using various NPs (particularly carbon-based nanomaterials), BFs and  
446 experimental conditions. According to the findings of those studies, the formation of a semi-  
447 solid layer on the surface of NPs increases TC, allowing NFs to store energy faster than BF.  
448 Almanassra, et al. [42] measured  $c_p$  of water/CNT (0.1-1wt.%) NF using a DSC and they  
449 understood that  $c_p$  increases for the NF adding particles marginally at low temperature (15-  
450 35°C) while the effect is more dominant at elevated temperature (35-75°C). The highest 65%  
451 enhanced  $c_p$  is noted at 0.1wt.% and 75°C while they also identified no prominent consequences  
452 to  $c_p$  adding stabilizers (GA, SDS and PVP) against temperature variation but little increment

453 of 3% is attained when NP: surfactant ratio is varied from 1:0.5 to 1:1, consistent with [113].  
 454 Tiwari, et al. [109] compared the  $c_p$  of three distinct hybrid water-based NFs containing  
 455 nanocomposites that were experimentally formulated (comprising MWCNT with CuO, MgO  
 456 and SiO<sub>2</sub> separately). Variation in  $c_p$  is observed against increasing  $\phi$  (0.25-1.5vol.%), altering  
 457 particle diameter (20-50 nm) and temperature (25-50°C). The obtained results imply that the  $c_p$   
 458 deteriorates raising  $\phi$  and the degradation appears further using larger particles while it  
 459 improves with temperature. The maximum drop is 12.84% at 25°C using an average size of 20  
 460 nm for CuO-MWCNT (1.5vol.%) composite and the decrement is lessened using 50 nm  
 461 particles at promoted temperature (**Fig. 11**). Analogous trends are noticed for the other two  
 462 NFs as well. More experimental studies on  $c_p$  of water-based NFs are reviewed in **Table. 4**.



463  
 464 **Fig. 11.** Variation of  $c_p$  with increasing  $\phi$ , NP diameter and temperature using  
 465 water/MWCNT-CuO NF , studied by [109].

466 Theoretical models along with experimental correlations are useful to estimate  $c_p$  of a wide  
 467 range of NFs that has been proposed in literature over the years. The first model presented by  
 468 Pak and Cho [114] is known as mixture theory to predict  $c_p$  of solid-liquid mixture at nonorange  
 469 scale.

$$470 \quad C_{p_{nf}} = \varphi C_{p_{np}} + (1 - \varphi) C_{p_{bf}} \quad (2)$$

471 Although this model is commonly used to predict the  $c_p$  of NFs, anomalies have been identified  
 472 due to the model's significant deviation from experimental results.

473 Xuan and Roetzel [115] proposed a thermal equilibrium model for various NFs based on  
 474 reviewed experimental results.

$$475 \quad \rho_{nf} C_{p_{nf}} = \rho_{np} C_{p_{np}} \varphi + (1 - \varphi) \rho_{bf} C_{p_{bf}} \quad (3)$$

$$476 \quad \text{where, } \rho_{nf} = (1 - \varphi) \rho_{bf} + \varphi \rho_{np}$$

477 This model performs better than mixture theory at predicting data. However, inconsistencies  
 478 up to a certain range are reported [116, 117].

479 Fakoor Pakdaman, et al. [118] investigated  $c_p$  of NF using MWCNT and developed a  
 480 correlation to predict  $c_p$ .

$$481 \quad \frac{C_{p_{bf}} - C_{p_{nf}}}{C_{p_{bf}}} = (0.0128 \times T + 1.83282) \times \varphi^{0.4779} \quad (4)$$

482 The equation is applicable for  $\varphi$  of 0-0.004wt.% and temperature range of 313-343K. Tiwari,  
 483 et al. [109] formed a correlation for several hybrid NFs considering experimental data ( $\varphi$ ,  
 484 particle size  $d_{np}$  and temperature). Valid for  $0.25 \leq \varphi \leq 1.5 \text{ vol. } \%$ ,  $d_{np} = 20 - 50 \text{ nm}$  and  
 485  $T = 20 - 50^\circ\text{C}$ , with maximum error of is 2.93%.

$$486 \quad C_{p_{nf}} = C_{p_{bf}} \left[ -10.6364 \times \left( \frac{T}{T_0} \right)^{-0.771} \times \varphi^{0.448} \times \left( \frac{d_{np}}{d_0} \right)^{-0.474} \times \left( \frac{C_{p_{np}}}{C_{p_{bf}}} \right)^{1.027} \times \right. \\ \left. \left( \frac{\rho_{nf}}{\rho_{bf}} \right)^{-2.742} \right] \quad (5)$$

488 Sekhar and Sharma [119] collected data from 81 different experiments studying  $c_p$  of NFs using  
 489  $\text{Al}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  to develop which can predict data with a deviation of +10% and -  
 490 8%.

$$491 \quad \frac{C_{p_{nf}}}{C_{p_{bf}}} = 0.8429 \left( 1 + \frac{T_{nf}}{50} \right)^{-0.3037} \left( 1 + \frac{d_{np}}{50} \right)^{0.4167} \left( 1 + \frac{\varphi}{100} \right)^{2.272} \quad (6)$$

492 This correlation is applicable for  $0.01 \leq \varphi \leq 4.0 \text{ vol. } \%$ ,  $d_{np} = 15 - 50 \text{ nm}$  and  $T = 20 -$   
 493  $50^\circ\text{C}$ .

494 **Table 4.** Summary of recent experimental studies on specific heat capacity ( $c_p$ ) of water-based with details information and important outcomes.

Reference	Nanofluids	Particle dimension and concentration	Surfactants/ Dispersants	Temperature range	Key findings
Sadri, et al. [75]	Water/GNPs /GAGNPs	200 nm $\Phi = 0.05$ vol.%	Gallic acid	20-50 °C	<ul style="list-style-type: none"> <li><math>c_p</math> of the NF is reduced with the inclusion of GNPs and enhanced slightly at raising temperature.</li> </ul>
Sabiha, et al. [80]	Water/SWCNT	500 nm $\times$ 1-2 nm $\Phi = 0.05$ -0.25 vol.%	SDS	20-60 °C	<ul style="list-style-type: none"> <li>The addition of SWNCT nanomaterial resulted in a decreasing trend of <math>c_p</math> for the NF, while an increasing temperature resulted in the opposite trend.</li> </ul>
Hussein, et al. [82]	Water/CF-MWCNT + CF-GNP + h-BN	5 $\mu$ m $\times$ 15 nm and 2 $\mu$ m respectively $\Phi = 0.05$ -0.1 wt.%	Tween-80	20-60 °C	<ul style="list-style-type: none"> <li>11% higher <math>c_p</math> is achieved at 0.1 wt.% and 60°C due to advanced surface energy and greater surface of the dispersed particles.</li> </ul>
Wole-Osho, et al. [110]	Water/Al <sub>2</sub> O <sub>3</sub> /ZnO /Al <sub>2</sub> O <sub>3</sub> -ZnO	29 and 70 nm respectively $\Phi = 0.33$ -1.67 vol.%	--	25-65 °C	<ul style="list-style-type: none"> <li><math>c_p</math> dropped by 30.12% at 25°C and 1.67 vol.% loading, but it increased at higher temperatures. However, Al<sub>2</sub>O<sub>3</sub> NF have a lower <math>c_p</math> compared to ZnO NF at the same temperature.</li> </ul>
Tiwari, et al. [109]	Water/CuO-MWCNT /MgO-MWCNT /SnO <sub>2</sub> -MWCNT	20-50 nm (CuO, MgO and SnO <sub>2</sub> ) 1-20 $\mu$ m $\times$ 20 nm (MWCNT) $\Phi = 0.25$ -1.5 vol.%	CTAB	20-50 °C	<ul style="list-style-type: none"> <li>The highest <math>\phi</math> of MgO-MWCNT composite reduced <math>c_p</math> about 15.09% relative to water at 25°C. When the particle diameter of CuO and MgO nanoparticles is increased from 20 to 50 nm, the deterioration rate decreases.</li> </ul>
Wang, et al. [120]	Water-EG/TiO <sub>2</sub> /Aminopropyl-TiO <sub>2</sub> /CD- TiO <sub>2</sub>	15 nm $\Phi = 0.2$ -0.1 vol.%	(3-aminopropyl) triethoxysilane	30-85 °C	<ul style="list-style-type: none"> <li><math>c_p</math> decreases when particles are added. However, average <math>c_p</math> of water/CD-TiO<sub>2</sub> NF is 3.186 J/g °C which is quite good for heat transfer applications. <math>c_p</math> of the nanofluids reduced at the increasing cooling rate.</li> </ul>
Fesenko, et al. [121]	Water/Graphene /Graphene-gold	150-200 nm $\Phi = 0.002$ wt.%	--	30-60 °C	<ul style="list-style-type: none"> <li><math>c_p</math> decreased when the nano-filters were added, but it increased marginally when the temperature was raised.</li> </ul>
Moldoveanu and Minea [112]	Water/Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> /TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub>	45, 20 and 30 nm respectively $\Phi = 1$ to 3 vol.%	--	--	<ul style="list-style-type: none"> <li><math>c_p</math> dropped substantially for both mono and hybrid NFs at higher <math>\phi</math>. Experimental data of the fluids depicted larger deviation from the correlation at higher <math>\phi</math> of the dispersed particles.</li> </ul>
Selvam, et al. [122]	Water-EG/Graphene	15 $\mu$ m $\times$ 5-10 nm $\Phi = 0.001$ to 0.45 vol.%	Sodium Deoxycholate	30 °C	<ul style="list-style-type: none"> <li><math>c_p</math> decreased by 8% than BF and was observed to be lower than the predicted values from the mixture rule</li> </ul>

					to calculate $c_p$ of homogenous NFs. More deviation is noticed when $\varphi$ is above 0.15 vol.%.
Murshed [117]	Water/TiO <sub>2</sub>	15 nm $\Phi = 1-5$ vol.%	--	--	<ul style="list-style-type: none"> <li>• A <math>c_p</math> reduction of 18% is measured for the NF as 5 vol.% of particles are added to the BF due to much lower <math>c_p</math> of solid material relative to water.</li> </ul>
O'Hanley, et al. [123]	Water/Alumina /Silica /CuO	50, 32 and 30 nm respectively $\Phi = 0-0.3$ vol.%	--	35-55 °C	<ul style="list-style-type: none"> <li>• The <math>c_p</math> data is compared to two widely used correlations. The results indicate that the calculated <math>c_p</math> of formulated NFs agrees very well with the thermal equilibrium-based model rather than the direct mixture model.</li> </ul>
Singh, et al. [124]	Water/MWCNT	30 nm $\Phi = 0.05-0.5$ wt.%	Arabic Gum	25-300 °C	<ul style="list-style-type: none"> <li>• <math>c_p</math> enhanced as <math>\varphi</math> increased, the highest augmentation is noted 3.1% relative to water. The improvement is attributed to semi-solid layer formed on the surface of the nanomaterial.</li> </ul>
Gao, et al. [125]	Water/ Al <sub>2</sub> O <sub>3</sub> - Graphene oxide	layer number <10 for Graphene oxide, Al <sub>2</sub> O <sub>3</sub> (30±5 nm) $\Phi = 0.05-0.15$ wt.%	SDS	20-70 °C	<ul style="list-style-type: none"> <li>• At lower temperatures, the decrease in <math>c_p</math> for the NFs is much greater (7%) and lessens as <math>c_p</math> increases at higher temperatures.</li> </ul>
Devarajan, et al. [126]	Water/CNT /CNT-Al <sub>2</sub> O <sub>3</sub>	20-30 and 25-40 nm respectively $\Phi = 0.05-0.1$ vol.%	--	0-100 °C	<ul style="list-style-type: none"> <li>• The <math>c_p</math> is found dominant to BF as it increased notably with the addition of <math>\varphi</math>. The increment is attributed to stability and absorptivity of the NFs.</li> </ul>
Mousavi, et al. [97]	Water/MgO-TiO <sub>2</sub>	25-45 and 18-23 nm respectively $\Phi = 0.1-0.5$ vol%	SDS	15-60 °C	<ul style="list-style-type: none"> <li>• The maximum 1.17% decrease of <math>c_p</math> is measured at 0.5 vol% and 30 °C. It also dropped with inclusion of nanomaterials.</li> </ul>

#### 496 4. Colloidal stability of NF

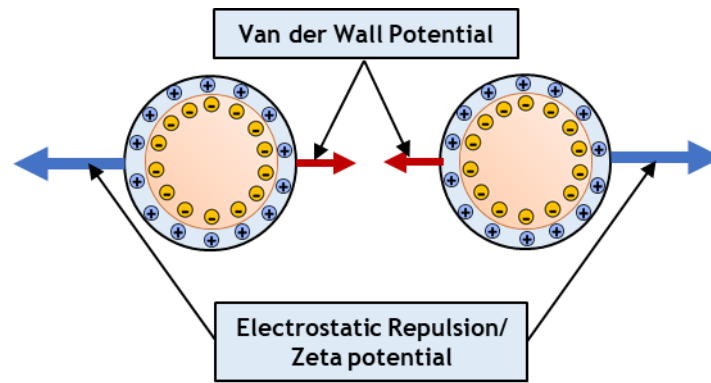
497 Stability is the most crucial hinder towards persistent application of the NFs for industrial  
498 purposes. The ability of NF to resist permanent distortion, i.e., the product of attraction and  
499 repulsion forces (between particle-particle and particle-fluid interface) over a given period, is  
500 known as its stability. The suspension stability of NPs distributed in BF greatly influences the  
501 performance of nanofluids. NPs are prone to instability and aggregation due to a variety of  
502 forces, including Van der Waals attraction, magnetic attraction, electrostatic attraction, bouncy  
503 and gravitational forces. These forces act against the stability of colloidal suspension and cause  
504 formation of large clusters, leading to deterioration of nanofluid performance. The proclivity  
505 of NPs to cluster results in the destabilization of nanofluid suspensions. The tendency of  
506 agglomeration is caused due to higher surface area as well as surface activity of original fluid  
507 with addition of NPs. Therefore, the agglomeration must be avoided to prepare a stable  
508 suspension that maintains stable dispersion of the nanomaterials in the pure fluid. The  
509 mechanism of dispersion of colloidal suspension is explained by the DLVO theory of particle  
510 dispersion [127]. The DLVO theory is based on the Van der Waals attractive force and  
511 electrostatic repulsive force that exist among colloidal particles. The net attraction or repulsion  
512 force depends on the distance between particles and the summation of Van der Waals attraction  
513 force and electrostatic repulsion force. However, this colloidal theory of nanoparticle  
514 dispersion is based on a few key assumptions: However, this colloidal theory of nanoparticle  
515 dispersion is based on a few key assumptions: (1) particle dispersion is homogeneous and  
516 dilute, (2) Van der Waals force and electrostatic force are the only forces acting on the  
517 suspension, (3) buoyancy and gravity forces are negligible, and (4) ion distribution in the  
518 suspension is controlled by factors such as Brownian motion, electrostatic force, and entropy  
519 influenced dispersion.

$$520 \quad F_T = F_{VdW} + F_{ES} \quad (7)$$

521 Where  $F_{VdW}$  and  $F_{ES}$  are the attractive and repulsive potential between the particles. If the  
522 attractive force is stronger than the repulsive potential, suspension will not be defined as  
523 unstable. From **Fig. 12**, it can be understood that when total interaction potential is high (i.e.,  
524 potential barrier is high), NPs are likely to remain stable preventing clusters due to higher  
525 separation distance, whereas low net interaction potential will result in unstable suspension.  
526 Nevertheless, if the particles collide beyond the potential barrier being affected by influential  
527 factors (e.g., temperature, chemical additives) than attractive potential will dominate (i.e.,  
528 separation distance is less) and form agglomeration (low zeta potential) to deteriorate

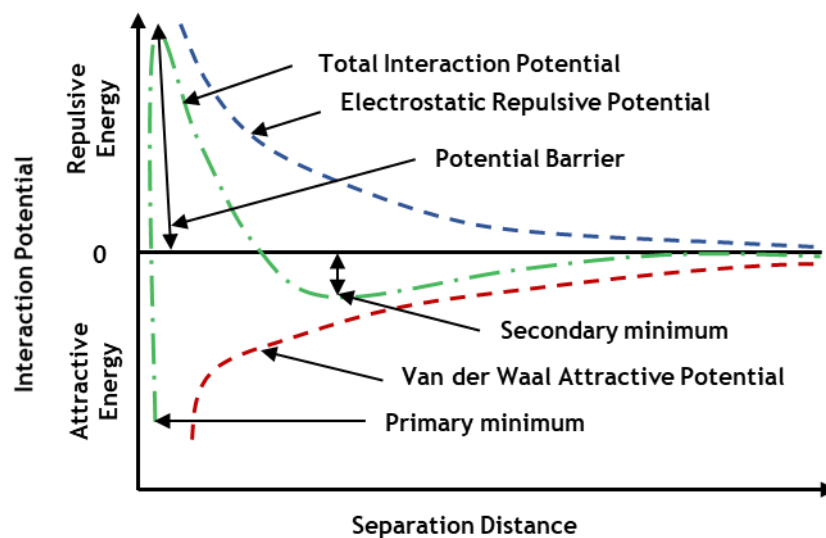


529 suspension homogeneous. Hence, the separation distance would be low, and it will cause  
 530 to emerge secondary minima which leads to further aggregation. Electrostatic repulsive  
 531 potential must be predominant over the attraction force to formulate stable NF. However,  
 532 mathematical expressions of Van der Waals attraction force and electrostatic repulsive force  
 533 vary depending on concentration, size, and shape of the particles.



534  
 535

(a)



536  
 537

(b)

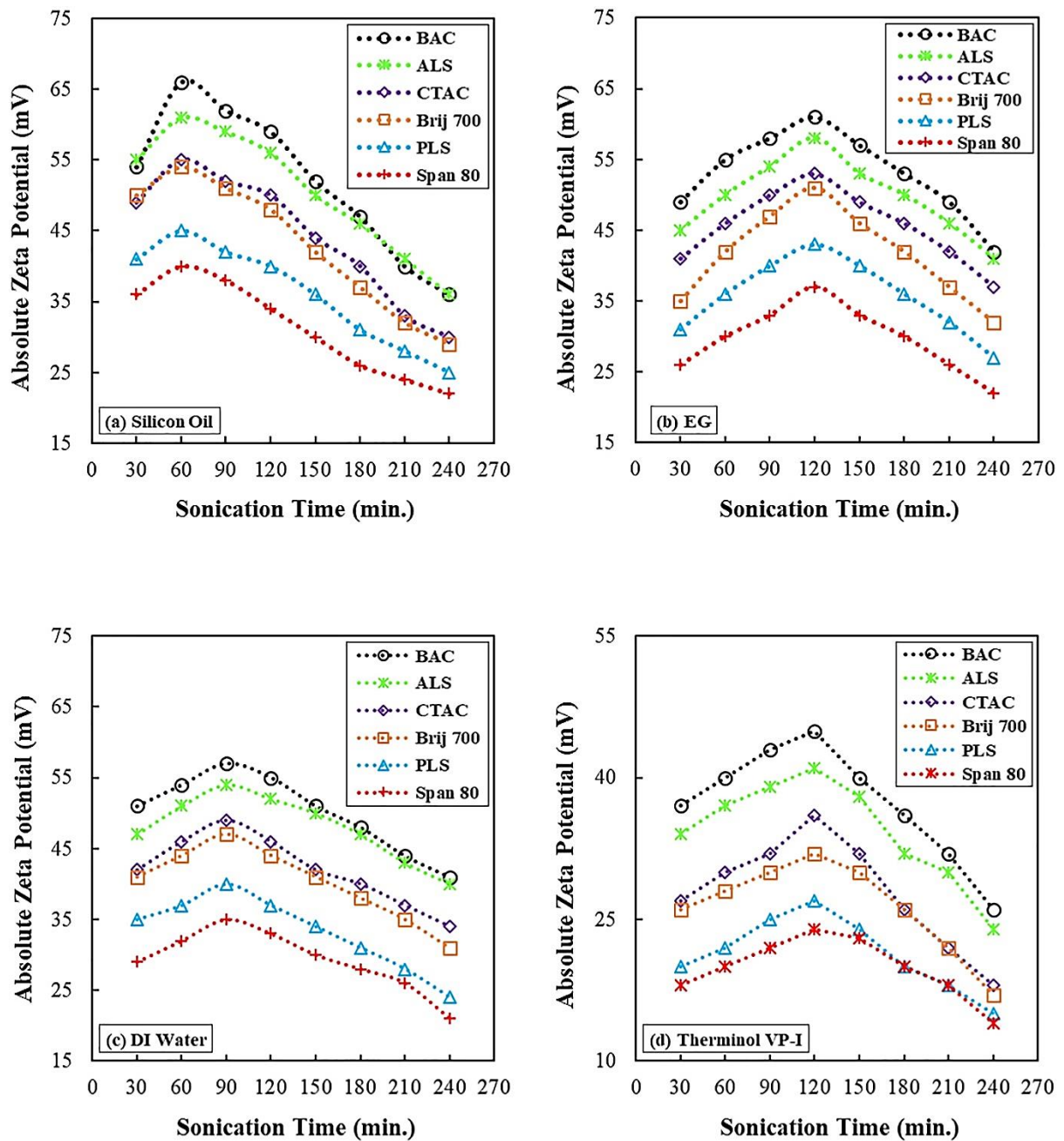
538 **Fig. 12.** (a) Interaction of two NF particles suspended in a BF (b) Schematic representation of  
 539 the interaction energy of stable NFs as a function of particle separation distance [8].

540 **4.1. Influential parameters effecting stability of NF**

541 Several factors have noteworthy effects on the colloidal stability of NF suspension. The  
 542 mechanism of some crucial factors influencing the colloidal stability of NF such as dielectric  
 543 constant ( $\epsilon$ ) of BFs,  $\phi$ , pH value, particle shape and size, temperature, Zeta potential ( $\zeta$ ),  
 544 stabilizing additives/surfactants, and stability evaluation techniques. For instance, various  
 545 types of BFs are used to formulate NFs based on the potential application of the fluids in low

546 to high temperature thermal heat transfer systems. The dielectric potential of fluids is an  
547 important property as it is directly related to repulsive potential which determines the stability  
548 of the fluid. The higher value of the  $\epsilon$  for fluid implies higher stability in suspension. Water  
549 has a  $\epsilon$  of approximately 78.5 at room temperature, which is the maximum among the generally  
550 used BF such as oils and glycols [128]. Deterioration of suspension stability of NFs due to  
551 addition of NPs is a chemical phenomenon, i.e., more the solid particles in BF, less the  
552 suspension stability [8, 11].

553 Choi, et al. [129] experimentally examined improved stability of water/MWCNT (0.0005-  
554 0.002vol.%) NF using different chemical dispersants (surfactants) e.g., SDBS, CTAB, SDS  
555 and TX-100. They revealed that the NFs were stable for over 30 days and exhibited improved  
556 absorbance property under the impact of surfactants. Tiwari, et al. [130] studied stability of  
557 four separate BF (water, EG, therminol-VP1 and silicon oil) based MWCNT-CeO<sub>2</sub> NFs using  
558 six unique surfactants (BAC, ALS, CTAC, Bri-700, PLS and Span-80) and substantial rang of  
559 ultrasonication period (30-240 minutes) for stabilization of the suspensions (**Fig. 13**). The  
560 obtained data elucidated that BAC was the most efficient stabilizer, as it the stability indicator  
561 ( $\zeta$ ) relative to other surfactants. Increased ultrasonication time results in a more homogeneous  
562 suspension up to a point where further ultrasonication deteriorates the stability of the dispersion  
563 due to the formation of clusters. Using BAC as surfactant, silicon oil-based NF performed best  
564 stability in terms of  $\zeta$ , duration and sonication time (66 mV, 30 days, 60 min) followed by EG  
565 (61 mV), water (57 mV) and therminol-VP1 (45 mV) based NFs at identical 0.75 vol.% of  
566 MWCNT-CeO<sub>2</sub>. The effect of increasing temperature (25-50°C) on stability was negative in  
567 this experiment, which could be attributed to the stabilizers' limitations at higher temperatures  
568 [131]. Similar positive effect of surfactants are observed using water/Al<sub>2</sub>O<sub>3</sub> and oil/Al<sub>2</sub>O<sub>3</sub> NFs  
569 by [132] and [133] respectively. The effect of low-high temperature using different surfactants  
570 can be understood from the experiment done by Choi, et al. [129] using water/MWCNT NFs.  
571 They stated that stability varies utilizing different dispersants in terms of temperature. In their  
572 case, SDBS performed well for low (10°C) and high (85°C) temperature whereas, CTAB and  
573 TX-100 showed well stability factor only at high temperature.



574

575 **Fig. 13.** The impacts of several BFs, surfactants and sonication period on suspension stability  
 576 of hybrid NFs using MWCNT-CeO<sub>2</sub> nanocomposite and different BFs, investigated by [130].

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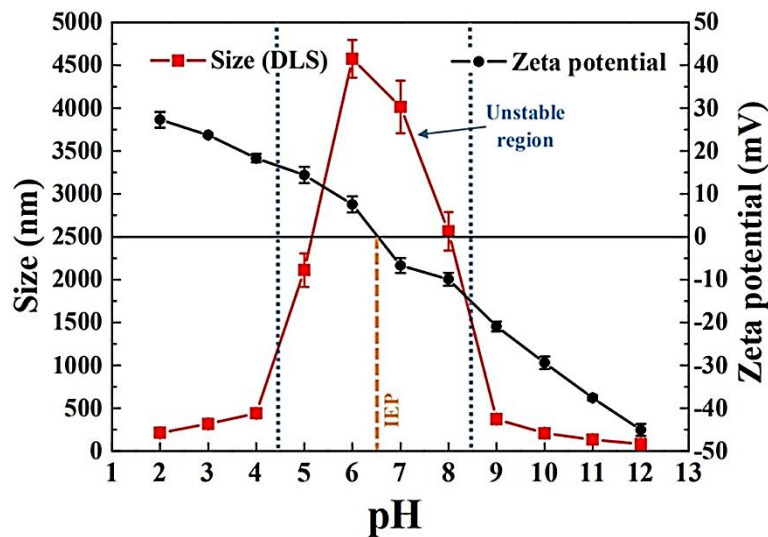
582

583

Almanassra, et al. [42] found excellent stability of water/CNT (0.1-1wt.%) NF adding GA, PVP and SDS as stabilizers using an optimum ration of 1:0.5 (NP: surfactant). The stability of GA and PVP-containing samples has been confirmed to exceed six and three months, respectively. Xian, et al. [58] experimentally evaluated the influence of various surfactants e.g., anionic (SDS, SDC and SDBS), cationic (CTAB) and non-ionic (PVP and Triton X-100) along with the effect of sonication time on water-EG based mono and hybrid NFs using functionalized graphene (COOH-GnP) and graphene (COOH-GnP)-TiO<sub>2</sub> NPs at 0.025-

584 0.1wt.%. Cationic CTAB and anionic SDBS stabilizers are found to be superior options for  
 585 homogenizing the suspension using a 90-minute sonication time. The obtained  $\zeta$  data  
 586 confirmed robust stability of single particle-based NF (-52 to -60 mV) rather than hybrid (-42  
 587 to -46 mV) at all NP loadings. Keklikcioglu Cakmak [60] demonstrated the opposite effect of  
 588 surfactants, as the stability and absorbance of water/GO NF decreased when CTAB, SDS, and  
 589 TX-100 were added regardless of  $\varphi$ .

590 Zhang, et al. [65] investigated the effect of pH variation on the suspension stability of  
 591 water/TiO<sub>2</sub> NF through sedimentation, TEM photos, DLS analysis, Brownian and settling  
 592 velocity ratios. NF sample with pH of 12 is observed to remain well dispersed for long time (>  
 593 30 days) with a  $\zeta$  value of -45.06 mV and smallest particle size of approximately 81.19 nm  
 594 while samples having pH values (4.5-8.5) around IEP 6.5 indicated lowest stability  
 595 demonstrated in Fig. 14.

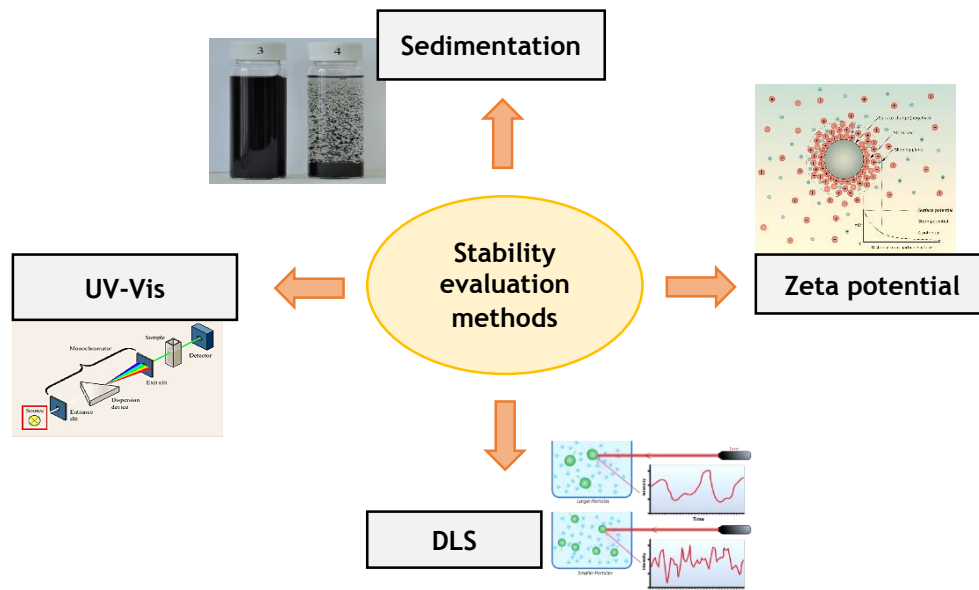


596  
 597 **Fig. 14.** Influence of pH values on Zeta potential and particle sizes of water/TiO<sub>2</sub> (20 nm,  
 598 0.025vol.%) NFs at 25°C [65].

599 Wang, et al. [66] observed variation in pH (3-11) and surfactant concentration (0-0.15wt.%)  
 600 noticeably alters suspension agglomeration of water/Cu and water/Al<sub>2</sub>O<sub>3</sub> NFs and optimum  
 601 combination of the parameters can deliver optimized particle distribution, stability, and  
 602 effective TC. At optimized pH condition (8.0 and 9.5 for alumina and Cu NFs respectively),  
 603 improved stability indicator value is achieved  $\zeta_{alumina} = 40.1$  and  $\zeta_{Cu} = 43.8$  mV. **Table. 5**  
 604 represents a summary of reviewed experimental works on stability of various NFs with detailed  
 605 specifications on the operating conditions. Details on stability evaluation methods and  
 606 stabilization techniques are covered in **Section 4.2 and Section 4.3**, respectively.

607 **4.2. Stability assessment techniques**

608 Different techniques are employed in investigations for assessment of nanofluids suspension  
 609 stability, i.e., sedimentation and centrifugation, Zeta potential measurement, transmission  
 610 electron microscopy, spectral absorbance, and transmittance measurement, 3- $\omega$  method and  
 611 dynamic light scattering technique (presented in **Fig. 15**). In the following sections, stability  
 612 measurement methods of NFs will be discussed briefly.



613  
 614 **Fig. 15.** Effective stability evaluation techniques for nanofluids.

615 **4.2.1. Sedimentation**

616 Sedimentation of NFs is important since it is directly related to their suspension stability. This  
 617 approach uses static nanofluid images to test the settling activity of NFs due to gravitational  
 618 force and the internal solid-liquid interaction between scattered particles and BF. Stability is  
 619 determined using this technique by the time required for the NF sample to precipitate. Stokes  
 620 law can be used to calculate the gravitational settling of spherical shaped particles:

621 
$$V_t = \frac{2r^2(\rho_p - \rho_b)g}{9\mu} \quad (8)$$

622 where  $V_t$ ,  $r$ ,  $\rho_p$ ,  $\rho_b$ ,  $g$  and  $\mu$  represent terminal velocity of spherical particles, radius of the  
 623 particles, density of solid particles, density of base fluid, gravity, and dynamic viscosity of the  
 624 base fluid, respectively. According to the equation, smaller particles have a lower terminal  
 625 velocity and a higher sedimentation rate than larger nanoparticles distributed in BF.  
 626 Additionally, it demonstrates that the dynamic viscosity of BF and the density of nanoparticles

627 are critical parameters for the formation of stable nanofluids. Stability can also be determined  
628 using this technique by comparing the height of the sedimented layer to the duration.  
629 Several studies on the stability characterization of NFs have been conducted using the  
630 sedimentation technique [134-136]. This approach is advantageous and cost-effective in  
631 comparison to other approaches for determining stability, such as zeta potential, UV-vis, and  
632 electron microscopy. Rehman, et al. [137] used the sedimentation approach to examine the  
633 stability of MWCNT/Jatropha oil nanofluids. For up to three weeks, the nanofluids exhibited  
634 no visible sedimentation and exhibited excellent stability over a one-month period. Ilyas, et al.  
635 [138] studied stability of Al<sub>2</sub>O<sub>3</sub>/thermal NFs at natural and functionalized conditions. They  
636 revealed that functionalized NFs exhibit suspension stability of more than 4 weeks whereas,  
637 natural samples aggregation within a few hours from the formulation of NFs. However, due to  
638 significant limitations, this approach is not widely reliable. Due to the impossibility of detecting  
639 internal dynamic solid-liquid interactions with the naked eye or by examining images, this  
640 method of determining suspension stability may not be predictable. Additionally, it is very  
641 difficult to detect sedimentation in dark nanomaterials solely by visualizing the NF samples.

#### 642 *4.2.2. Zeta potential ( $\zeta$ )*

643 As NPs are distributed in BF, the fluid surrounding the particles forms layers (i.e., stern and  
644 diffuse) that combine to form an electrical double layer (EDL). EDL produces a potential  
645 difference, referred to as the Zeta potential ( $\zeta$ ), which implies electrostatic attraction between  
646 scattered particles. Suspensions having a  $\zeta$  value of more than  $\pm 30$  mV are considered  
647 electrostatically stable and above  $\pm 60$  mV indicate very good stability. Suspensions having  $\zeta$   
648 value in the range of  $\pm 15$  mV are considered unstable [139]. At a particular pH value of  
649 nanosuspension,  $\zeta$  becomes zero and it is called isoelectric point (IEP). At the IEP, dispersed  
650 particles maintain an electrophoretic immobility. The possible electrostatically stable  
651 suspension can be obtained by adjusting the pH value in relation to the IEP value for  
652 electrostatically stabilized suspensions.

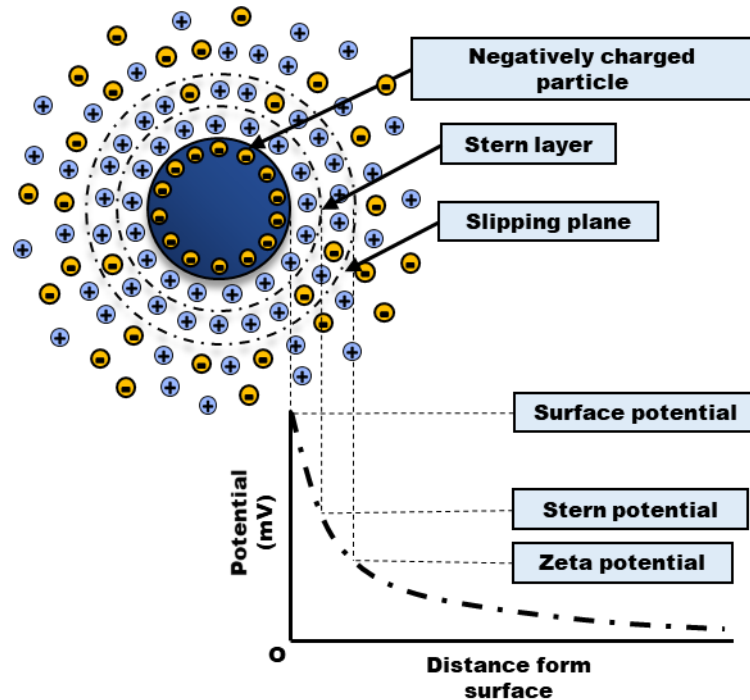
653 The  $\zeta$  indicate the potential difference between the stationary layer (stern layer) of mobile  
654 particles and the layer of dispersant (diffuse layer) around the particles at the slipping plane.  
655 The Stern layer is tightly bound to the surface of the particles by oppositely charged ions, while  
656 the diffuse layer is weakly bonded and consists of both neutrally distributed positive and  
657 negative ions (demonstrated in **Fig. 16**). The ZP can be calculated using following equations:

$$658 \quad \mu_e = \frac{V}{E} \quad (9)$$

659 where  $V$  = particle velocity ( $\mu\text{m/s}$ ),  $E$  = electric field strength (Volt/cm). The  $\zeta$  can be  
 660 calculated from the obtained  $\mu_e$  by the Henry's equation.

$$661 \quad \mu_e = \frac{2\varepsilon_r\varepsilon_0\zeta f(ka)}{3\eta} \quad (10)$$

662 where  $\varepsilon_r$  = relative permittivity/dielectric constant,  $\varepsilon_0$  = permittivity of vacuum,  $f(ka) =$   
 663 Henry's function and  $\eta$  = viscosity at experimental temperature. The  $\zeta$  value significantly  
 664 effects the colloidal stability of nanofluids [140]. A higher absolute value of  $\zeta$  indicates more  
 665 stable suspension, whereas low  $\zeta$  depicts unstable nanoparticles distribution into the pure fluid  
 666 [132]. A stable nanofluid possesses higher repulsive force among the dispersed particles  
 667 because of higher absolute potential difference. According to the most widely accepted DLVO  
 668 theory, colloid stability depends on the sum of Van der Waals attractive forces and electrostatic  
 669 repulsive forces due to the EDL. However, the limitations of this theory are stated by  
 670 Bhattacharjee [141] as it does not provide details on Van der Waals interactions among the  
 671 dispersed particles. In addition, it should be noted that, in contrast to common practice  
 672 regarding stability of NFs,  $\zeta$  value should not be taken as the ultimate indicator of suspension  
 673 stability of NFs unless the NFs are stabilized by electrostatic repulsion between the particles.



674  
 675 **Fig. 16.** Charged layers of nanoparticle dispersed in bulk base fluid.

676 **4.2.3. Dynamic light scattering (DLS)**

677 The DLS technique can be utilized to determine particle size distributing of any colloidal  
 678 solution transmitting a monochromatic beam of light across suspension containing NPs. Light



679 diffuses in all directions depending on the size and shape of dispersed particles. The intensity  
680 of scattered light fluctuates due to Brownian motion of the particles and is then investigated by  
681 a photon detector to evaluate the particle size distribution by analyzing the diffusion coefficient  
682 ( $D_\tau$ ) which is a function of critical parameters such as particle hydrodynamic size, temperature,  
683 and absolute viscosity of the NF. and can be calculated using the Stokes-Einstein equation  
684 [141]:

$$685 \quad D_\tau = \frac{k_B T}{6\pi\mu R_h} \quad (11)$$

686 where  $k_B$ ,  $T$ ,  $\mu$  and  $R_h$  are the Boltzmann constant, temperature, viscosity hydrodynamic radius  
687 of particles. The particle size distribution of a suspension shows the stability of the dispersion  
688 by determining the cluster size of the scattered particle over time intervals. Particles with a  
689 large cluster size indicate that the suspension is unstable, resulting in sedimentation and  
690 agglomeration of scattered particles. Investigations with nanofluids, DLS technique is being  
691 used to successfully determine the particle distribution in order to define suspension stability.  
692 Anushree and Philip [142] observed the hydrodynamic size of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> NFs decreases  
693 significantly with time, implying significant sedimentation and unstable dispersion of the  
694 nanofluids. Navarrete, et al. [143] experimentally measured particle size distribution for molten  
695 salt-based NFs using a DLS set-up which is designed to perform up to 500°C. Nevertheless,  
696 the DLS technique may interpret inconsistent results when particle concentration is high, and  
697 sizes of dispersed multiple nanomaterials are not identical.

#### 698 **4.2.4. Spectral absorbance measurement**

699 The stability of NFs can be determined by measuring the spectral absorbance over a specific  
700 band of wavelengths. UV-Vis spectral analysis is often used to determine stability by  
701 estimating spectral absorption between 190 and 1100 nm [144]. Stability is evaluated using  
702 this technique by analyzing the absorption profiles of NF samples with varying solid  
703 concentrations over a specified period. An UV-Vis spectrophotometer uses the fact that the  
704 light intensity turns out to be different by absorption and scattering of light passing through a  
705 fluid. Stability is determined by assessing the variation in absorption peak characteristics for  
706 the fluid against time. Lower value of absorbance after a certain period indicates instability of  
707 NF suspension. Absorbance ( $A_\lambda$ ) can be estimated using the following equation:

$$708 \quad A_\lambda = \log_{10}(I_0/I) = \alpha \times l \times c \quad (12)$$

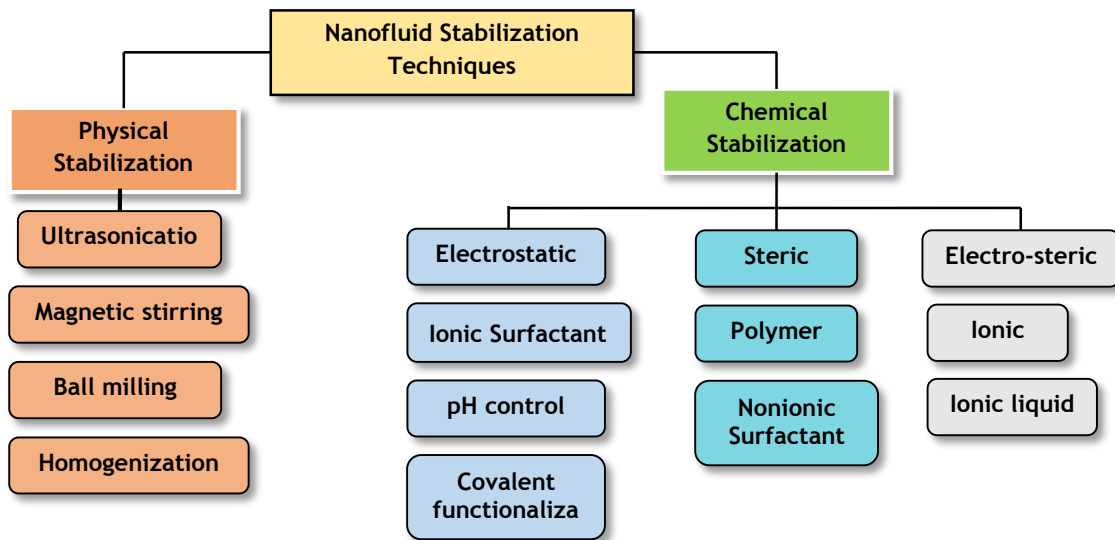
709 Absorbance ( $A_\lambda$ ) is proportional to particles concentration ( $c$ ), absorptivity ( $\alpha$ ) distance  
710 traveled by the light source.  $I_0$  and  $I$  are the intensity of light beam before and after passing



711 through the fluid sample. The reduction of solid concentration in the suspension over time is  
712 reflected in decreased absorbance due to agglomeration in the suspension. This approach has  
713 been shown to be useful in determining the stability of NF in several studies [145, 146].  
714 However, the technique is ineffective for samples with high NF concentrations or dark  
715 suspensions because it is difficult to distinguish sediment visibility at high solid concentrations  
716 [147].

### 717 *4.3. Nanofluids stabilization techniques*

718 A thorough understanding of colloidal dispersion mechanisms is needed to clarify the  
719 suspension stability of NFs. The dispersion or suspension stability of NF is directly associated  
720 to inter-particle interaction and active microscopic forces acting on dispersed nanoparticles in  
721 the base fluid. NFs are inherently unstable due to the gravitational force acting on each  
722 NP which causes sedimentation of the particles. However, random thermal motion, i.e.,  
723 Brownian motion of NPs can counterbalance the sedimentation and stabilize the suspension.  
724 Along with force action on single NP, interaction forces between the particles in the suspension  
725 play a dominant role in the dispersion characteristics of NF [26]. During inter-molecular  
726 interaction among adjacent particles, NPs tend to form aggregation due to ubiquitous Van der  
727 Waals attraction forces ( $F_{VdW}$ ). The magnitude of  $F_{VdW}$  depends on different factors such as;  
728 dielectric constant of the solvent, interfacial interaction between the NP and dispersion medium  
729 [148]. In contrary, the electrostatic potential between adjacent particles stabilizes the colloidal  
730 suspension through repulsive intermolecular interaction. The resultant potential of these inter-  
731 molecular forces is a function of a few key parameters as discussed in **Section 4**. Different  
732 effective stabilization techniques for improved stability of NF are summarized and  
733 classification of the techniques is shown in **Fig. 17**. In the following sections, these stabilization  
734 techniques are enlightened.



735  
736

**Fig. 17.** Stability enhancement techniques for nanofluids.

737 **4.3.1. Physical stabilization**

738 Different physical techniques are often used to stabilize NF suspensions. Mechanical methods  
739 such as ultrasonic vibration, magnetic stirring, and homogenization are often used to disperse  
740 colloidal mixtures homogeneously.

741 Ultrasonication is an important mechanical dispersion technique for achieving a homogeneous  
742 mixture of NPs and base fluid. Ultrasonication methods, both direct (ultrasonic bath) and  
743 indirect (probe sonication), can be used to stabilize colloidal suspensions by dissolving particle  
744 clusters and reducing the average particle size distribution. The indirect ultrasonication  
745 approach using high frequency probe sonication exhibits superior output in various studies  
746 involving NF dispersion. Ultrasonication of colloidal suspensions results in a more  
747 homogeneous distribution of NPs within the mixture, resulting in a smaller average cluster size,  
748 which has a significant effect on the NP's heat transfer properties [149]. Asadi, et al. [150]  
749 reviewed the remarkable effect of ultrasonication on the colloidal dispersion and heat transfer  
750 characteristics of NF, highlighting the significant effect of ultrasonication time and power  
751 variation on the effective dispersion of NPs into BF. In another article, Asadi, et al. [151]  
752 revealed that the optimal time for sonication is 60 minutes for MWCNT/water NFs with the  
753 highest thermal conductivity. However, beyond a certain amount of ultrasonication, dispersion  
754 characteristics and thermophysical behavior deteriorate noticeably, and this stage is considered  
755 the optimal time for stabilization [152].

756 Magnetic stirring is a fundamental technique for achieving homogeneous dispersion of NPs in  
757 a base liquid solvent. A spinning magnetic bead rotates at varying speeds in this process, using

758 an external magnetic field to break up clusters and disperse the NPs. Studies has shown that  
759 effective stirring technique depends on two crucial parameters such as stirring speed and  
760 stirring time. Usually, high speed of stirring and longer time of stirring yield better performance  
761 dispersing NP clusters. At elevated speed and longer stirring time more NPs can come into  
762 contact to the magnetic bead and break apart into smaller particles. Kamalgharibi, et al. [153]  
763 reported better stabilization of CuO/water-EG NFs at higher stirring speed. At 700 rpm, they  
764 observed the lowest height of sedimentation while lower rpm showed a rise in sedimentation  
765 and instability of the suspension. Chen, et al. [154] investigated dispersion stabilization of  
766 Al<sub>2</sub>O<sub>3</sub>/liquid paraffin NF at different stirring periods. They observed that stirring for a longer  
767 period increases stability by using stirring in two stages of the stabilization process. They noted  
768 that increasing stirring time by 30 to 40 minutes yields 3.14% more thermal conductivity for  
769 the studied NFs. In addition, stirring is found to be more effective at elevated temperatures and  
770 lower concentration of NPs. To formulate stable NFs, few other effective stabilization methods,  
771 for instance; high-pressure homogenization and ball milling are employed in various studies  
772 and found prominent improvement of dispersion characteristics [155-157]. However, the  
773 stability of NFs remains a challenging issue since the physical maintenance techniques often  
774 fall short of providing suspensions that are stable for the long term.

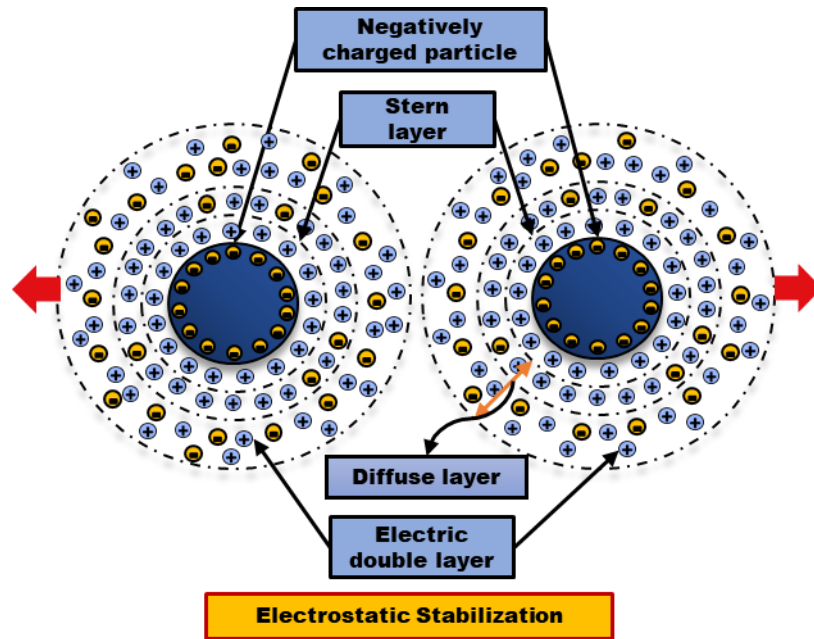
#### 775 **4.3.2 Chemical stabilization**

776 Chemical techniques for stabilization i.e., electrostatic, steric, or electro-steric strategies  
777 include surface functionalization, surfactants inclusion, pH control, acid treatment and so on.  
778 The sections that follow provide a thorough understanding of these stabilization techniques.

##### 779 **4.3.2.1. Electrostatic stabilization**

780 Electrostatic stabilization of NFs can be obtained when attractive Van der Waals force is  
781 stabilized by reciprocal repulsive potential between the identically (positive or negative)  
782 charged particles demonstrated in **Fig. 18**. The surface charges of the NPs can be induced by  
783 several approaches such as: (a) ionization of surface groups, (b) adsorption of ions from ionic  
784 surfactants, (c) substitute of ions, (d) dissociate surface charged parts, (e) physically adsorbed  
785 ions, and (f) accumulation or depletion of electrons at surfaces. In liquid suspension, charged  
786 NPs are surrounded by opposite charges to sustain charge neutrality of the dispersion and to  
787 form the electric double layer (EDL) with a strongly bonded stern layer and diffuse layer. The  
788 stern layer contains opposite ions whereas, diffuse layer consists of weakly attached both  
789 positive and negatively charged ions due to electrostatic force of the particles. The electric

790 potential is maximum at the surface of the particles and drops steadily away from the surface  
 791 to EDL. The electric potential at the outer layer of EDL is defined as Zeta potential, which  
 792 value is used to estimate the dispersion stability of NF suspension. The objective of electrostatic  
 793 stabilization is to increase the electric potential between the particles to minimize the attraction  
 794 force so that particles cannot form agglomeration and disperse homogenously in the liquid  
 795 medium. The higher the potential, the higher the electrostatic stability of the NFs.



796  
 797 **Fig. 18.** Electrostatic stabilization technique for nanofluid suspension.

798 Electrostatic stabilization includes the addition of ionic surfactants to the NF. Several  
 799 categories such as cationic, anionic, non-ionic, and amphoteric surfactants are employed in BF  
 800 [158-161]. Amphoteric surfactants, also known as zwitterionic, are surfactants containing both  
 801 cationic and anionic hydrophilic functional groups in their chemical structure. This class of  
 802 surfactants can produce cations and anions depending on the acidity (pH) of the suspension.  
 803 These surfactants exhibit low toxicity, good anti-bacterial characteristics, resistance to the  
 804 hardness of water and are well-suited with other forms of surfactants. Amiri, et al. [161]  
 805 reviewed stable liquid-phase exfoliation of two-dimensional graphene using several classes of  
 806 ionic and non-ionic surfactant stabilizers such as pluronic P-123, Triton X-100,  
 807 Polyvinylpyrrolidone (PVP), n-Dodecyl  $\beta$ -D-maltoside, Polysodium4-Styrenesulfonate (PSS),  
 808 Sodium deoxycholate (DOC), Sodium taurodeoxycholate hydrate and so on. Furthermore,  
 809 pyrene derivative dispersion stabilizers are also used for effective suspension stabilization.  
 810 Parviz, et al. [162] investigated different pyrene-based stabilizers such as 1-Pyrenesulfonic acid  
 811 sodium salts (Py-1SO<sub>3</sub>), 1-Pyrenesulfonic acid hydrate (Py-SAH), 1,3,6,8-Pyrenetetrasulfonic

812 acid (Py-4SO<sub>3</sub>) and 1-Pyrenecarboxylic acid (PCA) with high concentration of graphene  
813 nanosheets. They concluded that pyrene derivatives attached with sulfonyl groups yield the  
814 most stable dispersion of NPs over a wide range of pH. Aromatic stabilizers are generally  
815 utilized for homogenous dispersion of carbon-based NPs in different BFs [163, 164].  
816 Pyrene derived stabilizers are also considered as anionic surfactant and used as non-covalent  
817 functionalization method of NF stabilization. Ionic and non-ionic surfactants are used to obtain  
818 electrostatic and steric stabilization of NF dispersion. Non-covalent functionalization can be  
819 accomplished by various way such as anionic and cationic surfactant, non-ionic surfactant,  
820 polymer, and aromatic surfactant. For carbon-based NFs, the main shortcoming of non-  
821 covalent functionalization is the formation of foam inside thermal apparatus leading to  
822 lessening in effective heat transfer performance [165, 166]. In contrary, covalent  
823 functionalization of carbon-based NF can overcome these shortcomings [74, 167]. The most  
824 frequently utilized stabilizers for covalent functionalization of carbon-based NPs are Sodium  
825 Dodecyl Sulfate (SDS), Sodium Dodecyl Benzene Sulphonate (SDBS), Gum Arabic (GA) and  
826 Triton X-100. Among them, SDBS offers finest dispersion stability of carbon-based NP in  
827 water due to strong  $\pi$ - $\pi$  interaction between the carbon particles [168].  
828 Stability of NFs can also be obtained by substituting the functional groups on the surface of  
829 NPs using acid or alkali solution and employing plasma treatment as well. Several functional  
830 groups for instance; hydroxyl ( $-OH$ ), carboxylic ( $-COOH$ ), carbonyl ( $C = O$ ), sulphate ( $SO_4^{2-}$ )  
831 and amine ( $N - H$ ) leads to advance suspension stability in the polar solvents. Such form of  
832 functionalization is identified as the covalent functionalization [161, 169]. Amiri, et al. [167]  
833 investigated effect of covalent and non-covalent functionalization of CNT NPs using Gum  
834 Arabic and Cysteine respectively. Amiri, et al. [170] reported improvement of dispersion  
835 stability of graphene (doped with nitrogen)/ethylene glycol-water NF using cyanamide as  
836 stabilizer. Etefaghi, et al. [171] prepared environment friendly stable graphene-water NF  
837 without using citric acid as precursor. They reported NFs were stable for six months at low-  
838 cost to formulate the ecofriendly NFs.  
839 pH of NF suspension plays an essential role in terms of stability of the dispersion therefore, pH  
840 adjustment of NF mixture leads to attain considerable homogenous dispersion characteristics  
841 of the mixture. To obtain good suspension stability pH should be controlled either at higher  
842 value or lower value with respect to pH value of isoelectric point (IEP) for the suspension. At  
843 IEP, zeta potential for any suspension is zero which implies absence of repulsive force in the  
844 mixture hence, the mixture is at unstable state in terms of homogenous dispersion. Lee, et al.  
845 [172] showed colloidal mixture performs better suspension stability and thermal performance

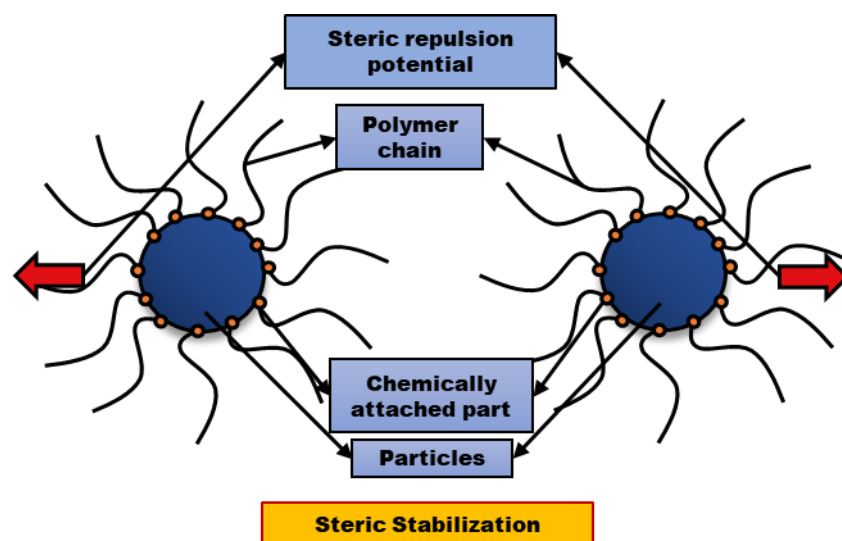
846 at pH value far from the value of IEP using CuO NF. They concluded surface charge as a basic  
847 key parameter towards improved thermal performance of NFs. Investigations on effect of pH  
848 control on dispersion stability of NF are performed to evaluate optimum pH value for NF under  
849 which it performs better suspension stability [66, 173-175].

850 Several oxidizing agents such as;  $\text{HNO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$  and so on are utilized to  
851 improve dispersion stability of colloidal mixture [176, 177]. Ghozatloo, et al. [178] used  
852  $\text{K}_2\text{S}_2\text{O}_8$  and KOH solution as oxidizer and pH control agent respectively for alkaline  
853 functionalization of hydrophobic graphene nanosheets into hydrophilic structure. The results  
854 exhibited improvement in dispersion as well as in thermal conductivity due to the inclusion of  
855  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{COOK}$  functional groups in the formulated NF.

856 However, electrostatic stabilization has some restrictions regarding the applicability of this  
857 dispersion technique in different medium as follows; (a) this technique is applicable for non-  
858 aqueous colloidal suspension, (b) limited to dilute nanoparticle dispersion, (c) not suitable for  
859 systems containing metal ions and saline medium and (d) stable dispersion of the agglomerated  
860 particles is not possible in this method of stabilization.

#### 861 4.3.2.2. Steric stabilization

862 The steric or polymeric technique of colloidal suspension stabilization is characterized as the  
863 addition of polymeric chains to the particle surface in order to generate repulsive forces  
864 between the dispersed particles and thus improve suspension stability. The polymer molecules  
865 use steric hinders to counteract the attraction force between the NPs (see **Fig. 19**). Non-ionic  
866 surfactants and polymers can be used to stabilize NFs sterically [161, 168, 179, 180]. Steric  
867 stabilization enables the stabilization of NFs at higher particle loadings than electrostatic  
868 stabilization.



869

870

**Fig. 19.** Steric stabilization technique for nanofluids stabilization.

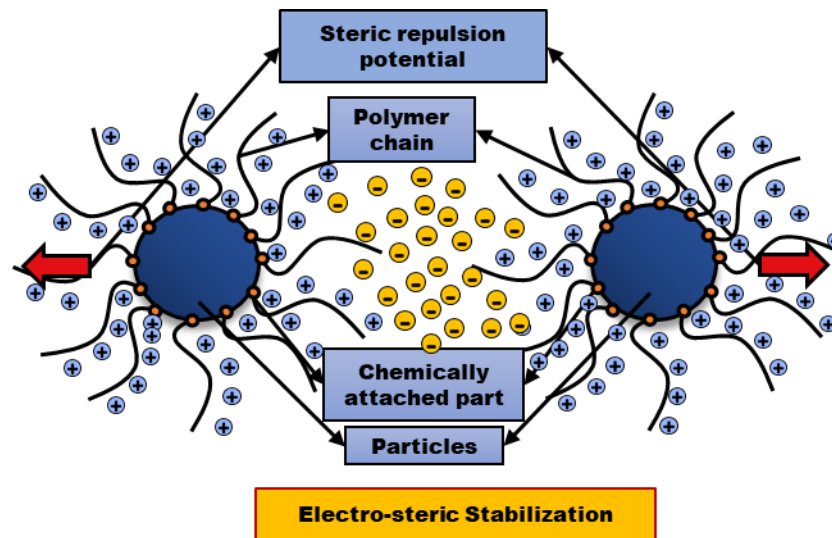
871 By grafting polymers or macromolecules onto the surface of NPs, a steric barrier is formed  
872 between the dispersed particles, significantly lowering the intermolecular Van der Waals  
873 potential [26, 181]. Via chemical or physical adsorption, the polymers become weakly bound  
874 to the NP surface. When polymers are grafted onto the surface of particles, they restrict particle  
875 movement in the base fluid, creating a barrier that prevents particle aggregation [182].  
876 Compatibility of polymeric additives with BF is critical for successful stabilization. Steric  
877 stabilization performance is highly dependent on the absorption properties and length of  
878 polymeric chains. For example, increased polymer absorption on the NP surface results in a  
879 larger grafted surface, which can result in an improved steric effect in the dispersion. The length  
880 of polymeric chains is critical since short polymers exhibit poor absorption properties. Thus, a  
881 longer polymeric chain and strong bonding to the NP surface are needed for effective steric  
882 stabilization.

883 Steric stabilization polymers are either homopolymers containing the same monomer or  
884 copolymers containing two dissimilar monomers in the same polymeric chain. Co-polymers  
885 are classified into three groups based on their monomer structure, namely random, block, and  
886 graft co-polymers. If random co-polymers are composed of several groups of monomers  
887 randomly assembled, block co-polymers are composed of two monomer blocks of repeating  
888 units. In contrast to random and block copolymers, graft copolymers have a main structure  
889 composed of one monomer and another monomer on the side chain. For possible steric  
890 stabilization, grafted and amphiphilic block polymers are optimal. The criteria for selecting co-  
891 polymers for steric technique are that one component should be attracted to the particle surface  
892 and the other component should be compatible with the BF medium. Gum Arabic, Oleylamine,  
893 Triton-X-100, Tween 20, Span 80, PVP, and oleic acid are all polymers that are often used for  
894 steric stabilization of NFs [91, 183, 184].

#### 895 **4.3.2.3. *Electro-steric stabilization***

896 Electro-steric stabilization is the combination of electrostatic and steric stabilization. Ionic  
897 polymers are absorbed by the charged particle surface in this technique, resulting in the  
898 formation of a steric barrier and electrostatic barriers that prevent the agglomeration of  
899 dispersed NPs. Apart from steric repulsion, the electrostatic double layer developed in this  
900 process enhances NF dispersion much further. Electro-steric stabilization is typically  
901 accomplished using ionic polymers that incorporate a charged anchor segment and an ionic

902 polymeric chain to simultaneously provide electrostatic and steric stabilization (illustrated in  
903 **Fig. 20**).



904

905

**Fig. 20.** Electro-steric stabilization for nanofluid suspension.

906 The polymer used in this method is identified as polyelectrolyte which is an amalgamation of  
907 repeating polymer units attached with at least one ionized functional group (such as;  
908 carboxylic, sulfonic acid group and so on) and different molecular structure [185]. The most  
909 used polyelectrolytes for the electro-steric stabilization of NPs in suspension are poly(styrene  
910 sulfonic acid) (PSS), polyacrylic acid (PAA) and poly(1-vinylpyrrolidone-co-acrylic acid)  
911 (PVcA) as anionic block co-polymers, poly(vinyl sulfonic acid) (PVSA), and  
912 polyethyleneimine (PEI) as cationic polyelectrolyte [185, 186]. The ionized function groups  
913 attached to the polymers dissociated into the base fluid to form EDL between the approaching  
914 particles. To achieve successful stabilization, the ionic polyelectrolytes and NP should be  
915 charged in the opposite direction. Polyampholyte can also be used for electro-steric  
916 stabilization because it contains both anionic and cationic functional groups. Owing to their  
917 high charge density and heavy chemisorption on the NP surface, ionic liquids are used to  
918 stabilize NFs by providing electrostatic repulsion and steric stabilization, respectively [187].  
919 Kong, et al. [188] stabilized cement and deionized water suspensions using melamine  
920 formaldehyde sulfonate (MFS) as a solid anionic polyelectrolyte.



921 **Table 5.** A summary of experimental studies on stability of nanofluids with detailed operating conditions and deployed stabilization techniques.

Reference	Examined nanofluids	Particle size and concentration ( $\phi$ )	Surfactant or chemical additives	Stability or Zeta potential ( $\zeta$ )	Stabilization techniques
Bandyopadhyaya, et al. [189]	Water/SWCNT	30-50 nm $\Phi = 0.05$ wt. %	GA, SDS and CTAC	3 months	Steric and electrostatic stabilization mild sonication
Abdelrazik, et al. [43]	DI water/rGo-Ag	n/a $\Phi = 0.0005$ -0.05 wt. %	SDBS	> two weeks	Electrostatic stabilization ultrasonication.
Akash, et al. [11]	DI water/MWCNT DI water/Al DI water/Cu	MWCNT (length = 6 $\mu$ m, diameter = 5 nm) Al (80 nm), Cu (40 nm) $\Phi = 0.3$ vol. %	SDS	$\zeta = -42.3, -41.2$ and $-38.4$ mV, respectively.	Electrostatic stabilization mechanical stirring, ultrasonication.
Zhao, et al. [47]	Water/G-BN	Graphite (40 $\mu$ m), BN (20 $\mu$ m) $\Phi = 0.05$ -5 vol. %	1M Hcl(aq) solution is used for covalent functionalization.	Several months, $\zeta = -48$ to $-31$ mV	Steric stabilization, ultrasonication Covalent functionalization, ultrasonication pH control.
Das, et al. [72]	Water-[MMIM][DMP]/MXene	1-10 $\mu$ m $\times$ 1 nm $\Phi = 0.05$ and 0.2 wt. %	--	$\zeta = -17.88$ to $-39.54$ mV	Physical stabilization: magnetic stirring and ultrasonication.
Zare, et al. [38]	Distilled water/ZnO/TiO <sub>2</sub> /MWCNT	ZnO (15-30 nm) TiO <sub>2</sub> (21 nm) MWCNT (10-20 nm) $\Phi = 0.15$ wt. %	MWCNTs were functionalized with -COOH group.	$\zeta = 32, 38.1$ and $42.3$ mV, respectively.	Chemical functionalization: -COOH group. Physical stabilization: magnetic stirring and ultrasonication.
Elminshawy, et al. [39]	Water/Al <sub>2</sub> O <sub>3</sub>	$\Phi = 1$ -3 vol. %	SDBS	$\zeta = -38.6$ mV	Electrostatic stabilization magnetic stirring, ultrasonication.
Islam, et al. [41]	Water/SWCNT	L = 20-50 nm $\Phi = \leq 1.0$ mg/mL	SDBS, SDS and TX-100	3 months	Electrostatic stabilization Ultrasonication
Amiri, et al. [74]	Water/GNP-COOH/GNP-SDBS	0.5-3 $\mu$ m $\times$ 0.55-3.74 nm $\Phi = 0.025$ -0.1 wt. %	SDBS	n/a	Electrostatic stabilization
Chakraborty, et al. [190]	Water/Cu-Zn-Al LHD	49 nm $\times$ 9 nm $\Phi = 200$ -800 ppm	SDS, Tween 20	$\zeta = -52.7$ mV	Steric and electrostatic stabilization magnetic stirring, ultrasonication.
Sarsam, et al. [30]	Water/GNPs	2 $\mu$ m $\times$ 2 nm $\Phi = 0.1$ wt. %	BS, SDS, CTAB, and GA	> two months	Electrostatic and steric stabilization. water bath, ultrasonication.

Sadri, et al. [75]	Water/GAGNPs	n/a $\Phi = 0.05$ vol.%	--	> 63 days	None Ultrasonication, centrifugation
Zhang, et al. [86]	Water/CRGO	Thickness (~4.3 nm) $\Phi = 0.2$ to 1 mg/ml	--	$\zeta = -44.68$ to $-54.52$ mV, 45 days	Physical stabilization Ultrasonic probe
Srinivas, et al. [88]	Carboxylated water/MWCNT	1-25 $\mu\text{m} \times 20$ -40 nm $\Phi = 0.025$ -1 wt.%	Sebacic Acid and 2-ethylexanoic Acid	$\zeta = 18.88$ to 30.11 mV	Electrostatic Ultrasonication
Wu, et al. [89]	Water/SWCNT /MWCNT	1-2 and 8 nm, length < 30 $\mu\text{m}$ $\Phi = 0.0962$ -0.3846 vol.%	Humic acid	10 days	Electrostatic stabilization Ultrasonication
Yu, et al. [191]	Water/MWCNT	10-20 nm $\times$ 5-10 nm $\Phi = 0.01$ -0.4 wt.%	SDS	3 months	Electrostatic stabilization Sonication
Wusiman, et al. [90]	Water/MWCNT	5 $\mu\text{m} \times 5$ -20 nm $\Phi = 0.1$ -1 wt.%	SDBS and SDS	1 month	Electrostatic stabilization Ultrasonication, stirring
Wang, et al. [66]	Water/Cu /Al <sub>2</sub> O <sub>3</sub>	25 nm $\Phi = 0.02$ -0.8 Wt.%	SDBS	$\zeta = -43.8$ mV	Electrostatic stabilization Ultrasonication, pH control
Sahooli, et al. [91]	Water/CuO	4 nm $\Phi = 1$ -6 vol.%	Polyvinylpyrrolidone	7 days $\zeta = 32.3$ mV	Steric stabilization Magnetic stirring, ultrasonication
Fedele, et al. [192]	Water/SWCNH /TiO <sub>2</sub> /CuO	100, 21 and 30-50 nm respectively $\Phi = 0.01$ -1 wt.%	SDS, hydrochloric acid and PEG	15 days	Electrostatic stabilization Homogenization, sonication, and mechanical shaking
Li, et al. [193]	Water/Cu	25 nm $\Phi = 0.05$ -0.1 wt.%	Triton X-100, CTAB and SDBS	7 days $\zeta = -43.8$ to 28.1 mV	Steric and electrostatic stabilization Ultrasonic vibration, pH control
Iqbal, et al. [194]	Saline water/Fe <sub>3</sub> O <sub>4</sub>	< 100 nm $\Phi = 0.1$ mg/ml	Poly (AMPS-co-AA)	1 month $\zeta = -53.6$ mV	Electrostatic stabilization Sonication,
Ghadimi and Metselaar [40]	Water/TiO <sub>2</sub>	25 nm $\Phi = 0.1$ wt.%	SDS	7 days $\zeta = -33.3$ to $-55$ mV	Electrostatic stabilization Ultrasonication
Song, et al. [92]	Water/stainless steel	70 nm $\Phi = 0.017$ wt.%	SDBS	10 days $\zeta = -70$ mV	Electrostatic stabilization Ultrasonication, pH control
Mousavi, et al. [97]	Water/MgO-TiO <sub>2</sub>	25-45 and 18-23 nm respectively $\Phi = 0.1$ -0.5 vol%	SDS	$\zeta = 30.02$ -40.87 mV	Electrostatic stabilization Ultrasonication, magnetic stirring

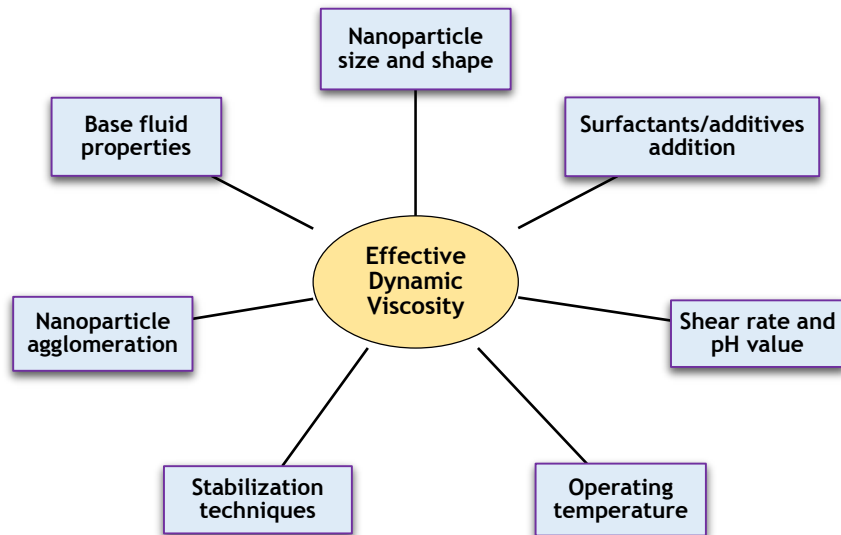
## 923 **5. Rheological behaviour of NFs**

924 Rheology is the study of how fluids flow when subjected to applied tensions. The relationship  
925 between shear stress and corresponding shear rate is used to assess rheological behavior, where  
926 shear stress is defined as the applied force per unit area and shear rate can be calculated by  
927 measuring the rate of change in strain. The ratio of these two parameters is defined as viscosity  
928 ( $\mu$ ) and it is one of the key parameters for rheological characteristics of fluids.

### 929 *5.1 Viscosity ( $\mu$ ), Newtonian and non-Newtonian behaviour*

930 The resistance force which causes deformation of fluids against the flow direction is defined  
931 as dynamic viscosity ( $\mu$ ). It is one of the key properties of NFs which has significant effect in  
932 convective heat transfer performance during implementation on thermal energy conversion  
933 systems due to its direct association to pressure drop and pumping power. Rheometers and  
934 different viscometers are commonly utilized to experimentally evaluate  $\mu$  of NFs [195-197].  
935 Rheometers are used to characterize the flow behavior of fluids over a broad range of shear  
936 rates and temperatures, while viscometers are used to measure the of fluids.

937 Considering the relationship between shear stress and shear rate, rheological behavior of fluids  
938 can be categorized into Newtonian and non-Newtonian nature. It is established that Newtonian  
939 fluids follow linear variation in shear stress against corresponding shear rate or the ratio of  
940 shear stress and shear rate i.e.,  $\mu$  of Newtonian fluids remain unchanged with variation of shear  
941 rate. Whereas the non-linear relationship of shear stress and shear rate i.e., variation of  $\mu$   
942 against corresponding shear rate results in non-Newtonian behavior of fluids. Rheological  
943 properties along with  $\mu$  of NFs is affected by several vital parameters depicted in **Fig. 21**.  
944 Numerous experimental and theoretical investigations are performed to scrutinize and estimate  
945 rheological characteristics and  $\mu$  of various NFs. Studies enlighten that the  $\mu$  of NFs generally  
946 increases with the inclusion of solid particles, however the flow characteristics i.e., rheology  
947 depends on several parameters and operating conditions, for instance, NFs tends to behave as  
948 Newtonian fluid at low particles concentration, high shear-rates and without surfactants or  
949 stabilizers while they act as non-Newtonian fluids at higher dispersed particles, low shear-rates,  
950 and addition of surfactants [198-200].



951  
952 **Fig. 21.** Key parameters effecting dynamic viscosity of nanofluid.

953 Nguyen, et al. [201] investigated impact of temperature and NP size on viscosity of water-  
954 based metal oxide NF using different size of Al<sub>2</sub>O<sub>3</sub> (36 and 47 nm) and CuO (29 nm) from 22  
955 to 75°C. At 4 vol.% or less, effect of particle size is unlikely while at higher loadings (>4vol.%)  
956 47 nm Al<sub>2</sub>O<sub>3</sub> based NF exhibited greater viscosity than 36 nm Al<sub>2</sub>O<sub>3</sub> particles. CuO NP showed  
957 more viscous property than the former. In addition, results showed the presence of a critical  
958 temperature beyond which NFs viscous property can alter radically. Barai, et al. [202] studied  
959 rheological properties of water dispersed graphene oxide and Fe<sub>3</sub>O<sub>4</sub> (10-20 nm) NF for 0.01-  
960 0.2 vol.% over a wide range of shear rate (0-10000 s<sup>-1</sup>). Findings showed 41% augmentation  
961 in  $\mu_{nf}$  and predominant shear thinning property at low shear rates while it altered and remain  
962 almost unchanged against higher shear rates and temperatures.

963 In a systematic experimental approach Minakov, et al. [203] studied several NFs based on three  
964 different base fluids (water, glycol and oil) dispersing seven different nanomaterials  
965 (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and diamond NPs). The NFs are formulated using two-  
966 step method dispersing the NPs at concentration of 0.25-8 vol.% and the size of the  
967 nanomaterials differs from 5-150 nm. Considerable augmentation is reported for all the samples  
968 when NPs are dispersed in all three liquid mediums. In case of impact of NP size, the results  
969 revealed that smaller the NPs higher the  $\mu_{nf}$  while influence of materials type found to be  
970 evident on viscosity as at the same particle size (150 nm). Water-TiO<sub>2</sub> NF exhibited  
971 substantially higher viscosity than water-Al<sub>2</sub>O<sub>3</sub>, also supported by related studies using  
972 molecular dynamic method [204, 205]. Effect of BFs also performed and detected that greater  
973 viscosity of pure fluids yields overall higher viscosity of NFs e.g., since water has a very low

974  $\mu$  in comparison with others traditional fluids, water adopted NFs are suitable in multifarious  
975 thermal applications. Furthermore, rheological assessment of the NFs elucidated that using  
976 smaller NPs and higher loading of particles can alter Newtonian behaviour to non-Newtonian  
977 while, using identical size of NPs of different class of nanomaterials can also show substantial  
978 divergence in rheological behaviour. Although the temperature relationship demonstrated a  
979 clear decreasing trend at elevated temperatures, the fascinating fact is that excess dispersed  
980 particles can result in hysteresis loss during heating and cooling operations [206], and viscosity  
981 of NF is demonstrated in terms of base liquid,  $\varphi$  and size using  $\mu_{nf}(T) = \mu_{bf}(T)f(\phi, D)$   
982 [207]. Addition of stabilizing surfactants from 0-100 mg/l in water-TiO<sub>2</sub> (150 nm, 2 vol.%) NF  
983 shifted Newtonian behaviour to shear thinning property in shear rate of 0-120 s<sup>-1</sup> and intensified  
984 the  $\mu_{nf}$  by 18% and adding 40 mg/l of polyacrylamide and nearly twice by xanthan surfactant.  
985 Jarahnejad, et al. [208] studied the influence of several factors (temperature, NP concentration,  
986 size, and surfactant) on effective viscosity of water-Al<sub>2</sub>O<sub>3</sub> and water-TiO<sub>2</sub> NFs for 20-50°C at  
987 NP concentration of 3-14.3 wt.%. Different surfactants (octyl-silane, polycarboxylate and  
988 trioxadecane acid) were added to formulate the NFs dispersing various sizes of Al<sub>2</sub>O<sub>3</sub> (200,  
989 250 and 300 nm) and TiO<sub>2</sub> (140, 200 and 90 nm) NPs. The results confirmed that the rise in  
990  $\mu_{nf}$  with 200 nm is lower than the NF with 250 and 300 nm particle sizes at 2.4 vol% loading  
991 for water-Al<sub>2</sub>O<sub>3</sub>, although a general trend was not mentioned explicitly. Impact of surfactants  
992 resulted an increase in the  $\mu_{nf}$ , TiO<sub>2</sub> NF using polycarboxylate surfactant had greater  $\mu$  than  
993 the TiO<sub>2</sub> NF using trioxadecane acid. However, association of  $\mu$  dependency between  
994 surfactant and NP size was not clarified. Hence, it cannot be stated that the viscosity increment  
995 of nanofluids is completely reliant on the type of stabilizer. Koca, et al. [209] reviewed impact  
996 of NP sizes on  $\mu$  of NFs based on the data from the literatures. They concluded inconsistencies  
997 among the studied investigations regarding different particles sizes at similar concentration and  
998 altering the NP size can results either increase or decrease of  $\mu$  by 40%. Timofeeva, et al. [63]  
999 experimentally studied effect of four different NP shapes (platelets, blades, cylinders, and  
1000 bricks) and solution pH for alumina/EG-water. They revealed that with addition of NPs at 1-7  
1001 vol.%, platelet-like particles exhibited largest  $\mu_{nf}$  followed by cylindrical, bricklike, and  
1002 bladelike particles. NFs using identical NP concentration, platelet-like and blade shaped  
1003 particles showed Newtonian property while cylindrical and bricklike NP contained NF  
1004 signifies shear-thinning characteristic above loading of 3 vol.%. Maximizing the pH value  
1005 resulted substantial 31% reduction in  $\mu_{nf}$ .

1006 Carbon-based nanomaterials that have been extensively studied exhibit both Newtonian and  
1007 non-Newtonian behavior in suspension, depending on the particle concentration, distributed  
1008 medium, size, and shear rate. Sadri, et al. [210] revealed that water-MWCNT NF at 0.5 wt.%  
1009 shows non-Newtonian shear thinning behavior as  $\mu_{nf}$  decreases against applied shear-rate up  
1010 to  $140 \text{ s}^{-1}$ . In addition, they found that  $\mu_{nf}$  enhances due to dispersion of NPs and surfactant  
1011 which can be reduced by optimum sonication of the samples. In a recent 3S research, Tiwari,  
1012 et al. [130] evaluated impacts of several surfactants, base fluids (water, EG, thermanol-VP1  
1013 and silicon oil) and sonication time on viscosity of hybrid MWCNT-CeO<sub>2</sub> nanocomposite  
1014 based NFs. Measurements revealed that increasing ultrasonication time for the samples  
1015 decreases  $\frac{\mu_{nf}}{\mu_{bf}}$  up to an optimum period and further ultrasonication offers opposite consequences  
1016 due to formation of clusters at longer sonication periods while, addition of nanocomposite  
1017 (0.25-1.50 vol.%) and surfactants reasonably rises the ratio. Water is found to be most efficient  
1018 as BF in terms of viscosity and lowest sonication time relative to other fluids although  
1019 water/MWCNT-CeO<sub>2</sub> NFs exhibited non-Newtonian rheological property under applied shear  
1020 rates ( $0-174 \text{ s}^{-1}$ ) with 0.025-2 vol.% at 25 and 80°C. Phuoc, et al. [211] experimentally studied  
1021 the rheological property of aqueous MWCNT (0.5-3wt.%) NF using cationic chitosan (0.1-0.2  
1022 wt.%) as stabilizer and found both Newtonian and non-Newtonian behavior. The measurement  
1023 showed that NF exhibit Newtonian behavior up to  $200 \text{ s}^{-1}$  shear-rate at lowest concentration of  
1024 nanomaterial and surfactant whereas, shear thinning property is found to be dominant at higher  
1025 loadings of CNT and chitosan. Zhang, et al. [65] studied pH effect on  $\mu_{nf}$  of water/TiO<sub>2</sub> at  
1026 three different points (2,7 and 12) for 0.08-2 vol.% and 25-60 °C. Results revealed that higher  
1027 pH value contributed to lower  $\mu_{nf}$  for a certain temperature which contradict with [130] and  
1028 particle loading whereas  $\mu_{nf}$  near IEP-6.5 is reasonably higher due to aggregation.

1029 Parallel to theoretical developments in NF's rheology, numerical simulations and molecular  
1030 dynamics approaches have also aided in this field's advancements. Wu, et al. [212] performed  
1031 numerical study on rheology of graphene-PAO NF using nonequilibrium molecular dynamics  
1032 analysis utilizing statistical data from previous experimental and numerical works. The model  
1033 was validated, and the results confirmed an improvement in  $\mu_{nf}$  at higher temperature and  
1034 shear thinning property is identified for NF samples. Azmi, et al. [213] recommended a  $\mu$  model  
1035 obtained by analyzing different experimental data of several water-based metal oxide (Al<sub>2</sub>O<sub>3</sub>,  
1036 CuO, SiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>) NFs using a non-linear regression method for particle sizes varying  
1037 from 20-170 nm and loading of below 4 vol.%. The model was integrated with various  
1038 parameters ( $\phi$ , temperature, and NP size) of the NFs.

1039 Nevertheless, studies on rheology of NF somewhat inconsistent and disorganized in terms of  
1040 key influential parameters and characteristics of various category of NFs. **Table. 6** represents  
1041 summary of reviewed works on rheology and viscosity of water-based NFs using wide range  
1042 of NPs and **Table. 7** and **Table. 8** demonstrate summary of empirical and classical correlations  
1043 obtained from available studies on this topic.

**Table 6.** Summary of reviewed experimental studies on viscosity and rheological behavior of various water-based nanofluids.

Reference	Nanofluids	Size and concentration ( $\phi$ )	Temperature range	Surfactants	Rheological behavior and shear rate (1/s)	Key findings
Minakov, et al. [214]	Water/SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> /ZrO <sub>2</sub> /C	10-100, 50-150, 71-150, 44-105 and 5 nm respectively $\Phi = 0.25-2$ vol.%	25 °C	--	Non-Newtonian 0-120	• NFs showed degree of shear thinning property even at lowest loading of NPs and non-Newtonian behaviour keep dominating at raising $\phi$ as well.
Singh, et al. [76]	Water/rGO-Al <sub>2</sub> O <sub>3</sub>	4-5 nm $\Phi = 0.01-0.52$ vol.%	25 °C	--	Non-Newtonian 0-2000	• The major pseudoplastic non-Newtonian property of the NF is observed up to 1500 s <sup>-1</sup> and then achieved the highest shear ordering of the molecules.
Sarsam, et al. [30]	Water/GNPs	2 nm × 2 $\mu$ m $\Phi = 0.1$ wt.%	25-55 °C	DBS, GA, CTAB, and SDS	Newtonian 20-200	• CTAB based NF exhibited non-Newtonian for certain range of share rate whereas, other surfactant-based NFs showed almost Newtonian behaviour.
Chakraborty, et al. [71]	Water/TiO <sub>2</sub>	< 100 nm $\Phi = 0-100$ ppm	30-50 °C	Polyvinylpyrrolidone and Tween 20	Non-Newtonian 0.1-100	• $\mu_{nf}$ increases with addition of TiO <sub>2</sub> however, it dropped adding one of the surfactants (Tween 20) into water.
Das, et al. [72]	Water-[MMIM][DMP]/MXene	1–10 $\mu$ m × 1 nm $\Phi = 0.05-0.2$ wt.%	20-50 °C	--	Newtonian 30-100	• $\mu_{nf}$ found to be higher for NF samples while rise in temperature reduces it substantially.
Alshayji, et al. [73]	DI water/Diamond	3-10 nm $\Phi = 0.125-1.25$ vol.%	20-60 °C	--	Newtonian n/a	• The experiment showed that the $\mu_{nf}$ decreased notably with temperature while it increased by 36% at maximum $\phi$ .
Amiri, et al. [74]	Water/GNP-COOH /GNP-SDBS	0.5-3 $\mu$ m × 0.55-3.74 nm $\Phi = 0.025-0.1$ wt.%	20-80 °C	SDBS	n/a 300	• Non-covalent NFs found to be more viscous than covalent NFs. Highest 136.4% growth of $\mu_{nf}$ is observed with GNP-SDBS particles at 0.1 wt.% while, GNP-COOH exhibited 29.4% increment.



Singh, et al. [76]	Water/rGO- Al <sub>2</sub> O <sub>3</sub>	4-5 nm $\Phi = 0.1$ vol.%	25 °C	--	Non-Newtonian 0 to 2000	<ul style="list-style-type: none"> <li>Rheology of the nanocomposite exhibited non-Newtonian (0-1500 S<sup>-1</sup>) behaviour although at higher shear rates <math>\mu_{nf}</math> tends to remain constant.</li> </ul>
Sabiha, et al. [80]	Water/SWCNT	500 nm × 1-2 nm $\Phi = 0.05-0.25$ vol.%	20-60 °C	SDS	Non-Newtonian 24.46-293.5	<ul style="list-style-type: none"> <li>NF showed significantly low <math>\mu_{nf}</math> at high temperature and reduced nonlinearly with increasing shear-rate which implies shear thinning fluid flow behaviour.</li> </ul>
Hussein, et al. [82]	Water/CF-MWCNT + CF-GNP + h-BN	5 $\mu$ m × 15 nm and 2 $\mu$ m respectively $\Phi = 0.05-0.1$ wt.%	20-60 °C	Tween-80	Non-Newtonian 50-200	<ul style="list-style-type: none"> <li>NF performed non-Newtonian shear-thickening behaviour as <math>\mu_{nf}</math> rises with corresponding growth of shear-rates.</li> </ul>
Zhang, et al. [86]	Water/CRGO	Thickness (~4.3 nm) $\Phi = 0.2-1$ mg/ml	10-60 °C	--	Newtonian 0-140	<ul style="list-style-type: none"> <li><math>\mu_{nf}</math> linearly decreased at elevated temperature and all the NFs behaved as Newtonian fluid at higher shear-rate (60 to 140 s<sup>-1</sup>).</li> </ul>
Shahsavari, et al. [93]	Water/CNT-Fe <sub>3</sub> O <sub>4</sub>	10 $\mu$ m × 10-30 nm and 13 nm respectively $\Phi = 0.9-2.25$ vol.%	25-35 °C	Gum Arabic and Tetramethylammonium hydroxide	Newtonian 1-100	<ul style="list-style-type: none"> <li><math>\mu_{nf}</math> of CNT- Fe<sub>3</sub>O<sub>4</sub> increased when strength of magnetic field raised, whereas it decreased at elevated temperature. Furthermore, shear thinning behaviour is observed at low shear-rates.</li> </ul>
Garg, et al. [94]	Water/MWCNT	0.5-40 $\mu$ m × 10-20 nm $\Phi = 1$ wt.%	15-35 °C	Gum Arabic	Non-Newtonian 10-80	<ul style="list-style-type: none"> <li>Shear thinning and thickening was noticed for 10-60 and 60-75 s<sup>-1</sup> shear-rate, respectively.</li> </ul>
Phuoc, et al. [211]	Water/MWCNT	10-30 $\mu$ m × 20-30 nm $\Phi = 0.5-3$ wt.%	25 °C	Chitosan	Non-Newtonian 20-200	<ul style="list-style-type: none"> <li>Addition of dispersant and nanomaterials enhance the <math>\mu_{nf}</math> notably and lead to non-Newtonian characteristic.</li> </ul>
Wang, et al. [215]	Water/MWCNT	5-30 $\mu$ m × 20-30 nm $\Phi = 0.05-1.27$ vol.%	20-50 °C	TritonX-100 and SDBS	Newtonian to non-Newtonian 1-120	<ul style="list-style-type: none"> <li>Shear-thinning behaviour is observed for high <math>\phi</math>. Addition of dispersants yielded better NF stability but increased <math>\mu_{nf}</math>.</li> </ul>
Mondragon, et al. [216]	Water/SiO <sub>2</sub>	12 nm $\Phi = 0.002-0.132$ vol.%	n/a	--	Newtonian to non-Newtonian 0.1-1000	<ul style="list-style-type: none"> <li>The NF depicted Newtonian behaviour at below 0.069% vol.%, while shear-thinning behaviour is detected at higher <math>\phi</math>.</li> </ul>

Aladag, et al. [217]	Water/Al <sub>2</sub> O <sub>3</sub> /CNT	30 nm and 200 μm × 9 μm respectively Φ = 1 wt.%	2-10 °C	--	Newtonian and non-Newtonian 0.1 to 5000	<ul style="list-style-type: none"> <li>• NF comprising CNTs shows approximately Newtonian behaviour at &gt; 100s<sup>-1</sup> and exhibits a non-Newtonian behaviour at low shear rates. Al<sub>2</sub>O<sub>3</sub> NF exhibits shear-thickening behaviour. Both NFs are thixotropic.</li> </ul>
Abdelhalim, et al. [218]	Water/Au	10-50 nm Φ = 0.01 vol.%	37-42 °C	--	Newtonian 200 to 2000	<ul style="list-style-type: none"> <li>• NF containing NPs of 50 nm performed higher viscosity than NF using 10 and 20 nm size of particles. As the temperature grows, the μ<sub>nf</sub> drops.</li> </ul>
Jeong, et al. [219]	Water/ZnO	90-210 nm (Rectangular) and 20-40 nm (Spherical) Φ = 0.05-5 vol.%	22 °C	Ammonium polymethacrylate	--	<ul style="list-style-type: none"> <li>• Rectangular shaped NPs exhibited more μ<sub>nf</sub> relative to spherical, maximum increment at 5 vol% is found 19.8 and 16% respectively.</li> </ul>
Eshgarf and Afrand [220]	Water-EG/SiO <sub>2</sub> -MWCNT	20-30 nm and 50 μm 5-15 nm respectively Φ = 0.0625-2 vol.%	27.5-50 °C	--	Non-Newtonian 0.612-122.3	<ul style="list-style-type: none"> <li>• NF revealed pseudoplastic behaviour for φ. NF follows power-law model and shear-thinning behaviour is dominant for the studied range of shear-rate.</li> </ul>
Yang, et al. [221]	Aqueous CTAC-NaSal/Cu	50 nm Φ = 0.05-2.5 vol.%	298.15-318.15 K	Cetyltrimethylammonium chloride/sodium salicylate	Non-Newtonian 0-1000	<ul style="list-style-type: none"> <li>• The μ<sub>nf</sub> of the measured NF is marginally higher than its BF and it raises with the φ and decreases with the escalating temperature.</li> </ul>
Bahrami, et al. [222]	Water-EG/Fe-CuO	35-45 and 25-55 nm respectively Φ = 0.05-1.5 vol.%	25-50 °C	--	Non-Newtonian to Newtonian 3.669-122.3	<ul style="list-style-type: none"> <li>• The measurements revealed that the NF has Newtonian behaviour at low φ and non-Newtonian behaviour at high φ.</li> </ul>
Omrani, et al. [223]	Water/MWCNT	0.5-30 μm × < 50 nm Φ = 0.05 vol.%	10-45 °C	SDBS and Triton X-100	Newtonian 100-1000	<ul style="list-style-type: none"> <li>• Linear relationship between shear stress and shear-rate indicates Newtonian behaviour of nanofluids. μ<sub>nf</sub> declined with increasing aspect ratio of CNTs.</li> </ul>
Barai, et al. [202]	Water/rGO-Fe <sub>3</sub> O <sub>4</sub>	10-20 nm Φ = 0.01-0.2 vol.%	18-45 °C	--	Non-Newtonian 0-10000	<ul style="list-style-type: none"> <li>• μ<sub>nf</sub> exponentially dropped with raising shear-rates i.e., shear thinning flow behaviour whereas, at high shear-rates (6000-10000s<sup>-1</sup>) it remained almost unchanged.</li> </ul>

**Table. 7.** A summary of reviewed correlations proposed based on experimental data to estimate the viscosity of nanofluids.

Reference	Nanofluid	Correlation	Applicability	Accuracy
Garoosi [67]	Water/Ag, Cu, Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , CuO, SiO <sub>2</sub> , ZnO, MgO, Fe, Fe <sub>3</sub> O <sub>4</sub> , Al, AlN, CaCO <sub>3</sub>	$\frac{\mu_{nf}}{\mu_{bf}} = 1 + 49.6 \times \left(\frac{d_p}{d_f}\right)^{-0.414} \phi^{0.908} e^{10.8\phi}$ where, $d_f = 0.1 \left(\frac{6M}{N\pi\rho_f}\right)^{1/3}$	$0 \leq \phi \leq 12 \text{ vol. \%}$ $10 \text{ nm} \leq d_p \leq 12 \mu\text{m}$	Standard deviation = 2.88%
Tiwari, et al. [130]	Water/MWCNT-CeO <sub>2</sub>	$\frac{\mu_{nf}}{\mu_{bf}} = 1 + 5.01795 \times \left(\frac{T}{T_a}\right)^{0.321298} \times \phi^{0.153641}$	$0 \leq \phi \leq 1.50 \text{ vol. \%}$ $55 \leq \phi \leq 80 \text{ }^\circ\text{C}$	Average deviation = 2.39%
Azmi, et al. [213]	Water/Al <sub>2</sub> O <sub>3</sub> /ZnO /TiO <sub>2</sub>	$\mu_{nf} = \mu_{bf} \left(1 + \frac{\phi}{100}\right)^{11.3} \left(1 + \frac{T_{nf}}{70}\right)^{-0.038} \left(1 + \frac{d_p}{170}\right)^{-0.061}$	$\Phi < 4 \text{ vol. \%}$ $T = 0\text{-}100 \text{ }^\circ\text{C}$	Max. error = 3.5%
Khanafar and Vafai [224]	Water/Al <sub>2</sub> O <sub>3</sub>	$\mu_{eff} = -0.4491 + \frac{28.837}{T} + 0.574\phi_p - 0.1634\phi_p^2$ $+ 23.053 \frac{\phi_p^2}{T^2} + 0.0132\phi_p^3 - 2354.735 \frac{\phi_p}{T^3} + 23.498 \frac{\phi_p^2}{d_p^2}$ $- 3.0185 \frac{\phi_p^3}{d_p^2}$	$1 \leq \Phi \leq 9 \text{ vol. \%}$ $T = 20\text{-}70 \text{ }^\circ\text{C}$ $13 \leq d_p \leq 131 \text{ nm}$	$R^2 = 0.99$
Corcione [225]	Water/Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> /SiO <sub>2</sub> /Cu	$\mu_{nf} = \frac{\mu_{bf}}{1 - 34.87 \left(\frac{d_p}{d_f}\right)^{-0.3} \phi^{1.03}}$ where, $d_f = 0.1 \left(\frac{6M}{N\pi\rho_f}\right)^{1/3}$	$\Phi = 0.1\text{-}7.1 \text{ vol. \%}$ $T = 293\text{-}333 \text{ K}$ $25 \leq d_p \leq 200 \text{ nm}$	Standard deviation = 1.84%
Sekhar and Sharma [119]	Water/Al <sub>2</sub> O <sub>3</sub>	$\frac{\mu_{nf}}{\mu_{bf}} = 0.935 \left(1 + \frac{T_{nf}}{70}\right)^{0.5602} \left(1 + \frac{d_p}{80}\right)^{-0.05915} \left(1 + \frac{\phi}{100}\right)^{10.51}$	$0.01 \leq \Phi \leq 5 \text{ vol. \%}$ $T = 20\text{-}70 \text{ }^\circ\text{C}$ $13 \leq d_p \leq 100 \text{ nm}$	Standard deviation = 15%

Syam Sundar, et al. [226]	Water/Fe <sub>3</sub> O <sub>4</sub>	$\mu_{nf} = \mu_{bf} \left(1 + \frac{\varphi}{12.5}\right)^{6.356}$	$\Phi = 0-2$ vol.% T = 20-60 °C	Standard deviation = 7.62%
Hemmat Esfe, et al. [227]	Water-EG/MWCNT- TiO <sub>2</sub>	$\mu_{nf} = 6.35 + 2.56\varphi - 0.24T - 0.068\varphi T + 0.905\varphi^2 + 0.0027T^2$	$\Phi = 0.05-0.85$ vol.% T = 10-50 °C	R <sup>2</sup> = 0.9913

1047

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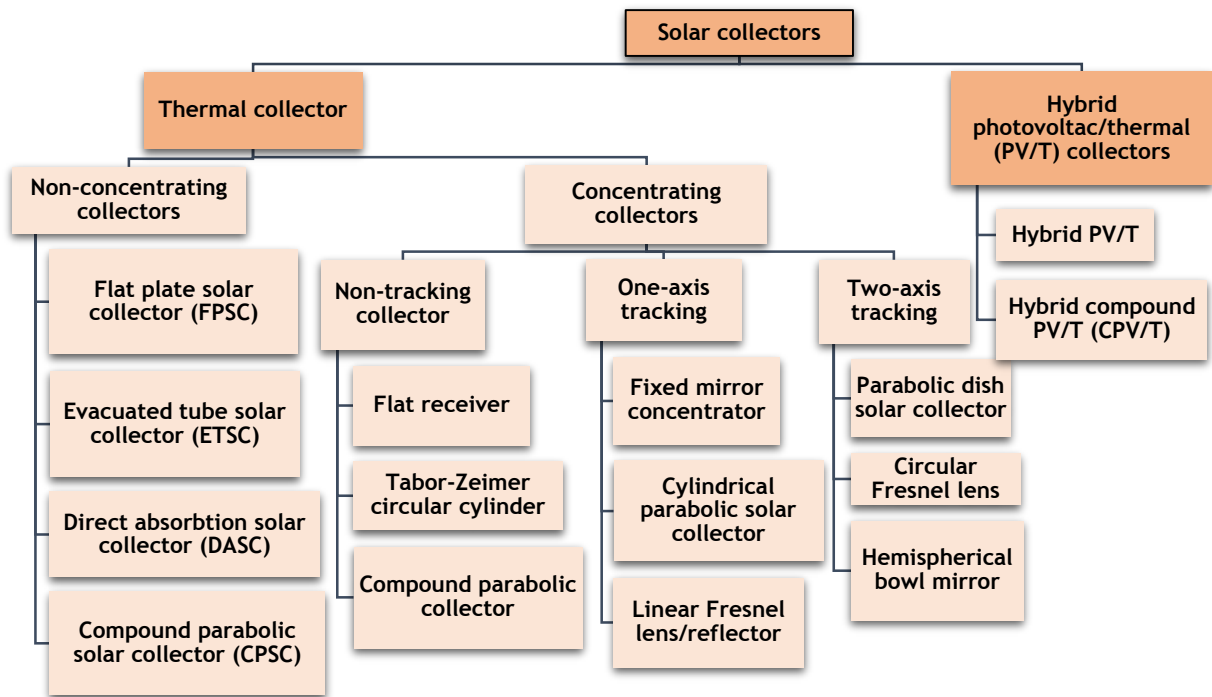
**Table. 8.** Summary of classical models of viscosity estimation for NFs.

Reference	Model	Applicability
Einstein [228]	$\mu_{eff} = \mu_{bf}(1 + 2.5\varphi)$	Dilute suspension of spherical particle with low solid concentration of < 1 vol.%
Brinkman [229]	$\mu_{eff} = \mu_{bf}(1 - \varphi)^{-2.5}$	Extended form of the Einstein model, applicable for even less dilute suspensions.
Roscoe [230]	$\mu_{eff} = \mu_{bf} \left(1 - \frac{\varphi}{\varphi_m}\right)^{-2.5}$	This model is appropriate for suspensions of equal sized rigid sphere particles at low to high concentrations.
Krieger and Dougherty [231]	$\mu_{eff} = \mu_{bf} \left(1 - \frac{\varphi}{\varphi_m}\right)^{-[\mu]\varphi_m}$	Power law-based semi-empirical to predict viscosity containing any volumetric concentration of particles.
Brenner and Condiff [232]	$\mu_{eff} = \mu_{bf}(1 + \eta\varphi)$	Suitable for rod-shaped particles suspensions at higher shear rate. Applicable for up to $1/\gamma^2$ volume concentration.
Jeffrey and Acrivos [233]	$\mu_{eff} = \mu_{bf} \left[3 + \frac{4}{3} \left(\frac{\varphi r^2}{\ln(\frac{\pi}{\varphi})}\right)\right]$	To predict the viscosity of non-dilute suspension rod-shaped in extensional flow.
Batchelor [234]	$\mu_{eff} = \mu_{bf}(1 + 2.5\varphi + 6.2\varphi^2)$	Brownian motion is considered in this model to predict the viscosity of dilute suspensions.
Graham [235]	$\mu_{eff} = \mu_{bf} \left[ (1 + 2.5\varphi) + \frac{2.25}{\left(1 + \frac{h}{2a}\right)} \times \left[ \frac{1}{\frac{h}{a}} - \frac{1}{\left(1 + \frac{h}{a}\right)} - \frac{1}{\left(1 + \frac{h}{a}\right)^2} \right] \right]$	This model is applicable for spherical particles. Intermolecular spacing and particle radius is considered to predict viscosity by this formula.

1049

1050 **6. Application of water-based NFs on non-concentrating solar collectors**

1051 Solar collectors (SCs) are advanced types of heat exchangers capable of spontaneously  
 1052 absorbing and converting solar irradiation into usable thermal energy in the case of thermal  
 1053 collectors, or into thermal and electrical energy utilizing photovoltaic/thermal hybrid SCs.  
 1054 Solar energy incident on the surface of the SC is converted to heat through a working fluid  
 1055 flowing through integrated copper tubes in the SCs [236]. SC is one of the most simple,  
 1056 sustainable, environmentally friendly, and efficient renewable thermal energy conversion  
 1057 systems available. It can be used in a wide variety of applications, including but not limited to  
 1058 domestic and industrial heating processes. SCs are primarily known as thermal or hybrid  
 1059 collectors (a combination of photovoltaic panel and thermal collector). Alternatively, thermal  
 1060 collectors are classified as non-concentrating or concentrating based on the concentration of  
 1061 incident solar radiation on the collector's specific surface area. Several forms of SCs are  
 1062 classified and illustrated in **Fig. 22**.



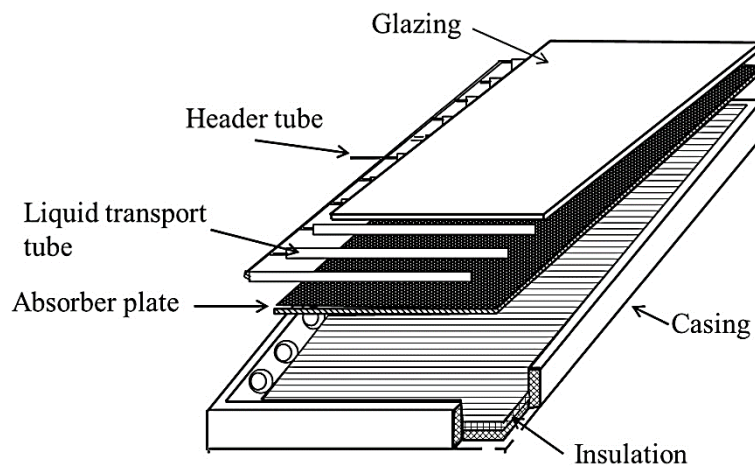
1063  
 1064 **Fig. 22.** Classification of solar thermal collectors.

1065 The performance of solar collectors is determined by a variety of factors, including the  
 1066 collector's configuration and, most significantly, the amount of energy absorbed by the  
 1067 working fluid from intercepted solar irradiation on the receiver surface. However, the thermal  
 1068 energy efficiency of SCs is heavily influenced by the heat transfer properties of the working  
 1069 fluids. For the last decade or so, extensive research has been conducted on the use of numerous

1070 NFs in place of traditional heating or cooling fluids in SC technology [237]. In recent years,  
1071 the use of advanced nanomaterials and BFs to develop and implement superior working fluids  
1072 on SCs has been extensively investigated. The aim of this review is to examine the potency and  
1073 effect of advanced water-based NFs as working fluids in low temperature SC systems. In  
1074 general, water-based NFs are frequently utilized in non-concentrating i.e., low-temperature  
1075 solar thermal collectors like FPSC, ETSC, DASC, CPSC and hybrid PV/T due to their superior  
1076 thermal and optical behavior. The following sections explain various types of NF-based solar  
1077 collectors that use water as the BF, and **Table. 9** summarizes previous research with main  
1078 findings.

### 1079 **6.1. Flat plate solar collector (FPSC)**

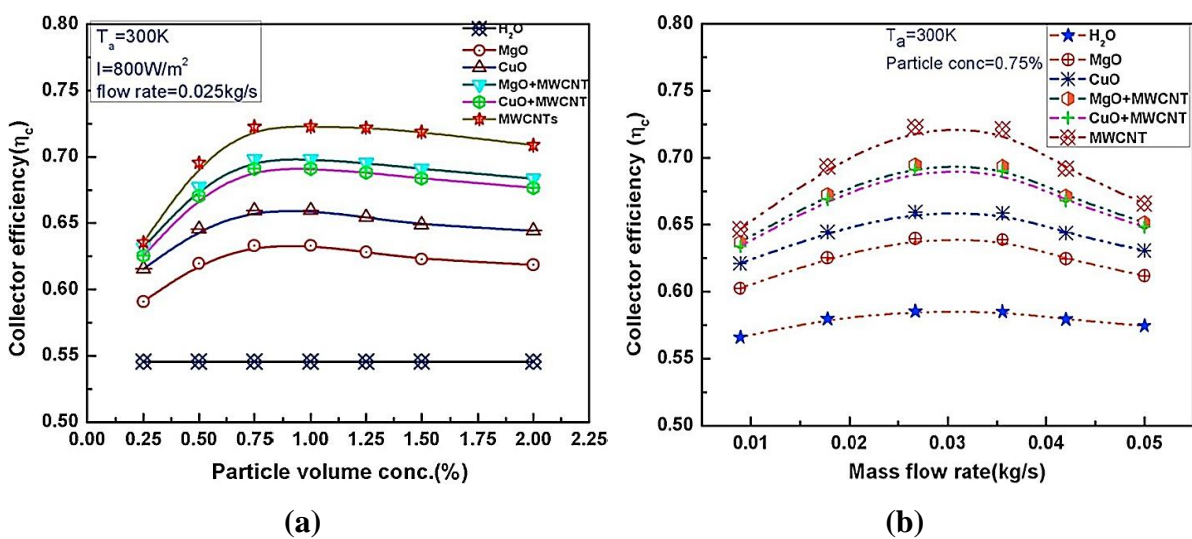
1080 FPSC is the simplest, most primitive, cost-effective, and most commonly used SC in a variety  
1081 of domestic and industrial heating applications. Solar irradiation is absorbed on the absorber  
1082 plate and transferred and stored in the SC's working fluid through the tubes. FPSC consists of  
1083 five important components (see **Fig. 23**) such as (i) transparent glass surface (glazing) to  
1084 capture incident irradianations and inhibit heat loss by radiation and convection to the  
1085 environment (ii) absorber plate (made from copper, aluminum or other metal coating) to absorb  
1086 solar energy (iii) header and raiser tubes to exchange the heat energy to circulating working  
1087 fluid passing through the tubes (iv) insulation materials to minimize the heat loss (v) an overall  
1088 encapsulation or casing to protect the collector from external hindlers and hold all the integrated  
1089 components together.

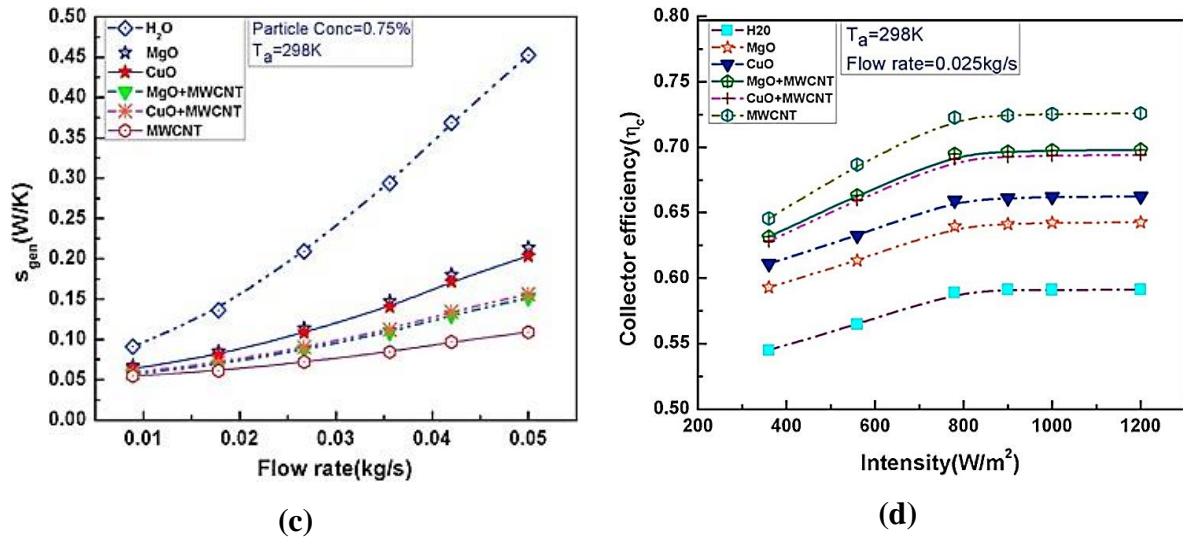


1090  
1091 **Fig. 23.** Structure of a typical flat-plate solar collector [238].

1092 To improve the performance of a FPSC, research is being conducted in structural design, heat  
1093 loss reduction due to convection heat transfer, and the use of advanced working fluids such as

1094 nanofluid [239]. Generally, water, oils and ethylene glycol are employed as working fluid.  
 1095 However, poor heat transport properties of these fluids restrict the performance of the SCs.  
 1096 Researchers and engineers in recent studies on solar collectors have strongly suggested that  
 1097 emerging nanomaterial-based NFs can be implemented on SC systems for performance  
 1098 enhancement [240]. Yousefi, et al. [241] experimentally studied effect of Al<sub>2</sub>O<sub>3</sub>-water NF on  
 1099 a FPSC. Their results revealed that the inclusion of Al<sub>2</sub>O<sub>3</sub> NPs into water led the instantaneous  
 1100 energy efficiency of the thermal collector to 28.3% higher relative to conventional water driven  
 1101 FPSC. Fraction (weight or volume) of dispersed NPs, type of nanomaterials, mass flow rate  
 1102 and intensity of solar irradiations are the important parameters that governs the effectiveness  
 1103 of a FPSC. Verma, et al. [242] investigated the effect of metal oxide (MgO and CuO) and  
 1104 MWCNT-based NFs on FPSC as a high-performance working fluid. They examined the effect  
 1105 of collector efficiency and entropy production on two metal oxide, one carbon nanotube, and  
 1106 two hybrid NFs, as illustrated in **Fig. 24**. They revealed that increasing the particle loading in  
 1107 the base fluid initially increases efficiency before it reaches an optimal level, at which point  
 1108 efficiency degrades due to agglomeration and clustering. For both sole and hybrid NFs, a  
 1109 similar pattern is observed with varying mass flow rates. Colangelo and Milanese [243]  
 1110 numerically evaluated the impact of concentration (1-3 vol.%) of Al<sub>2</sub>O<sub>3</sub> nanoparticles on FPSC  
 1111 using water-based NF. The investigation was performed considering practical weather  
 1112 conditions for summer and winter solstices, with inlet temperatures ranging from 30 to 65°C  
 1113 and a steady flow rate of 0.02 kg/s. Using 3 vol.% of Al<sub>2</sub>O<sub>3</sub> NPs, a maximum 7.54% augmented  
 1114 efficiency was achieved, while efficiencies were much lower at lower concentrations (1-2  
 1115 vol.%). The obtained results, however, are based on the assumption of uniform particle  
 1116 dispersion in the BF.





1117 **Fig. 24.** Influence of important parameters on efficiency of FPSC [242] (a) variation of  
 1118 collector efficiency with raising concentration of nanomaterials (a) variation of collector  
 1119 efficiency at various mass flow rates (c) entropy generation at various flow rate (d) variation  
 1120 of efficiency at elevating solar intensity.

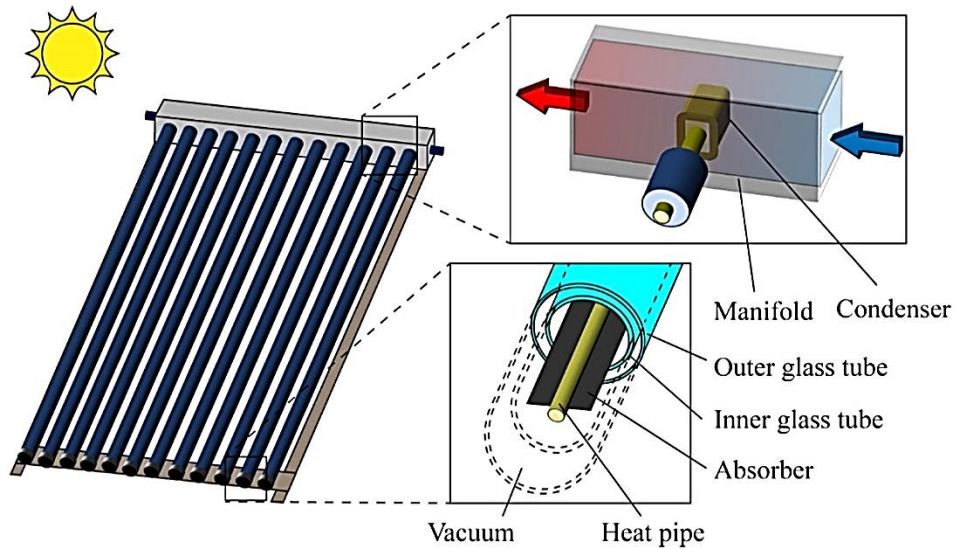
1121 Akram, et al. [244] experimentally investigated the performance of FPSC using water NFs  
 1122 incorporated with metal oxides ( $SiO_2$  and  $ZnO$ ) carbon-based (GNP) materials. The results  
 1123 show that carbon material has a greater impact than metal oxides, with the highest  
 1124 enhancements of 17.45, 13.05, and 12.36% obtained using the particles, respectively. In a  
 1125 recent comparative investigation between ETSC and FPSC, Eltaweel, et al. [245] reported that  
 1126 FPSC showed superior performance than ETSC in terms of overall heat loss coefficient, heat  
 1127 removal factor, thermal and exergy efficiency using MWCNT NF. Furthermore, increasing the  
 1128 heat flux rate improves the heat removal factor, which reduces total heat loss and increases the  
 1129 collector's performance. The use of NF on the collectors often results in a decrease in the size  
 1130 of the SCs. **Table. 9** summarizes recent experimental findings on NF-based FPSC.

## 1131 6.2. Evacuated tube solar collector (ETSC)

1132 ETSC is the more efficient form of solar energy conversion system which can provide more  
 1133 thermal energy relative to conventional FPSC due to low heat dissipation because of the  
 1134 existence of its vacuum insulation system. A vacuum separation between the glass tube and  
 1135 absorber surface integrated with pipe (thermosyphon, U-pipe or heat pipe) demotes heat losses  
 1136 caused by conduction and convection. Absorber plate and incorporated pipe are placed inside  
 1137 the innertube and generally made of copper or aluminum materials. The working fluid  
 1138 circulates through the heat pipes in a closed loop and absorbs the energy from solar radiation,



1139 condenses in the manifold and returns to heat pipes for the next cycle (a typical ETSC is  
1140 demonstrated in **Fig. 25**).



1141

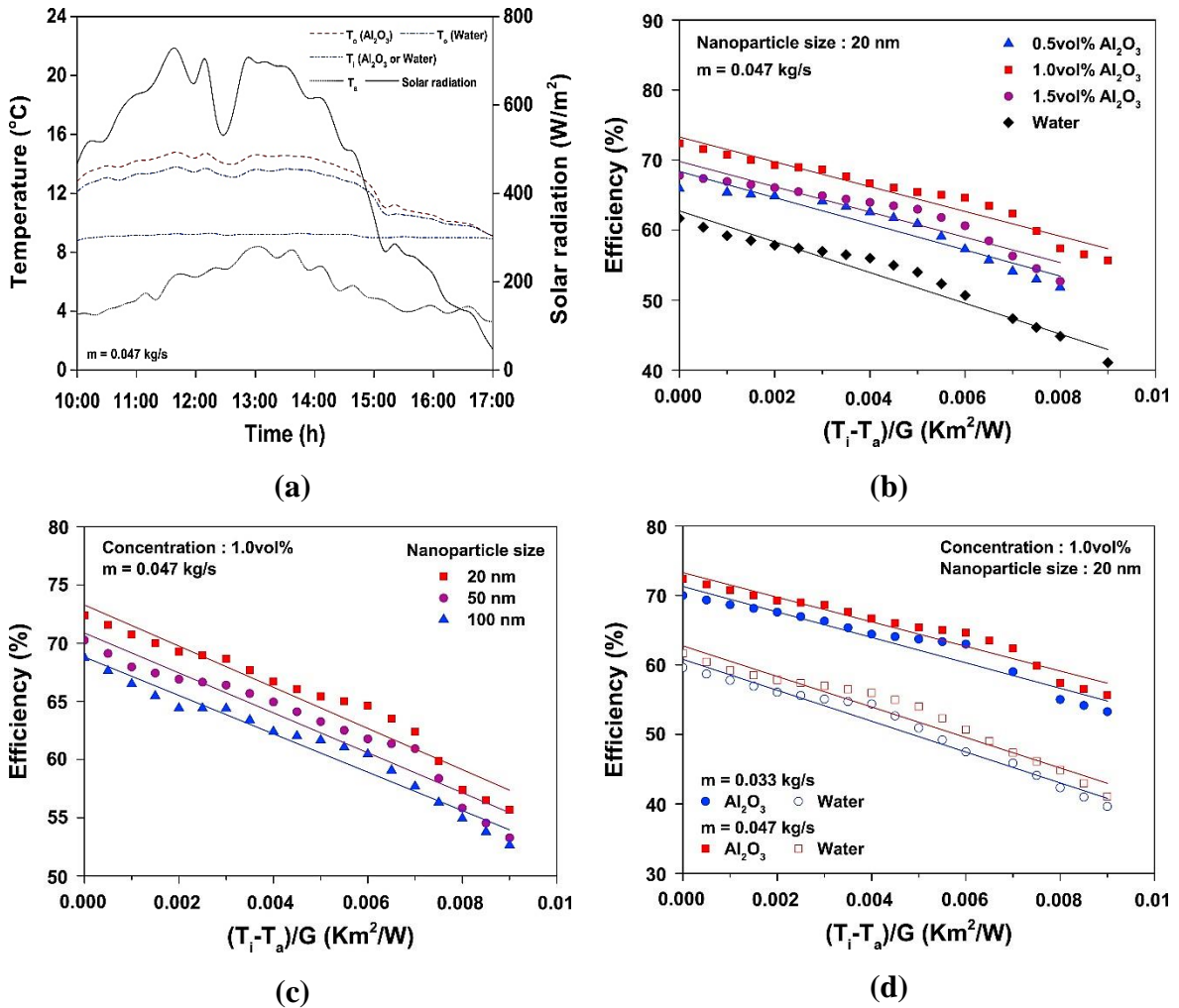
1142

**Fig. 25.** Main components evacuated tube solar collector system [237].

1143 Ghaderian, et al. [246] evaluated the efficiency of ETSC experimentally using water/CuO NF.  
1144 The ETSC was equipped with a thermosyphon, and circulating NF as the absorption medium  
1145 at a concentration of 0.03-0.06 vol.% of CuO nanomaterials and a mass flow rate of 20-60 L/h.  
1146 The attained results showed that ETSC delivers highest 14% improved thermal efficiency at  
1147 0.03vol.% and 20 L/h relative to water. Investigation impact of water/WO<sub>3</sub> NF on ETSC,  
1148 Sharafeldin and Gróf [247] revealed heat gain and output temperature has intensified by 23 and  
1149 21% respectively when WO<sub>3</sub> NPs (0.014-0.042vol.%) were added at 900 W/m<sup>2</sup>. In addition,  
1150 19.3% supplemented thermal-optical efficiency is achieved over conventional collector.  
1151 Sabiha, et al. [248] measured output of ETSC comprised with heat pipe by employing  
1152 water/SWCNT (0.05-0.2vol.%). They observed thermal efficiency of ETSC enhances with  
1153 increasing flow rate (0.0008-0.025kg/s) and  $\phi$ . A maximum 93.43% augmentation is  
1154 achieved at 0.2vol.%, which is 39.06% beyond the water based ETSC at 0.025kg/s.  
1155 Furthermore, the NF based was collector found to be 4.5% more effective even on cloudy days  
1156 than water based ETSC on sunny days.

1157 Kim, et al. [249] assessed impacts of several parameters (e.g., solar irradiation,  $\phi$ , NP size and  
1158 flow rate) on effectiveness of an evacuated U-tube solar collector substituting water with water/  
1159 Al<sub>2</sub>O<sub>3</sub> (20-10 nm, 0.5-1.5vol.%) NF at 0.033-0.047 kg/s flow rate (see **Fig. 26**). Average outlet  
1160 temperature is improved by 1.2% although effect was minimal at low solar radiations. The  
1161 elevated efficiency of the ETSC is observed at optimum  $\phi$  of 1.5vol.%, smallest diameter of  
1162 NPs (20 nm) and highest flow rate of 0.047 kg/s. 72.4% elevated output is measured at

1163 optimized conditions which is considerably superior to water as working fluid. Natividade, et  
 1164 al. [250] reported notable intensification in efficiency of ETSC integrated with parabolic  
 1165 concentrator and multi-layered graphene/water as operating fluid. Combined effect of  
 1166 concentrator and NF caused 298% enhanced efficiency than water as working fluid without  
 1167 concentrator.

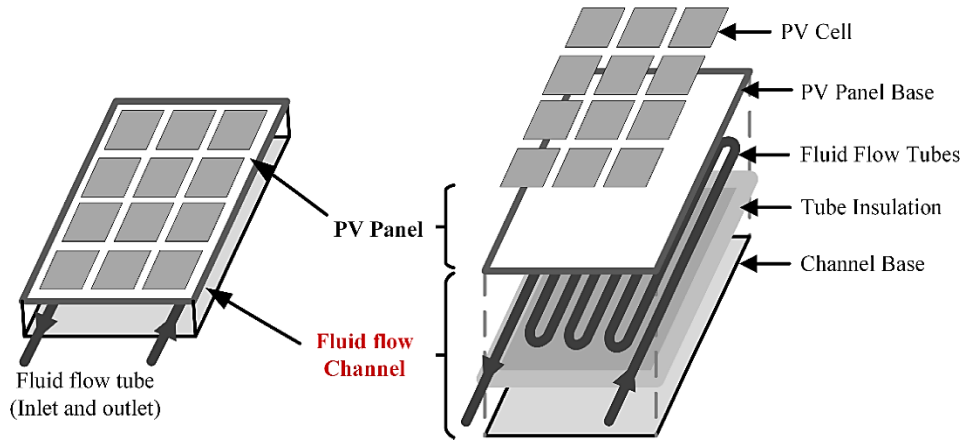


1168 **Fig. 26.** Effect of various parameters on efficiency of evacuated U-tube solar system;  
 1169 variation of (a) outlet temperatures against corresponding time and solar irradiances (b)  
 1170 efficiency using different vol.% of particles (c) efficiency for different sizes of Al<sub>2</sub>O<sub>3</sub>  
 1171 particles (d) efficiency boosting mas flow rate [249].

### 1172 6.3. Photovoltaic thermal (PV/T) collector

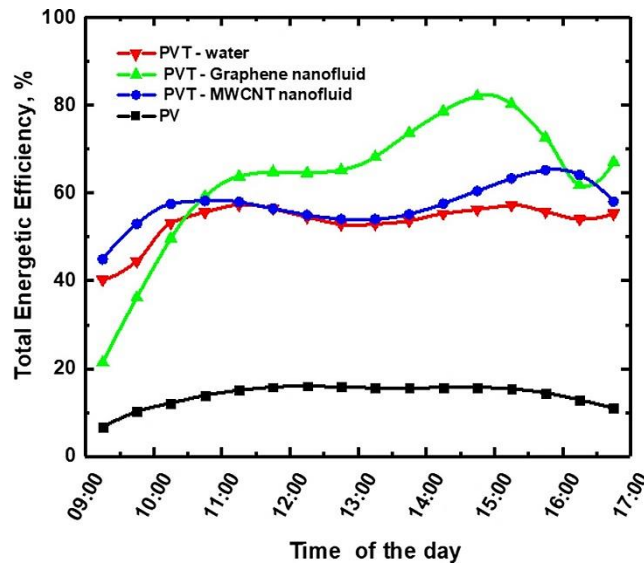
1173 Photovoltaic (PV) thermal hybrid systems can concurrently produce thermal and electrical  
 1174 energy by capturing and converting the renewable solar irradiances to useable forms.  
 1175 Traditional PV modules are adversely affected at high temperature as excessive heat reduces  
 1176 the overall efficiency of the panel. Hybrid PV/T technology allows extraction of surplus heat

1177 assimilating a cooling unit with improved properties to advance the thermal-electrical output  
1178 of the PV/T compared to PV module and conventional fluid equipped systems. The thermal  
1179 unit of the collector absorbs the additional heat generated from the PV module to optimize the  
1180 effectiveness of the system. A typical hybrid PV/T solar collector is illustrated in **Fig. 27**.



1181  
1182 **Fig. 27.** Schematic of hybrid PV/T collector, PV panel integrated with thermal cooling  
1183 system using nanofluid [72].

1184 Aberoumand, et al. [251] experimentally examined energy and exergy performance of PV/T  
1185 collector operating water/Ag NF at 2-4wt.% for laminar-transient-turbulent (0.0085-0.029  
1186 kg/s) flow regimes. They noted excellent effect of NF on performance as NF controlled system  
1187 offers maximum 10 and 30% higher energy and exergy efficiencies at 0.029 kg/s (turbulent)  
1188 flow rate relative to collector operated by water. In an outdoor experiment using water-based  
1189 graphene and MWCNT NFs, Alous, et al. [252] revealed that overall (i.e., thermal, electrical  
1190 and cooling) performance of PV/T enhanced (see **Fig. 28**). The results indicate up to 16°C  
1191 temperatures drop of the PV module using MWCNT particles and advanced energetic and  
1192 energetic efficiencies of 22.1 and 20.6% for the graphene NF compared to the water-cooled  
1193 system.

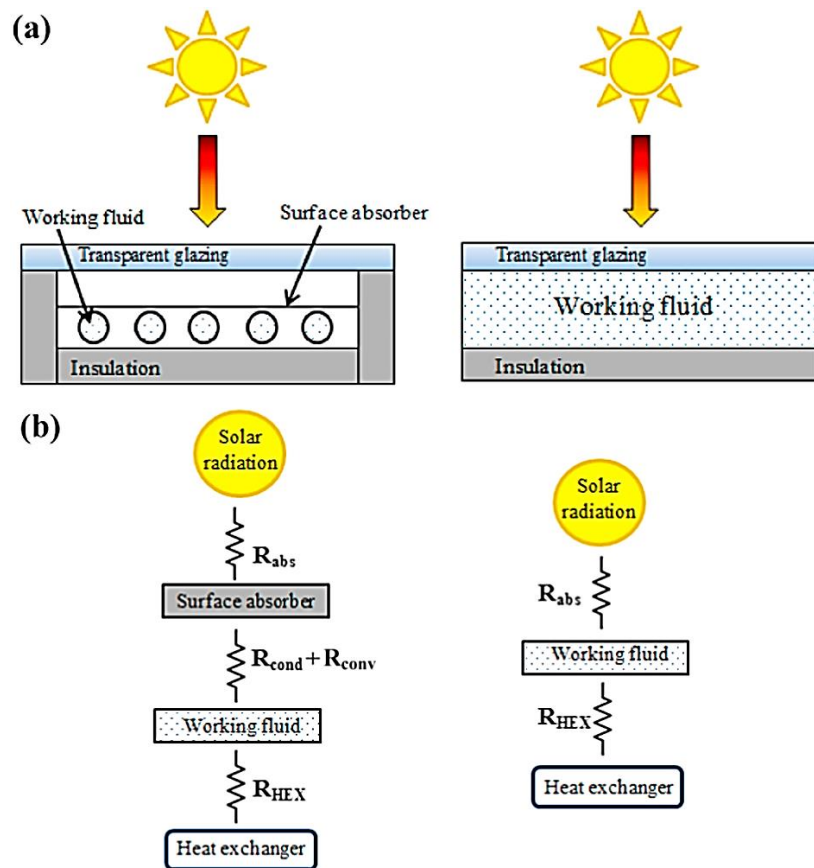


1194

1195 **Fig. 28.** Variation in efficiency of standalone PV and hybrid PV/T collectors operated with  
 1196 water-based NFs [252].

1197 **6.4. Direct absorption solar collector (DASC)**

1198 Traditional non-concentrating solar collector technologies employ solid absorber surfaces  
 1199 made of selective materials (e.g., polymer, copper, titanium, still and black carbon-based  
 1200 coatings) and circulate HTFs through tubes enclosed in an encapsulated insulation to exchange  
 1201 solar energy absorbed by the absorber surface. This technique results in low solar collector  
 1202 efficiency since substantial heat is lost from the hot absorber plate to the collector's other  
 1203 components (via conductions) and to the atmosphere (by convection and radiation). The  
 1204 volumetric DASC, on the other hand, is an advanced system where operating fluid is directly  
 1205 exposed to solar radiation that allows to eliminate thermal resistance formed by absorber  
 1206 surface in indirect collectors [253]. **Fig. 29** presents a schematic and thermal resistance diagram  
 1207 of indirect and DASC systems. Nevertheless, the concern with DASCs is that the employed  
 1208 regular HTFs have weak photothermal characteristics including low absorbance capacity for  
 1209 visible range of solar spectrum. Replacing conventional fluids with advance NFs as absorption  
 1210 medium can boost the absorptivity and performance of the DASCs due to supplemented optical  
 1211 effect of dispersed nanoscale particles.



1212

1213 **Fig. 29.** (a) Schematic illustration of surface absorption based and DASC system (b) thermal  
 1214 resistance networks [25].

1215 Milanese, et al. [254] experimentally assessed the optical merit of several water-based NFs  
 1216 using six different nanomaterials (CuO, CeO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO and Fe<sub>2</sub>O<sub>3</sub>) to determine their  
 1217 potential use in DASC. The extinction distance, transmittance and/or absorbance  
 1218 measurements were performed for all the NFs using volumetric concentrations of 0.05-1% for  
 1219 each of the NPs. The measurements were conducted over a limited range of solar irradiation  
 1220 from 200-1300 nm. The results revealed distinct optical characteristics of the NFs depending  
 1221 on nanomaterials and their concentrations. They found that at lower vol.% of NPs, the  
 1222 extinction distance exceeds the typical diameter (1cm) of a collector receiver. CuO and Fe<sub>2</sub>O<sub>3</sub>  
 1223 dispersed NFs exhibited better absorbance relative to other NFs, while TiO<sub>2</sub> based NF was  
 1224 reported as the best alternative due to its ability to absorb nearly 100% of solar radiation at a  
 1225 low concentration (0.05 vol.%) within the absorption depth. In their subsequent study [255],  
 1226 they evaluated the optical properties and stability of these NPs (ZnO, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>) with  
 1227 respect to temperature (25-500°C). The obtained results suggest that there was no substantial  
 1228 shift in the optical properties of the NPs at elevated temperatures, as the absorption coefficient  
 1229 remained nearly constant. **Chen, et al. [256] conducted a systematic study of the solar**

1230 absorbance of 13 distinct plasmonic nanoparticles and revealed that Cu@SiO<sub>2</sub> NPs with a core-  
1231 shell structure were the most efficient at a 5:7 ratio. The NPs are proposed as potential energy  
1232 conversion materials for application in DASC.

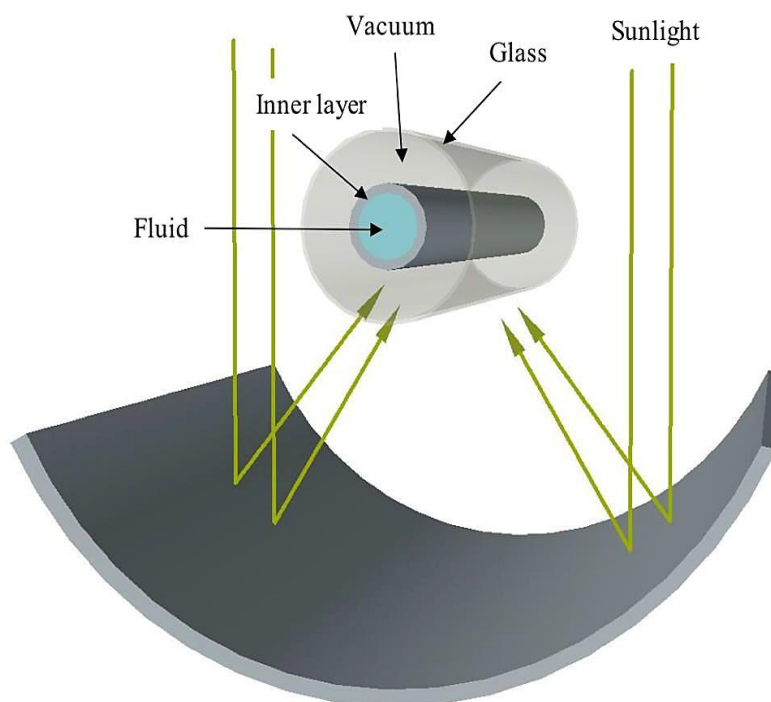
1233 Guo, et al. [257] revealed that using 0.005-0.05wt.% of MWCNT (5-30 nm) in water  
1234 substantially augments photothermal conversion relative to water based DASC. The results  
1235 exhibited that inclusion of 15 nm MWCNT at 0.01wt.% produced optimum photothermal  
1236 conversion of 65.4%. Karami [258] revealed 21.7 and 66.4% augmented efficiencies of DASC  
1237 using hybrid NF dispersing Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> NPs. They also checked the performance using  
1238 CuO [259] and MWCNT [260] based NFs at identical conditions in separate articles where it  
1239 is noticed that CNT nanomaterial outstrip the former one (see **Table. 9**). Li, et al. [261]  
1240 performed an experimental and numerical comparison study between volumetric and surface  
1241 absorption based solar collector operated with water (low-temperature) or Therminol-55 (high-  
1242 temperature) based MWCNT NF. The surface absorber is comprised of a chrome-coated  
1243 copper tube. Simulation findings indicated that in the 50–250 °C, the global heat deficit in the  
1244 NF based absorber was approximately twice greater than the coated absorber, because of the  
1245 glass tube have greater emissivity than surface absorber. They recommended using vacuum  
1246 installation across the receivers and a low emissive coating on the tubes to improve the  
1247 volumetric system as it resulted in significantly lessened convective heat loss consequences.  
1248 On-sun measurements on the two prototypes revealed that the volumetric absorber performed  
1249 poorly than the surface absorber. At 80°C, the exterior absorber gained 68% efficiency, while  
1250 the NF-based absorber gained just 54% efficiency. When vacuum packaging is used at 200°C,  
1251 the outputs were 47 and 26%, respectively. To cope with surface absorbers, it is suggested that  
1252 NF absorbers require anti-reflective and selective coatings. Wang, et al. [262] investigated the  
1253 photothermal energy conversion efficiency of two-dimensional multi-layered MXene and  
1254 graphene NFs in water to optimize DASC performance. They achieved a maximum  
1255 photothermal efficiency of 63.35 and 60.92%, respectively, when using MXene and graphene-  
1256 incorporated NFs.

### 1257 **6.5. Parabolic trough solar collector (PTSC)**

1258 The PTSC is considered as the future of sustainable renewable energy resources that can be  
1259 implemented commercially to develop sustainable solar energy conversion systems. PTSC is  
1260 the one of the concentrating solar system of solar collector technologies comprised with  
1261 parabolic shaped mirror reflector and cylindrical absorber surrounded by anti-reflecting glass  
1262 layer to prevent heat loss due to convection and radiation (depicted in **Fig. 30**). Solar energy is



1263 concentrated on the receiver and then transformed to a working fluid that flows through it,  
1264 converting solar energy to thermal energy. [263]. The performance of PTSCs is determined by  
1265 the photothermal properties of the working fluid used in the cycle. Water-based NFs are  
1266 commonly used in PTSC at temperatures below 100°C as they are the most innovative and  
1267 effective medium for light-to-heat conversion [22]. Although PTSC is capable of operating at  
1268 higher temperatures, water-based NFs have a small temperature range due to their low boiling  
1269 point.



1270  
1271

**Fig. 30.** Schematic diagram of the PTSC system [22].

1272 Menbari, et al. [264] investigated low-temperature direct absorption PTSCs by operating with  
1273 water/CuO NF at a concentration of 0.002-0.008 vol.% and a flow rate of 10-100 L/h to  
1274 increase the collector's thermal effectiveness and absorption property. The results demonstrate  
1275 an increase in thermal efficiency of up to 52% compared to BF at the peak loading of 0.008  
1276 vol.%. Hachicha, et al. [265] recently investigated the impact of experimentally formulated  
1277 water-based NF on the optical and thermo-hydraulic efficiency of PTSC dispersing low-cost  
1278 industrial-grade MWCNT (0.05-0.3 vol.%) nanomaterial. The numerical application of the  
1279 fluids is performed at four different locations in UAE and 49.52% thermal efficiency is  
1280 achieved with 21% increment in Nusselt number. In addition, parametric analysis showed that  
1281 thermo-hydraulic performance of the system increases at lower flow rates (below 0.2 L/s) and  
1282 low concentration of NPs while, higher concentrations can be effective for further increase in

1283 flow rate. Okonkwo, et al. [266] evaluated performance of the LS-2 PTSC system employing  
1284 water/SiO<sub>2</sub> and water/TiO<sub>2</sub> NFs synthesized from olive leaf and barley husk. Green  
1285 formulation techniques result in a decrease in thermal losses and an increase in energy and  
1286 exergy efficiency. The proposed NFs improved heat transfer efficiency by 128 and 138%,  
1287 respectively. Sekhar, et al. [267] used several NPs (CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) with water at 0.5-3  
1288 vol.% to evaluate the output of the PTSC system. In comparison to water as working fluid, the  
1289 thermal efficiency of the system was augmented by 27, 25 and 23% for the NFs, respectively.  
1290 Subramani, et al. [268] investigated the heat transfer properties of PTSC under turbulent flow  
1291 conditions using water/Al<sub>2</sub>O<sub>3</sub> NF. They observed up to 8.54% increment in efficiency at a flow  
1292 rate of 0.05 kg/s and 0.5 vol.% of NP. Nusselt number and overall heat transfer coefficient of  
1293 the collector are found to be improved as well. In a numerical fluid dynamics investigation,  
1294 Ghasemi and Ranjbar [269] examined heat transfer and friction factor characteristic of PTSC  
1295 using water/Al<sub>2</sub>O<sub>3</sub> and water/CuO NF. The obtained results showed 28 and 35% enhanced heat  
1296 transfer coefficient using the NFs, respectively. Moreover, lower friction factor is caused by  
1297 water/Al<sub>2</sub>O<sub>3</sub> than that of water/CuO.

1298 The studies concluded that the PTSC solar collector based on water-NF outperformed the  
1299 traditional fluid-based system in terms of energy and exergetic efficiency. However, one of the  
1300 major disadvantages of water-based NFs is that, due to their restricted low boiling point, they  
1301 are not suitable for use at medium-high temperatures on PTSC. **Table. 9** summarizes recent  
1302 research on PTSC using water-based NFs, including comprehensive details and key results.



1303

**Table. 9.** Summary of key findings from recent experimental studies on various water-based NFs in low-temperature application on non-

1304

concentrating thermal solar collectors.

Reference	Nanofluids	Particle size and concentration ( $\phi$ )	Solar collector	Operating temperature	Flow rate	Key findings
Verma, et al. [270]	Water/CuO Al <sub>2</sub> O <sub>3</sub> TiO <sub>2</sub> SiO <sub>2</sub> Graphene MWCNT	42, 45, 44, 10, 20 nm, respectively. MWCNT (AR=200, dia 7nm) $\Phi = 0.25$ to 2 vol.%	FPSC	< 80 °C	0.01-0.05 kg/s	<ul style="list-style-type: none"> <li>• MWCNT-based NF produced the highest efficiencies, with improved exergy and energy efficiency relative to water of 29.3 and 23.47%, respectively.</li> <li>• 19.01% reduction in area is observed using MWCNT NF, which is optimum among the studied NFs.</li> </ul>
Sarsam, et al. [271]	Water/Ala-MWCNT	< 8 nm and 20-30 nm $\Phi = 0.025$ to 0.1 wt.%	FPSC	< 80 °C	0.6-1.4 kg/min	<ul style="list-style-type: none"> <li>• Functionalized MWCNT NPs lifted the output of FPSC up to 9.55% with 0.1 wt.% at 1.4 kg/min.</li> <li>• MWCNT particles with a smaller diameter (8 nm) performed significantly better than those with a larger diameter (20-30 nm).</li> </ul>
Choudhary, et al. [272]	Water/MgO	40 nm $\Phi = 0.1$ to 0.3 vol.%	FPSC	< 80 °C	0.5-1.5 L/min	<ul style="list-style-type: none"> <li>• Higher thermal conductivity and <math>c_p</math> of NF at elevated temperature enhanced thermal efficiency which is approximately 70.4% at 3 vol.% on the day NF was prepared.</li> <li>• Thermal output declined by 13.1% after a 10-day period at 0.3 vol.% while it decreased slightly using 0.1 vol.% loading.</li> </ul>
Hussein, et al. [82]	Water/CF-MWCNT+ CF-GNP	Diameter 15 nm, length 5 $\mu$ m $\Phi = 0.05$ -0.1 wt. %	FPSC	< 80 °C	2-4 L/min	<ul style="list-style-type: none"> <li>• Hybrid nanocomposite at 0.1 wt.% of MWCNT and GNP, augmented thermal efficiency of the collector by 20% relative to water as working fluid.</li> <li>• The highest increase for <math>F_R (\tau\alpha)</math> and <math>F_{RUL}</math> were 21.9 and 78.3%.</li> </ul>
Gad and Said [273]	Water/Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	25 nm $\Phi = 2$ wt. %	FPSC	< 80 °C	2-6L/min	<ul style="list-style-type: none"> <li>• Both metal oxide particles improved effectiveness of the FPSC being maximum 30 and 32% at 2 l/m mass flow rate for Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> NF, respectively.</li> </ul>

						<ul style="list-style-type: none"> <li>● Efficiency decreased as the flow rate of NFs increased as well as the Reynolds number increased from 4500-11000.</li> </ul>
Sundar, et al. [274]	Water/Nano-diamond	10 nm $\Phi = 0.2-1$ vol.%	FPSC	$< 80$ °C	0.033- 0.083 kg/s	<ul style="list-style-type: none"> <li>● Inclusion of 1 vol.% of nano-diamond intensified the collector efficiency by 39.62% than water. Solar absorbance also contributed to the rise in efficiency.</li> <li>● Heat transfer and Nusselt number increased by 52.33 and 32.31%, respectively, at Reynold number 12766.</li> </ul>
Moravej, et al. [275]	Water/TiO <sub>2</sub>	n/a $\Phi = 1-5$ wt.%	FPSC	$< 80$ °C	0.015-0.045 L/s	<ul style="list-style-type: none"> <li>● Highest 33.54% energy gained using 5 wt.% of water/TiO<sub>2</sub> replacing water as working fluid.</li> <li>● Efficiency increases from 0.53 to 0.65 with raising solar irradiance from 195 to 888 W.</li> </ul>
Alklaibi, et al. [276]	Water/Nano-diamond	100 nm $\Phi = 0.2-1$ vol.%	FPSC	$< 80$ °C	0.02 kg/s	<ul style="list-style-type: none"> <li>● 12.7% higher with addition of optimum 1 vol.% diamond particles.</li> <li>● Entropy of generation decreased using water/ND nanofluid although frictional entropy increased by 16.59% relative to water as working fluid.</li> </ul>
Yousefi, et al. [241]	Water/Al <sub>2</sub> O <sub>3</sub>	15 nm $\Phi = 0.2$ wt.%	FPSC	$< 80$ °C	1-3 L/min	<ul style="list-style-type: none"> <li>● Al<sub>2</sub>O<sub>3</sub> particles enhanced the performance of the collector by 28.3% over the water based FPSC system.</li> </ul>
Tong, et al. [277]	Water/MWCNT Al <sub>2</sub> O <sub>3</sub> CuO Fe <sub>3</sub> O <sub>4</sub>	20, 20, 40 and 30 nm $\Phi = 0.005, 0.1, 0.5$ and 0.015 vol.% respectively.	FPSC	$< 80$ °C	0.47 kg/s	<ul style="list-style-type: none"> <li>● Maximum efficiency of the collector is achieved with MWCNT nanofluid which is 25% higher than water based FPSC.</li> <li>● Efficiency found to be reduced by increasing the size of all the dispersed particles. Highest 7.9% reduction is observed for 500% increase (20-100nm) of Al<sub>2</sub>O<sub>3</sub> particles.</li> </ul>
Allouhi and Benzakour Amine [278]	Water/CuO Al <sub>2</sub> O <sub>3</sub> TiO <sub>2</sub>	n/a $\Phi = 0-3$ vol.%	FPSC	$< 80$ °C	0.018-0.036 kg/s	<ul style="list-style-type: none"> <li>● Less cp of NF yielded higher performance increment of the FPSC. CuO exhibited best enhancement in energy and exergy efficiency by 2.7 and 11.1% correspondingly.</li> </ul>

						<ul style="list-style-type: none"> <li>• More energy gained at increasing flow rate of NFs; 2.95% better energy attained with CuO NF at 0.036 kg/s. However, maximum 13.26% for CuO NF.</li> </ul>
Choudhary, et al. [279]	Water-EG/Fe <sub>3</sub> O <sub>4</sub>	n/a Φ = 0.2-1 vol.%	FPSC	< 80 °C	30-150 L/h	<ul style="list-style-type: none"> <li>• Highest outlet temperature of the collector is achieved 350.26K, which is 15.98K higher than water-EG.</li> <li>• Thermal performance was increased by 15.27 % and remained nearly constant for 15 days. Furthermore, 17.05% increment in absorption and 40.17% drop of heat loss at 1 vol.% and 30 L/h.</li> </ul>
Verma, et al. [242]	Water/ /MgO /CuO /MWCNT /MgO-MWCNT /CuO-MWCNT	CuO (42 nm) MWCNT (AR=200, dia 7 nm) Φ = 0.25-2 vol.%	FPSC	< 80 °C	0.5-2 L/min	<ul style="list-style-type: none"> <li>• Hybrid CuO and MgO with MWCNT exhibited performed better than solo CuO and MgO based NFs although MWCNT alone observed to be most efficient NF among all.</li> <li>• MgO and CuO-based hybrid NFs exhibit the highest thermal efficiency increments of 20.52 and 18.05%, and exergy efficiency increments of 33.78 and 30.09%, respectively.</li> </ul>
Eltaweel, et al. [245]	Water/MWCNT	Length 20 μm, diameter 10-40 nm Φ = 0.005 to 0.05 wt.%	FPSC and ETSC	< 80 °C	0.0097-0.0338 kg/s m <sup>2</sup> (FPSC) 0.0133-0.0464 kg/s m <sup>2</sup> (ETSC)	<ul style="list-style-type: none"> <li>• The maximum average energy efficiency obtained using the 0.05 wt.% of Water/MWCNT was 55% and 59%, respectively, and the exergy efficiency was 10% and 11.5% for ETSC and FPSC.</li> <li>• The inclusion of NF leads to a size reduction in ETSC and FPSC by 29.5% and 26.7%, respectively.</li> </ul>
Hosseini and Shafiey Dehaj [280]	Water/TiO <sub>2</sub> (spherical) /TiO <sub>2</sub> (wire-like)	40-60 and 14.2 nm Φ = 1 vol.%	ETSC	20-60 °C	0.1-0.5 L/min	<ul style="list-style-type: none"> <li>• Both wire-like and spherical titania particles demonstrated superior efficiency, with the highest values being 21.1 and 12.2%, respectively. The flow rate was also added to the performance index.</li> </ul>
Mahbubul, et al. [281]	Water/SWCNT	1-2 nm Φ = 0.05-0.2 vol.%	ETSC	< 80 °C	0.265 kg/s	<ul style="list-style-type: none"> <li>• Using NF at 0.2vol.% intensified the efficiency by 10%. Most significant increment is observed at irradiance of 900 W/m<sup>2</sup>.</li> </ul>
Ozsoy and Corumlu [282]	Water/Ag	60 nm Φ = 20 ppm	ETSC	< 80 °C	n/a	<ul style="list-style-type: none"> <li>• Replacing water with NF produced up to 40% increment in the efficiency. It is understood that NP</li> </ul>

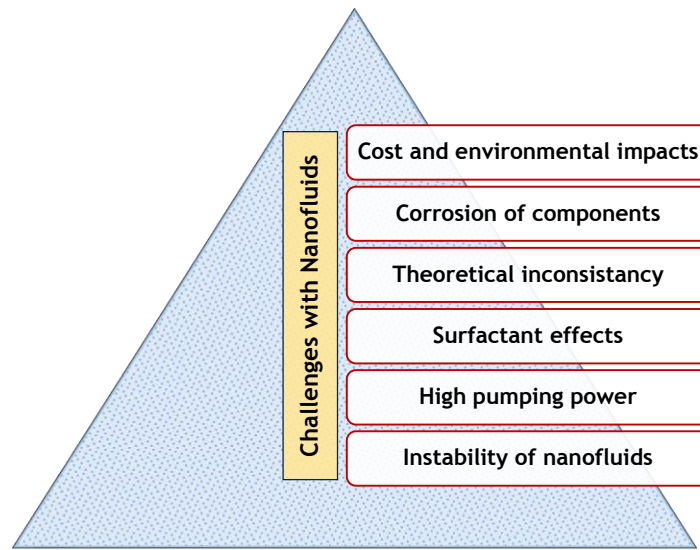
						layers accumulated on the evaporator surface clearly affect the heat transfer.
Daghigh and Zandi [283]	Water/MWCNT /CuO /TiO <sub>2</sub>	n/a Φ = 0.1 vol.%	ETSC	< 80 °C	n/a	<ul style="list-style-type: none"> <li>● Output of the ETSC augmented more using carbon based MWCNT dispersed NF (25%) relative to CuO (12%) and TiO<sub>2</sub> (5%) based NFs.</li> <li>● Fuel consumption was reduced by 67.7% using the designed solar system.</li> </ul>
Sharafeldin, et al. [284]	Water/Cu	50 nm Φ = 0.01-0.03 vol.%	ETSC	< 80 °C	0.6-0.8 L/min	<ul style="list-style-type: none"> <li>● Using NF, temperature raised by 50% in the outlet and removal factor increased significantly to reach the highest value of 0.97. Maximum efficiency intensified by 51% at 0.03vol.% and 0.8 L/min.</li> <li>● Positive impact of Cu NPs is observed in CO<sub>2</sub> reduction and economic perspective.</li> </ul>
Dehaj and Mohiabadi [285]	Water/MgO	74.5 nm Φ = 0.014-0.032 vol.%	ETSC/HPSC	< 80 °C	5 to 14 L/min	<ul style="list-style-type: none"> <li>● Efficiency stands high at higher flow rate; 77% effectiveness is obtained at 14L/m using 0.032 vol.% of MgO along with superior absorption capacity of the NF.</li> </ul>
Sadeghi, et al. [286]	Water/Cu <sub>2</sub> O	15-20 nm Φ = 0.04-0.08 vol.%	ETSC	< 80 °C	10-50 L/h	<ul style="list-style-type: none"> <li>● 28% augmented efficiency is achieved using parabolic concentrator and NF at 0.08 vol.% and 50 L/h replacing water. Furthermore, 3.7% supplemented exergy output.</li> </ul>
Al-Waeli, et al. [287]	Water/SiC	40-60 nm Φ = 3 wt.%	Hybrid PV/T	< 80 °C	-	<ul style="list-style-type: none"> <li>● Overall effectiveness was strengthened by 88.9 employing NF relative to standalone PV unit.</li> </ul>
Alous, et al. [252]	Water/MWCNT /Graphene	8-35 μm×18-28 nm and 1-12 μm×0.55-1.12 nm respectively Φ = 0.5 wt.%	Hybrid PV/T	< 80 °C	0.5 L/m	<ul style="list-style-type: none"> <li>● The highest 16°C temperature drop of a PV unit was obtained with MWCNT dispersed NF, while graphene dispersed NF revealed superior efficiencies of 63.1 and 20.6% in terms of energetic and energetic standpoint.</li> </ul>
Al-Shamani, et al. [288]	Water/SiO <sub>2</sub> /TiO <sub>2</sub> /SiC	< 100 nm Φ = 0.5-2 wt.%	Hybrid PV/T	< 80 °C	0.068-0.17 kg/s	<ul style="list-style-type: none"> <li>● Highest combined efficiency is achieved 81.73% with SiC NF at 0.17 kg/s and 1000 W/m<sup>2</sup> solar irradiance. Overall energy coefficient is 0.93.</li> </ul>

Rajendiran, et al. [289]	Water/CuO	27 nm $\Phi = 0.05-0.2$ vol.%	Hybrid PV/T	45-65 °C	40 L/h	<ul style="list-style-type: none"> <li>Higher sonication time provided optimized performance of the PV/T system. 95.8% maximum overall efficiency of the PV/T collector was found for 0.2% CuO/water NF after 4 h of sonication.</li> </ul>
Abdelrazik, et al. [43]	DI water/rGo-Ag	$\Phi = 0.0005-0.05$ wt.%	Hybrid PV/T	< 80 °C	n/a	<ul style="list-style-type: none"> <li>NFs produced more thermal and electrical efficiency relative to water-based PV/T collector and standalone PV panel without thermal cooling component.</li> </ul>
Wole-Osho, et al. [290]	Water/Al <sub>2</sub> O <sub>3</sub> -ZnO	29 and 70 nm respectively $\Phi = 0.01-1$ vol.%	Hybrid PV/T	< 80 °C	0.01-0.1 kg/s	<ul style="list-style-type: none"> <li>The hybrid NF had significant influence at optimum conditions of 0.01 vol.%, 0.1 kg/s flow rate and 0.47 mixture ratio (Al<sub>2</sub>O<sub>3</sub>: ZnO). 34% optimized energetic efficiency is remarked.</li> </ul>
Das, et al. [72]	Water-[MMIM][DMP]/MXene	1–10 $\mu\text{m} \times 1$ nm $\Phi = 0.05-0.2$ wt.%	Hybrid PV/T	< 80 °C	0.01-0.07 kg/s	<ul style="list-style-type: none"> <li>14 and 14.4% higher thermal and electrical efficiency is achieved relative to metallic alumina/water NF.</li> <li>PV cell temperature dropped by 12.5 °C using NF instead of water as cooling fluid.</li> </ul>
Elminshawy, et al. [39]	Water/Al <sub>2</sub> O <sub>3</sub>	$\Phi = 1-3$ vol.%	Low photovoltaic concentrator (LCPV)	< 80 °C	0.01 kg/s	<ul style="list-style-type: none"> <li>Temperature of the collector cooled by 16.47 °C in comparison with uncooled system.</li> <li>In addition, daily electrical output was augmented by 13.58% using NF instead of water.</li> </ul>
Li, et al. [291]	DI water/MXene	MAX-phase (25 $\mu\text{m}$ ) $\Phi = 10$ to 200 ppm	DASC	300-370 K	36 L/h	<ul style="list-style-type: none"> <li>Water/MXene NFs exhibited superior photothermal conversion efficiency of the DASC relative to water-based system due to distinct absorption of solar radiation with the NFs.</li> <li>Highest intercept efficiency is obtained 77.49% at 100 ppm loading of MXene flakes which is significantly higher than the base fluid.</li> </ul>
Esmaeili, et al. [292]	Water/CuO CuO foam	30 nm $\Phi = 0.01-0.1$ vol.%	DASC	< 80 °C	0.0075-0.0225 kg/s	<ul style="list-style-type: none"> <li>CuO NFs produced better output than metal oxide foam based working fluid. Maximum improvement is achieved 26.8% higher than water and 3% higher than metal oxide foam.</li> </ul>

Wang, et al. [293]	Water/ZrC	40 nm $\Phi = 10-100$ ppm	DASC	$< 80$ °C	--	<ul style="list-style-type: none"> <li>Reverse illumination is recommended for NF-based DASCs. The highest conversion effectiveness is increased up to 51.9%.</li> </ul>
Karami, et al. [259]	Water-EG/CuO	40 nm $\Phi = 25-100$ ppm	DASC	$< 80$ °C	50-90 L/h	<ul style="list-style-type: none"> <li>Efficiency of the DASC raised with addition of NPs and speeding up the flow rate and up to 17% supplemented efficiency is achieved during solar water heating.</li> </ul>
Delfani, et al. [260]	Water-EG/CuO	40 nm $\Phi = 25-100$ ppm	DASC	$< 80$ °C	50-90 L/h	<ul style="list-style-type: none"> <li>MWCNT dispersed NF produced better output (up to 29%) relative to CuO [259] at identical conditions indicates superior absorption of carbon nanomaterials.</li> </ul>
Karami [258]	Water/Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub>	30 and 15 nm respectively $\Phi = 500-200$ ppm	DASC	$< 80$ °C	0.0075-0.0225 kg/s	<ul style="list-style-type: none"> <li>Energy and exergy efficiencies augmented by 21.7 and 66.4% at maximum <math>\phi</math> and flow rate. Entropy generation was reduced using NF and contribution of pressure drop was insignificant.</li> </ul>
Hachicha, et al. [265]	Water/MWCNT	30-50 $\mu\text{m} \times 8-15$ nm $\Phi = 0.05-0.3$ vol.%	PTSC	35-55 °C	0.08-1 L/s	<ul style="list-style-type: none"> <li>Nusselt number improved against increasing Reynolds number and particle concentration. The Cost is considerably lower than research grade MWCNT.</li> </ul>
Minea and El-Maghlany [294]	Water:EG/Ag-MgO, Al <sub>2</sub> O <sub>3</sub> -Cu, GO-Co <sub>3</sub> O <sub>4</sub>	$< 100$ nm $\Phi = 0.05-2$ vol.%	PTSC	$< 100$ °C	--	<ul style="list-style-type: none"> <li>The hybrid NFs performed better when water was used as BF due to low pressure drop relative to EG. 115-125% augmented heat transfer coefficient is obtained using water-EG/GO-Co<sub>3</sub>O<sub>4</sub> at 0.15 vol.%.</li> </ul>
Ehyaiei, et al. [295]	Water/Al <sub>2</sub> O <sub>3</sub> , /CuO, Therminol VP-1/ Al <sub>2</sub> O <sub>3</sub> , /CuO	$< 100$ nm $\Phi = 1-5$ vol.%	PTSC	$< 80$ °C	0.08 kg/s	<ul style="list-style-type: none"> <li>Water performed better than the oil as BF. CuO NPs showed higher energy and exergy output than Al<sub>2</sub>O<sub>3</sub> particles due to higher TC of CuO.</li> </ul>
Bretado de los Rios, et al. [296]	Water/Al <sub>2</sub> O <sub>3</sub>	10 nm $\Phi = 1-3$ vol.%	PTSC	$< 80$ °C	--	<ul style="list-style-type: none"> <li>Replacing water with the NF resulted in 11.6% enhancement in thermal efficiency as well as outlet temperature using 3 vol.% of NPs.</li> </ul>
Rehan, et al. [297]	Water/Al <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>	20 and 20-40 nm $\Phi = 0.2-0.3$ wt.%	PTSC	$< 60$ °C	1-2 L/min	<ul style="list-style-type: none"> <li>13 and 11% elevated thermal efficiency is attained, respectively. Temperature difference increased dispersing NPs, while it declined raising the flow rate.</li> </ul>

1306 **7. Challenges with NFs and its application**

1307 NFs are the latest promising thermo-fluids which are evolving at considerable pace to establish  
1308 its place in impending practical applications. Nevertheless, over the last decade, researchers  
1309 and engineers have identified many critical issues with NF in terms of its advanced  
1310 characteristics and successful implementation in real-world solar thermal engineering  
1311 applications. Numerous sophisticated issues posed in numerous studies on NF are summarized  
1312 in the following points (also depicted in **Fig. 31**).



1313  
1314

**Fig. 31.** Identified challenges with nanofluids.

- 1315
- 1316 • Inadequate stability of NF suspensions (as stated in **Section 3**) is a fundamental  
1317 shortcoming as it degrades major properties and dictates essential implementation of  
1318 the NF in any solar thermal systems. The majority of available techniques for stabilizing  
1319 NF suspension fall short of providing industrial standard stable NF. Some techniques  
1320 including surfactant or chemical stabilizers addition and pH modulation are reported to  
1321 have positive impact on stability within certain conditions. Yet, consequences (i.e.,  
1322 thermal, and optical properties degradation, foam formation, corrosion, and fouling  
1323 factors) of these methods are responsible for deterioration of the properties at critical  
1324 operating conditions like high temperature and high particle loading. Conventional NP  
1325 synthesis and NF formulation procedures should be improved to produce more stable  
1326 suspension. Furthermore, there are no standard indicator for reporting stability that can  
1327 indisputably interpret suspension stability characteristic in terms of duration (days or  
1328 months), hence, rigorous observation approach is essential to report accurate  
assessments. Zeta potential ( $\zeta$ ) is often proposed as an ideal indicator of NF stability in

1329 literatures; however, it is not appropriate since high  $\zeta$  value does not necessary implies  
1330 high suspension stability. Rather, it indicates electrostatic repulsion potential between  
1331 NPs. In the in case steric stabilization technique,  $\zeta$  can be low while remaining  
1332 completely stable [298]. Therefore, reporting of stability is still in an ambiguous state  
1333 and needs to be construed with generic standard to allow comparisons across a broad  
1334 range of NFs.

- 1335 • Dispersion of nanoscale particles results in an increment of BF viscosity ( $\mu$ ) which in  
1336 turn escalates pressure drop in the NF-operated dynamic systems, i.e., solar collectors.  
1337 Inevitably, the drop extends further as particle loading and mass flow rate increase.  
1338 Since a dynamic system's pumping power is directly related to pressure drop and flow  
1339 rate, an increase in pressure drop implies an increase in pumping power demand [299].
- 1340 • Surfactants or chemical stabilizing additives are deployed to ameliorate the stability of  
1341 NFs. However, the stabilizers often result in penalties in terms of thermo-optical  
1342 properties and performance. Although most of the studies concur regarding positive  
1343 impact on stabilization, notable limitations (i.e., ineffectiveness above 50-60°C and non-  
1344 Newtonian flow property) and conflicts among reported studies due to diverse  
1345 classification of the surfactants make it difficult to select an ideal stabilizer for a  
1346 particular NF.
- 1347 • Theoretical unpredictability reflected in literature regarding interactions among  
1348 thermophysical properties (particularly, TC and  $c_p$ ) and affecting constraints is another  
1349 crucial challenge to conquer. Numerical based models and correlations developed for  
1350 an individual combination of BF and NP i.e., NF under specific conditions could not  
1351 provide accurate estimation of data for other NFs due to interactions of an extensive  
1352 number of dependent variables. Therefore, advanced ANN and machine learning  
1353 models must be developed that incorporate a variety of variables with NF properties  
1354 and make use of accumulated practical data to strengthen the prediction.
- 1355 • Several NFs exhibited perceptible corrosivity operating as working fluid in thermal  
1356 devices which can lead to significant damage to the entire system. Chemical  
1357 interactions, pH value variation and mechanical stabilization of the fluids are the  
1358 culpable factors that cause surface degradation [300]. To avoid this sort of  
1359 inconvenience, additional maintenance is necessary.
- 1360 • NFs comprised of nanoscale particles may cause toxic environmental and biological  
1361 effects. Due to the tiny size of NPs, it is reasonable that the particles can get into human



1362 skin and cause respiratory, inflammation and carcinogenic infections [301]. In future  
1363 research on NF, scientists and engineers should consider green synthesis techniques to  
1364 develop NFs that are non-toxic, ecologically beneficial, and safe for industrial usage.  
1365 Besides, the potential challenge of high production costs must be reduced since it  
1366 hinders application of NF on energy conversion systems, including but not restricted to  
1367 SCs.

## 1368 **8. Conclusions and recommendations**

1369 This study of the thermophysical properties, stability phenomena, and development of water-  
1370 dependent NFs on low temperature SCs includes causes and effects analyses based on detailed  
1371 experimental and numerical investigations. Due to their superior potency and influence at low  
1372 temperatures, this analysis focuses on the most frequently used water-based and hybrid NFs.  
1373 Several critical areas are examined and discussed, including thermophysical properties,  
1374 suspension stability and mechanisms, and application to solar collector products. Nevertheless,  
1375 research needs to progress in right directions for further advancement in the field of NF and its  
1376 utilization on solar thermal collector devices. Several critical areas are examined and discussed,  
1377 including thermophysical properties, suspension stability and mechanisms, and application to  
1378 solar collector products. Nonetheless, research must continue in the right direction to advance  
1379 the sector. In this regard, the authors have drawn some critical conclusions and  
1380 recommendations about the current state of research in this field and possible research  
1381 directions.

1382 On synthesis and formulation of NF:

- 1383 • The single-step method produces more stable NFs, while the two-step method produces  
1384 NF with more efficient thermal properties. Given the limitations of both approaches in  
1385 terms of concurrently formulating stable and thermally optimized NF, a systematic  
1386 approach should be applied considering critical parameters, operating conditions, and  
1387 desired performance (described in **Section 2**). Further research is needed to develop a  
1388 process for producing NF that is sustainable, cost efficient, and scalable. Carrillo-  
1389 Berdugo, et al. [302] recently revealed a novel interface based three step techniques to  
1390 formulate stable NF that produced optimized thermo-optical properties.

1391 On thermo-physical characteristics of NF:

- 1392 • Effective TC of water and water-based NFs amplifies prominently dispersing carbon  
1393 contained nanomaterials rather than traditional metal and metal-oxides. Nevertheless,  
1394 numerous works reveal chaotic conflicts with respects to few sophisticated factors

1395 (mentioned in **Section 3**) emerged from the diverse operating conditions. Therefore, a  
1396 comprehensive systematic approach should be performed considering the wide-ranging  
1397 finite variable operating conditions to establish fundamental relationship with TC of  
1398 diverse NFs. While TC intensifies dispersing nanomaterial in BF,  $c_p$  drops for most of  
1399 the NFs due to lower heat capacity of solid particles relative to liquids. Nevertheless,  
1400 opposite trends are reported in few studies using carbon-based particles. Since higher  
1401  $c_p$  value has remarkable impact on renewable energy sector, particularly energy storage  
1402 and SC devices, comprehensive experiments are required to come up with detailed  
1403 understanding on  $c_p$  enhancement of NFs.

- 1404 • The dynamic viscosity ( $\mu$ ) of water-based NFs enhances with the inclusion of  
1405 nanoscale materials but it declines noticeably at higher temperatures. Moreover,  
1406 Newtonian, and non-Newtonian properties are dominant at low to high  $\varphi$  respectively.  
1407 While hybrid NFs usually elucidate non-Newtonian flow characteristics.
- 1408 • Existing theoretical and empirical models derived for a specific NF are inaccurate to  
1409 estimate heat transfer behavior (Nusselt number, pressure drop and performance  
1410 factor), thermal conductivity,  $\mu$ , and  $c_p$  of other NFs when compared to experimental  
1411 data. This could be because only a few significant criteria and operating conditions are  
1412 considered. Analytical studies are needed to build specific models that analyze possible  
1413 factors to precisely estimate these critical properties.

1414 On suspension stability of NF:

- 1415 • Stability determines the overall performance of the NF and the thermal system on which  
1416 it operates, i.e., improved stability results in increased system efficiency. Generally,  
1417 most the formulated NFs reported in the studies exhibit short-term stability due to  
1418 agglomeration of dispersed particles caused by various factors. The instability of NFs  
1419 is identified as a function of multifarious variables, for instance formulation techniques,  
1420 BF, NPs ( $\varphi$ , size and shape), temperature, and stabilization methods (physical and  
1421 chemical). However, NFs containing very low  $\varphi$  of carbon nanomaterials in water  
1422 medium offer prominent suspension stability and effective performance augmentation  
1423 using in SC based energy conversion application. Further investigations should  
1424 emphasis on rigorous tracking of stability for longer periods employing techniques  
1425 associated with stabilizers and functionalization to provide explicit reports about the  
1426 impacts of stabilizing additives.

1427 • By evaluating related destabilization factors, comparisons between various NF  
1428 stabilization strategies (e.g., ionic, and non-ionic stabilizers, surface adjustment and  
1429 functionalization) should be made. Deployment of advance particle functionalization  
1430 using irreversible polymers grafting can during synthesis of NP may evade limitations  
1431 and provide robust protection against the undermining factors. Furthermore, there are  
1432 no clear analytical correlations linking NF stability, operating conditions, and  
1433 properties that can be addressed in future research.

1434 On implementation and performance evaluation of NF on various solar collector systems:

1435 • The selection of stable NF (i.e., BF and NP) is a critical precondition for their use in  
1436 solar energy conversion operations. The efficiency of several low flux SCs is  
1437 significantly enhanced when NFs are used in place of traditional HTFs. Desired  
1438 properties for SC application of NFs include high heat transport and energy storage  
1439 capacity (i.e., TC and  $c_p$ ) alongside low viscosity and Newtonian flow behavior which  
1440 are observed to have important impacts on the performance.

1441 • Water-based NFs are well suited for low temperature energy systems and SCs due to  
1442 their low viscosity and high thermo-optical properties. In low flux SCs such as FPSC,  
1443 ETSC, DASC, and hybrid PV/T, water-based NFs containing carbon nanomaterials  
1444 perform better.

1445 • Inadequate studies were observed estimating production cost, surface deterioration,  
1446 safety, and ecological aspects of NFs. Such instructive statistics would provide essential  
1447 assistance to determine prospective execution of the NFs in industrial sectors.

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