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Recent Developments in Heat Transfer Fluids Used for Solar Thermal Energy Applications

Umish Srivastva[1*], RK Malhotra[2] and SC Kaushik[3]

[1]*Indian Oil Corporation Limited, RandD Centre, Faridabad, Haryana, India*
[2]*MREI, Faridabad, Haryana, India*
[3]*Indian Institute of Technology Delhi, New Delhi, India*

Abstract

Solar thermal collectors are emerging as a prime mode of harnessing the solar radiations for generation of alternate energy. Heat transfer fluids (HTFs) are employed for transferring and utilizing the solar heat collected via solar thermal energy collectors. Solar thermal collectors are commonly categorized into low temperature collectors, medium temperature collectors and high temperature collectors. Low temperature solar collectors use phase changing refrigerants and water as heat transfer fluids. Degrading water quality in certain geographic locations and high freezing point is hampering its suitability and hence use of water-glycol mixtures as well as water-based nano fluids are gaining momentum in low temperature solar collector applications. Hydrocarbons like propane, pentane and butane are also used as refrigerants in many cases. HTFs used in medium temperature solar collectors include water, water-glycol mixtures – the emerging “green glycol” i.e., trimethylene glycol and also a whole range of naturally occurring hydrocarbon oils in various compositions such as aromatic oils, naphthenic oils and paraffinic oils in their increasing order of operating temperatures. In some cases, semi-synthetic heat transfer oils have also been reported to be used. HTFs for high temperature solar collectors are a high priority area and extensive investigations and developments are occurring globally. In this category, wide range of molecules starting from water in direct steam generation, air, synthetic hydrocarbon oils, nanofluid compositions, molten salts, molten metals, dense suspension of solid silicon carbide particles etc., are being explored and employed. Among these, synthetic hydrocarbon oils are used as a fluid of choice in majority of high temperature solar collector applications while other HTFs are being used with varying degree of experimental maturity and commercial viability – for maximizing their benefits and minimizing their disadvantages. Present paper reviews the recent developments taking place in the area of heat transfer fluids for harnessing solar thermal energy.

Keywords: Solar thermal energy; Solar thermal collectors; Heat transfer fluids

Introduction

Solar energy can be harnessed to generate power by way of either solar photo voltaic route or by concentrating the sun’s rays to generate high temperatures and high magnitude of heat (concentrated solar power or CSP). The concentrated heat generated by sun’s energy can be transported using suitable heat transfer fluids to heat exchanger where this heat is transferred to convert water into steam and steam turbine is then driven to produce electricity. Out of the two options of solar energy, PV and CSP, CSP based thermal route offers distinct advantages in bringing down the least cost of electricity generated by way of providing storage and dispatch ability of solar power during off-sun periods [1,2]. Solar thermal energy is utilized by capturing the heat of the sun in devices, generally known as solar collectors, designed to maximize the heat absorption through their surfaces exposed to the sun. The heat that is absorbed on the surfaces of such solar collectors is then transferred through a heat transfer media, generally liquid in nature, which takes the collected heat to the point of use. In most of the concentrating solar power plants, sun’s heat is captured by a receiver, transferred to a thermo fluid – also known as heat transfer fluid; and this heat from the thermo fluid is then used in a heat exchanger to convert steam from water [3-5]. Solar thermal collectors are defined by the USA Energy Information Administration as low-, medium- , or high-temperature collectors based on their temperatures of operation in the following manner [6].

Low temperature collector

They operate in a temperature range from above ambient to about ~80 °C, used primarily in solar water heating applications, solar based space heating and cooling applications, solar ice making etc. For such low temperature solar thermal applications, following are the heat transfer fluids which are being employed:

Refrigerants/phase changing materials: These are low boiling point but high heat capacity substances used in the solar collectors to transfer heat in applications like solar space cooling and heating, refrigerators, air conditioning, etc [7]. These materials absorb heat from the solar collectors, produce work either by expanding in a turbo-generator of a vapor compression cycle or by dissociating the refrigerant from its absorbent in a vapor absorption cycle [8]. In some of the relatively high temperature applications, higher boiling point refrigerants are used as indirect heat transfer fluids, wherein the heat collected from the solar collectors is transferred to another fluid like water from where the refrigerants pick-up heat to do the required work in the turbo-generators [9,10].

Traditionally, for refrigeration purposes, anhydrous ammonia (R-717) or sulphur dioxides (R-764) were used. However, they were found to have harmful effect when used in domestic application owing to their leakage during use and are thus now mostly used in industrial

***Corresponding author:** Srivastva U, Indian Oil Corporation Limited, RandD Centre, Faridabad, Haryana, India, E-mail: srivastavau@indianoil.in

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applications. For domestic applications, they were replaced by non-toxic, non-flammable, stable, noncorrosive, and non-freezing type's chlorofluorocarbon known as CFC refrigerants most common of them being Freon R-12 [11]. However, since the CFCs have a negative effect on the earth's ozone layer which is the cause of global warming, production of CFC is increasingly being banned in many parts of the world since early 1990s [12].

CFCs have been gradually replaced by the less harmful and comparatively low ozone layer depleting refrigerants' class hydro-chloro-fluoro-carbons known as HCFC such as tetra-fluoro-ethane (R-134a) which is still in use for refrigeration application though there are efforts to phase it out for the same reason [13]. Sometimes refrigerants like HCFC (R123) and HFC (R245fa) are chosen as the working fluids for the Organic Rankine Cycle / Vapor Compression Cycle systems. However, use of these refrigerants are now being restricted with increased environmental awareness. Since, hydrocarbons HCs are comparatively known to be more environmentally friendly, non-toxic, chemically stable and highly soluble in conventional mineral oil, they have also been used in several applications [14]. Owing to better flammability characteristics, hydrocarbons such as butane (R600) and isobutene (R600a) are also chosen as the refrigerants/working fluids for the ORC/VCC system for ice making [15].

Similarly, for solar absorption cooling purposes, refrigerant-absorbent pairs of LiBr-water or water-ammonia are used [16]. Infact, several researchers have used absorption/adsorption cycle as the preferred route of solar cooling and refrigeration. A large variety of working fluids such as activated carbon as adsorbent and ammonia were used, activated carbon/methanol, silica gel/water, olive waste as adsorbent with methanol as adsorbate, composite adsorbents of CaCl2 and BaCl2 developed by the matrix of expanded natural graphite have also been reported to be used [17,18].

Apart from the refrigerants, Phase-Changing-Materials (PCM), in conjunction with solar PV as well as thermal energy, have also been employed in several instances of designing active building architecture through devices known as PV-ST-PCM systems; wherein the heat generated in the solar panels is captured by the PCM which then transfers this heat to a suitable transfer medium such as air or water which can then be utilized for thermal applications in the building such as water heating, space heating, drying processes etc [19]. While PCMs have been used mainly with Building Integrated Photo Voltaics (BIPV) in BIPV-PCM systems at large [20], owing to the poor heat transfer capability, the innovative PV-ST-PCM systems play the dual role of increasing the PV efficiency on one hand and improving the thermal management of the building space on the other [21]. For storing the latent heat part of solar energy, the choice of suitable PCM to act as heat storage material as well as heat transfer fluid is important as by increasing the thermal storage capacity, the temperature variation can be reduced for long periods of time [22].

There are several materials such as Paraffins, Waxes, Salt Hydrates, Eutectic mixtures of Salt Hydrates etc which were traditionally used as PCMs. The major area of research in PCM integrated with solar energy systems is in finding material and engineering solutions for enhancing the heat transfer capabilities of these systems because while PCMs have exhibited good heat storage ability, their heat dissipation characteristics has not been satisfactory. In their efforts for increasing the heat storage capacity as well as heat transfer capacity of PCMs, incorporation of newer generation materials such as carbon fibres, metallic nano-powders, carbon nano tubes, encapsulated nano-materials, etc are now being increasingly experimented with [23,24].

The important properties such as phase change temperature and heat of fusion of some of the PCMs are listed in Table 1 [25].

Water: Water is the preferred fluid majorly used in low temperature solar collectors for applications such as domestic use, swimming pool heat, solar heating and cooling, etc. Water is abundantly available, is inexpensive and by nature nontoxic. It has high specific heat and is easy to pump owing to having very low viscosity [26]. However, it has a big disadvantage of operation in extreme conditions owing to having comparatively low boiling point (100°C) and high freezing point (0°C). Further, it is easily amenable to lose its neutrality in ph value very soon by picking up contamination thereby causing corrosion hazards and at the same time has a tendency to cause mineral deposits on heat transfer surfaces which reduces its heat transfer capability. The mineral deposits also cause blockages in the piping systems through which water moves within the solar thermal energy collection systems [27].

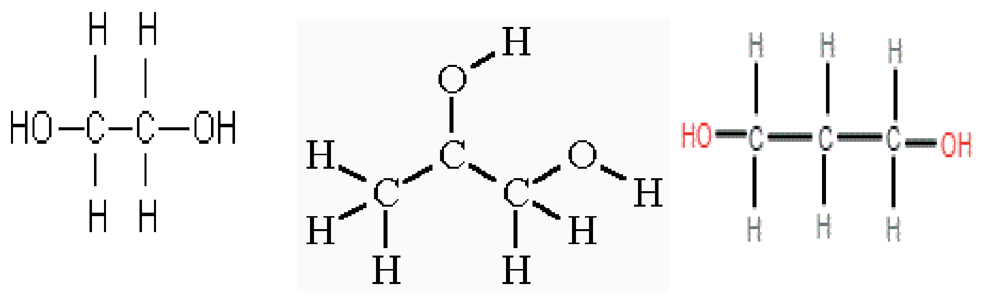
Water that is used in solar heating application is required to be non-contaminated and clean/treated so as to avoid scaling and mineral deposit formation. Generally, water quality with less than 200 ppm of hardness is used directly in solar water heaters [28,29]. When the incoming water quality is hard, it is recommended to either treat the water by provision of a separate water softener placed at the inlet of the cold tank or an intermediate heat transfer fluid, such as water glycol mixtures in an indirect or a closed loop circuit in the solar water heater [30-33].

Name	Type of Product	Melting Temp. (°C)	Heat of Fusion (kJ/kg)	Source
Astorstat HA17 Astorstat HA18	(Paraffins and Waxes)	21.7-22.8 - 27.2 - 28.3	-	Astor Wax by Honey well (PCM Thermal Solution)
RT26	Paraffin	24 - 26	232	Rubitherm GmbH
RT27		28	206	
Climsel C23	Salt Hydrate	23	148	Climator
Climsel C24		24	108	
STL27	Salt Hydrate	27	213	Mitsubishi Chemicals
S27	Salt Hydrate	27	207	Cristopia
TH29	Salt Hydrate	29	188	TEAP
	Mixture of Two Salt Hydrate	22-25	-	ZAE Bayern
E23	Plus ICE (Mixture of Non-Toxic Eutectic Solution)	23	155	Environmental process system (EPS)

Table 1. Phase Change Temperature and Heat of Fusion of Typical Commercial PCMs

	Water	Ethylene Glycol (% Volume)			Propylene Glycol (% Volume)			Trimethylene Glycol (% Volume)		
		40	50	60	40	50	60	40	50	60
Freezing point (°C)	**0**	**-24**	**-37**	**-53**	**-22**	**-34**	**-48**	**-21**	**-27**	**-38**
Viscosity (centipoises @ 4.4°C)	**1.55**	**4.8**	**6.5**	**9**	**-**	**-**	**-**	**8.4**	**11.5**	**16.9**
Specific gravity @ 4.4°C	**1**	**1.07**	**1.09**	**1.1**	**1.03**	**1.04**	**1.046**	**1.04**	**1.05**	**1.06**
Specific heat (Btu/lb.°F)	**1.004**	**0.84**	**0.79**	**0.75**	**0.89**	**0.85**	**0.81**	**0.87**	**0.83**	**0.78**
Boiling point (°C)	**100**	**104.4**	**107.2**	**111.1**	**103.9**	**105.6**	**107.2**	**-**	**-**	**-**
Toxicity	**Neutral**	**More**			**Less**			**Least**		

Table 2: Comparison of properties of heat transfer fluids used in low-medium temperature solar collectors.



Ethylene Glycol   Propylene Glycol   Trimethylene Glycol

Figure 1: Chemical Structure of different Glycols.

Properties	Aromatics	Naphthenes	Paraffins
Chemical structure	Benzene ring type	Cycloalkane type	Alkane type
Reactivity	Very high	High	Low
Solvency	Very high	High	Low
Oxidation stability	Low	High	Very high
Pour point	Very low	Low	High
Boiling point	Low	High	Very high
Viscosity index	Low	High	Very high
Heat transfer rate	Very high	High	Low
Wax content	Low	High	Very high
Heat transfer operating temperatures	105 – 160°C	150 – 210°C	180 – 280°C

Table 3: Comparison of aromatic, naphthenic and paraffinic heat transfer fluids.

Indirect or closed loop systems use a heat exchanger that separates the potable water from the intermediate fluid, also termed as the "heat-transfer fluid" (HTF), that circulates through the collector. The most common HTF is an antifreeze/water mix that typically uses non-toxic glycol. After being heated in the panels, the HTF travels to the heat exchanger, where its heat is transferred to the potable water. Though slightly more expensive, indirect systems offer freeze protection and typically offer overheat protection as well. Sometimes, water is flown in perpendicular direction through a larger diameter tube where it comes in contact with many small diameter pipes containing heat transfer fluid being heated in the solar heater and indirect heat transfer takes place. This way, periodic operation and maintenance of tube containing harder water becomes easy [34,35,36].

Water-nano fluids: Direct absorption of solar energy in the fluid volume, known as Direct Absorption Solar Collectors (DASC) [37] has been proposed as an effective approach to increase the efficiency of collectors. The concept of DASC was originally proposed by Minardi andChuang [38] in the 1970s as a simplified design of solar thermal collector and to appreciably enhance the efficiency by absorbing the energy with the fluid volume. They developed a direct collector that absorbed solar radiation by the black fluid (water with 3.0 g/L, Indiaink). However, later on, black fluid like India Ink, as well as other organic and inorganic chromophores have been shown to experience light- and temperature-induced degradation as well as low thermal conductivity [39].

Water-based nanofluids containing carbon nanotubes and stabilized by sodium dodecyl benzene sulfonate (SDBS) as surfactant, have also been experimentally studied. Low nanoparticle volume fraction, ranging from 0.0055% to 0.278%, showed positive effect on density, thermal conductivity and viscosity of nanofluids for temperature range of 20–40°C. Enhancement in density, thermal conductivity and viscosity of nanofluids with volume fraction in nanotubes was observed in comparison to base fluids [40- 42].

The effect of using nanofluids (aluminum/water) was investigated as the working fluid to increase the efficiency of low-temperature DASC [43]. The efficiency enhancement of 10% was obtained using nanofluid-based DASC in comparison with a conventional flat-plate collector. By introducing nanofluids as direct absorber of sunlight in solar collectors, their stability and optical properties as well as their thermal properties improve greatly [44]. However, it has also been reported that the ionic liquids of phosphates are not suitable for applications that require long-term stability at 200°C or more [45,46].

Glycol/water mixtures: Glycol, a synthetic chemical of origin, mixed along with water, often in ratios of 50:50 or 60:40, forms a solution for heat-transfer applications where the temperature in the heat transfer fluid can go below 0°C. Glycols of ethylene or propylene are generally used in heat transfer applications and are generally referred to as "antifreezes". While ethelyne-glycol is a common automotive anti-freeze and is extremely toxic , propylene glycol-water mixture is non-

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toxic and is used as food-grade anti-freeze [47].

Ethylene glycol-water mixture is traditionally a very commonly used heat transfer fluid in cars and other automobiles, which have to operate in very cold conditions to extremely hot operating temperatures. The properties of glycol-water mixtures varies depending upon the ratios of glycol and water; with the obvious increase in cost component with the increase of glycol content in the mixture [48].

Glycols are generally used in closed loop solar thermal systems using solar collectors that heat the glycol mixture. After getting heated in the collectors, the mixture is pumped in the system and used in a heat exchange to transfer its heat to water kept in the tank. Using glycol-water mixtures helps using the water in low temperature regions for round the clock domestic hot water applications. Glycol-water mixtures are also used for solar water heating applications when the operating temperatures of solar heaters rises beyond the low-temperature-collector region to low-medium-temperature collectors i.e. beyond 100°C [49-51].

Medium temperature collectors

These collectors operate in the temperature range from about 85°C – 270°C, used to supply process heat in various industries such as power, textiles, processing of raw materials etc. Such solar thermal hot water systems — where solar heating is used to provide hot water and low grade steam to process applications — are becoming increasingly common in industrial applications where hot water is at a premium and needed through green initiatives. An important step in optimizing the efficiency of a solar thermal hot water system ion the choice of proper fluid that can assist in transferring heat from the panel mounted on the rooftop down to the hot water heat exchanger.

Water-glycols

At times the temperatures in solar rooftop panels reach above 150°C and so long as the fluid is in circulation, there are no potential dangers at these temperatures. However, sometimes the circulation is interrupted owing to breakdown in power or pumps etc. In such cases the fluid gets stagnated and reaches higher temperatures whereby the glycols can cause a number of operational problems depending upon design of the solar rooftop water heating system. To deal with problems associated with such stagnant fluids, there are certain common designs such as drain back, boil back and allowing the fluid to fill the panel completely [52-56]. In fact, once a glycol based fluid reaches a bulk temperature of above 120°C, its degradation increases drastically making them turn acidic and causing corrosion issues, often needing replacement of the fluids as well as the panel components [57-59].

In order to retard the temperature linked degradation of glycols, corrosion inhibitors are added into them. The corrosion inhibitors are chemicals selected from a group consisting of a water- soluble, alkali metal phosphate, an alkali metal or ammonium hydroxide-neutralized aliphatic monocarboxylic acid having from 8 to 14 carbon atoms and a pH within a range of from 7 to 10; an alkali metal or ammonium hydroxide-neutralized aliphatic dicarboxylic acid having 8 to 14 carbon atoms and a pH within a range of from 7 to 10, an aromatic or substituted aromatic monocarboxylic acid that has from 7 to 14 carbon atoms or its alkali metal salt or ammonium salt, an alkali metal borate, an alkali metal silicate, an alkali metal molybdate, an alkali metal nitrate, and an alkali metal nitrite [60].

The inhibitor – propylene glycol package normally results into a reserve alkalinity of 10 sufficient to protect metals like copper and steel used in solar panel upto a temperature of 120°C. However, when the temperature exceeds 150°C owing to fluid stagnation, the reserve alkalinity is required to be adjusted between 18 to 25 depending upon the glycol being use, so as to minimize the acid formation and corrosion in the system. The following criteria is used to choose the correct glycol-inhibitor package in solar thermal applications:

Thermal stability at temperatures up to 175°C

Non-toxicity

Corrosion protection properties

Optimum reserve alkalinity

Types of glycols: The chemical structures of the three most commonly used glycols for heat transfer applications is given in Figure-1 below:

Ethylene glycol is the most common heat transfer fluid in the glycol family traditionally used automotive applications as well as in solar HVAC industries. Compared to other common types of glycols, it has good thermal and physical properties, is relatively toxic, is not normally used in domestic hot water systems and also degrades much faster at the higher temperature encountered in solar thermal systems [61-63].

Propylene glycol has become the most used antifreeze in some process heat transfer applications and most commercial HVAC systems. It is safe, nontoxic, commonly used in domestic hot water systems, degrades slowly than ethylene glycol but at the same time exhibits lower performance owing to its high viscosity and lower thermal conductivity [64,65].

Another important class of thermally stable glycol, derived from oil or natural gas is trimethylene glycol. Since, it can also be produced from corn sugar, it is known as bio-derived “green” glycol. Compared to propylene glycol manufacturing, there is 30 percent less greenhouse gases in the manufacturing of these green glycols. It has slower thermal degradation rate compared to the conventional glycols, and has superior viscosity at lower temperatures [66].

Table 2 gives a comparison of properties of glycol based heat transfer fluids used in low-medium temperature solar collectors [67].

Propylene glycol has a well-known chemistry and a proven record with process and HVAC systems in the past many years. For solar thermal applications, propylene glycol was most used traditionally but is now being increasingly replaced with the green glycol in developed world countries. Both propylene as well as trimethylene glycols, are

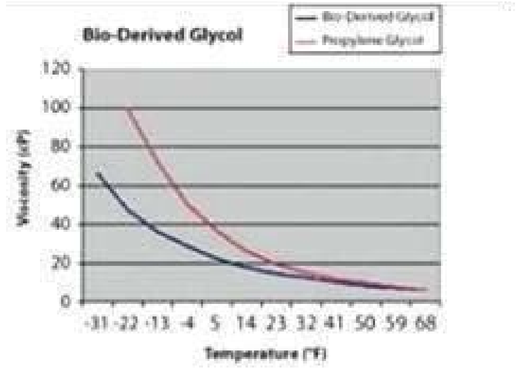

Figure 2: Comparison of Bio-derived Glycol with Conventional Glycol.

	Materials	Thermal conductivity (W/mk)
Metallic Materials	Copper	401
	Silver	429
Non-metallic Materials	Silicon	148
	Alumina (Al2O3)	40
Carbon	Carbon Nano Tubes (CNT)	2000
Base fluids	Water	0.613
	Ethylene glycol (EG)	0.253
	Engine oil (EO)	0.145
Nanofluids (Nanoparticle concentration %)	Water/Al2O3 (1.50)	0.629
	EG/ Al2O3 (3.00)	0.278
	EG-Water/Al2O3 (3.00)	0.382
	Water/TiO2 (0.75)	0.682
	Water/ CuO (1.00)	0.619

Table 4: Thermal conductivity of some materials, base fluids and nanofluids.

safe, non-toxic and are normally inhibited and adjusted for a higher reserve alkalinity to slow degradation. Though, the green glycol provides better thermal and physical properties while being renewable and more environment friendly than propylene glycol, but it has a higher cost. Figure 2 depicts a comparison of bio-derived glycol with the conventional glycol.

Hydrocarbon oils: Hydrocarbon oils can be either of petroleum origin or artificially synthesized in laboratories. As compared to water, the hydrocarbon oils have higher viscosity, lower specific heat and require more energy to pump. These oils are relatively cheap and have a low freezing point.

Most of the heat transfer fluids of petroleum hydrocarbon origin used in industrial applications operate within a temperature range from 120°C to 280°C and their choice for any particular application is governed by the nature of their composition. By this logic, wherever the industrial application uses solar energy for such heat transfers, these hydrocarbons based oils are used as heat transfer fluids. The petroleum hydrocarbon oils can be characterized based on their composition such as aromatic mineral oils, naphthenic oils or paraffinic oils in their respective increasing order of operational temperatures [68].

Though, the aromatic or naphthenic mineral oils are endowed with high heat transfer capacities and lower viscosities, they also have low operating temperatures ranges of say upto 210°C, beyond which these oils degrade very fast. These oils have low pour point and moderate viscosity helping in decreasing the pumping losses and power required for circulation in the system [69].

The paraffinic oils are more stable at low as well as higher temperatures and are thus used for high operating temperatures of about ~280°C despite of not having such good heat transfer properties. All the naturally occurring petroleum based heat transfer fluids are quite toxic by nature and are used in closed loop applications for several years altogether, virtually filled-for-life concept [70].

An indicative comparison of different types of naturally occurring hydrocarbon oils used for heat transfer applications is given in Table 3.

High temperature collectors

High temperature solar collectors are concentrating type high temperatures collectors generating temperatures exceeding 300°C used primarily for industrial processing heat and electricity generation. These solar collectors use different types of heat transfer fluids ranging from air, water, mineral oils, synthetic oils, molten salts, molten metal's, inorganic minerals, etc and are described below:

Hydrocarbon oils: While there are a few highly refined naturally occurring hydrocarbon oils, mostly paraffinic in nature, which are used in select solar collectors as heat transfer fluids for operating temperatures below 320°C, the high temperature solar collectors majorly uses hydrocarbon oils of synthetic origin. Synthetic fluids are relatively nontoxic and require little maintenance compared to their petroleum counterparts [71].

Synthetic heat transfer fluids are made of glycols, various synthetic fluids such as alkyleated aromatics, terphenyls, and mixtures of bi and diphenyls and their oxides. These are generally of two types - semi-synthetic oils having major constituent as naturally occurring petroleum based minerals oils and some synthetic fatty components added into it as additives to increase it heat transfer abilities or other necessary heat transport properties, - and - fully synthetic heat transfer oils where synthetic components such as eutectic mixtures of biphenyl and diphenyl oxides are most commonly used as heat transfer oils in parabolic trough based concentrated solar power plants round the world [72]. The fully synthetic heat transfer fluids used in parabolic CSP applications have high freezing point and in places where temperature falls below ~12°C. They pose a problem of getting solidified and require additional maintenance to keep them in fluidic conditions [73,74].

Compared to the petroleum based hydrocarbon oils, synthetic oils have excellent heat transfer properties, lower viscosities and high operating temperatures of upto 400°C. Using these synthetic hydrocarbon oils in solar collectors is most convenient in terms of operation and maintenance, but their use is hugely hampered by their maximum operating temperatures of 400°C beyond which these oils deteriorates very fast [75-77].

Researchers are also working to prove the feasibility of utilizing substituted polyaromatic hydrocarbons such as phenylnaphthalenes for solar heat transport application. These hydrocarbon derivatives are expected to retain favorable thermophysical properties and stabilities above 500°C, and can be derived as the byproducts of refining of clean-diesel. Thermophysical properties like low vapor pressure and high resistance to thermal decomposition may make polyaromatic hydrocarbons such as phenylnaphthalenes suitable for heat transfer applications in parabolic solar collectors. Since they are liquids at room temperatures and at the same time can withstand high temperatures of above 500°C, Phenylnaphthalene can potentially replace high-temperature inorganic salts in solar CSP aplications [78].

Nano-fluids: Nano-fluids are a colloidal mixture of base fluid containing nano-sized particles such as oxide ceramics, nitride ceramics, carbide ceramics, metals, semiconductors, carbon nanotubes and composite materials such as alloyed nanoparticles etc and have predominant characteristics because of nanoparticles' small size and high surface area [79]. Research studies on advanced high temperature heat transfer fluids by incorporation of metallic nanoparticles of copper, Al2O3, etc in concentrations of about ~5% by volume into conventional heat transfer fluids have been reported to be significantly improving the thermal transport properties of the HTFs [80,81]. Appreciable increase in thermal conductivity over the base fluids to the tune of about 20% at a 2 vol.% particle loading has been reported. When good dispersion of nanoparticles is obtained, based on the measurement of dynamic viscosity, the nano-fluids behave in a Newtonian manner and the dynamic viscosity increases over the base fluid are minor at

CSP Technology	Operating Pressures (Bar)	Operating Temperatures (°C)	HTF Commonly Used
Trough	15	400	Synthetic hydrocarbon oils
Trough	40	270	Saturated steam
Trough	50-100	400-500	Superheated steam
Tower/Trough	1	500-600	Salts
Tower	1	700-1000	Air
Tower	15	800-900	Air

Table 5: Indicative list of choice of CSP technology versus heat transfer fluids employed.

temperatures of 125°C and above [82-87].

Magnetic nanofluids (MNF) are a special class of nanofluids, exhibiting both magnetic as well as fluid properties. Possibility of using an external magnetic field to control the flow and heat transfer process of the MNF, makes it an interesting choice as a heat transfer medium [88]. Another novel nano-fluid is the carbon nano-tubes mixed nanofluids prepared by proper dispersion and stabilization of the CNT in base fluids (BF) commonly performed using ultrasonication [89]. Significantly higher thermal features of thermal conductivity, convective heat transfer coefficient and boiling critical heat flux compared to the base fluids have been reported n CNT based nano-fluids. Increasing of CNT concentration and temperature further enhances the haet atrsnport properties of CNT based nano-fluids. Increased thermal conductivity of nanofluid in comparison to base fluid by suspending particles is shown in Table 4 below [90]:

Discovered in early 2000's, carbon nano tubes and ionic liquids at room-temperature can be blended to form gels known as "bucky gels of ionic liquids" which has the potential for use in several engineering or chemical processing applications as advanced heat transfer fluids in numerous cooling technologies, heat exchangers, chemical engineering and green energy-based applications such as solar energy. CNT-ionanofluids also exhibit superior thermo-physical and heat transfer properties compared to base ionic liquids. Attractive features of ionanofluids are that they can be designed and fine-tuned through their base ionic liquids so as to obtain desired properties and tasks. These recent research finding on CNT based nanofluids and ionanofluids having ultra-high thermal conductivity, it is being forecasted that these types of fluids are the potential next generation heat transfer fluids [91-93].

Water

Water is being used in some of the high concentrated solar power plants for direct steam generation using linear Fresnel collectors, also in some of the parabolic trough systems as well as in few experimental solar towers. However, its use in CSP application remains in RandD stage and it is mostly used as a preferred heat transfer fluid in low and medium temperature solar collector [94,95].

Direct steam generation (DSG) from water eliminates the need for components like heat transfer fluid, heat exchangers, is non-toxic, have simpler overall plant configuration, allows the solar field to operate at higher temperatures, resulting in higher power cycle efficiencies and lower fluid pumping energies [96,97] Though, DSG still is one of the most promising opportunities for future cost reductions in high concentration solar collectors, it suffers from a number of operational issues such as two-phase flow, higher control requirement, difficult and expensive storage (mostly sensible heat storage), higher temperature gradients, high operating pressures resulting into frequent leakages etc. Compact Linear Fresnel Reflectors (CLFR) were designed to be using only water as its heat transfer fluid in direct steam generation and the trend of DSG is slowly being experimented in Parabolic Solar Collectors as well as in some of the Solar Towers [98].

Air and compressed gases

Air is one of the most abundantly available substances that can be used as heat transfer fluid. It does not freeze, does not boil and is non-corrosive by nature. However, it has poor heat transport properties in terms of very low heat capacity, poor thermal conductivity and tends to leak out of collectors, ducts and dampers. The system size and engineering requirement for using air as heat transfer fluid is very high and thereby costly in most cases [99].

For very high temperatures such as concentrated solar collectors, there are few experimental projects, where air is being reported to be used directly as heat transfer fluids, especially in concentrated solar towers, where volumetric air receivers are being and the operating temperatures achieved are as high as 550°C. In such high temperature applications, the high cost of engineering systems to handle air as heat transfer fluid can get suitably justified [100].

Simulation methods to comparatively study use of pressurized nitrogen in place of conventional synthetic oil based HTF in parabolic-trough plants using the coordinates of an existing Spanish 50 MWe parabolic-trough plants with 6 h of thermal storage and observed that almost similar net annual electricity productions can happen by replacing the conventional synthetic HTF with pressurized nitrogen which will also be environmentally safe HTF has also been experimented [101].

Another study by theoretical substitution of gas as working fluid in a parabolic trough solar power plant for overcoming flammability and environmental problems associated with conventional synthetic oils was done [102]. The researchers also described a test loop developed at solar research centre of Plataforma Solar de Almería (PSA Spain) for evaluating the effects and technical feasibility of such new concepts in heat transfer oils. They concluded that the high gas pressure can offset pumping power to better acceptable levels but also reported absence of technique to detect the gas leakages from ball joints as a major drawback of using gas in place of oil as HTF.

Molten salts

Salts of sodium or potassium in liquid forms are used as heat transfer fluids in concentrating solar power (CSP) plants as they are able to operate at temperatures well beyond 500°C, improves the power cycle efficiencies to about 40% range, improve the system performance and reduce the Levelized Electricity Cost (LEC). Molten salts are more user friendly and environmentally benign than oils, are easily available in nature and are thus less expensive. However, salts suffer from certain major disadvantages in that they have a high freezing point of about 250°C, which requires lot of auxiliary power during shut-off periods to keep them in molten state and is thus a huge maintenance problem. Further, owing to their corrosive nature, they require expensive operational machineries and system engineering in terms of pipings, pumps, joints etc for their efficient operation [103- 110].

Molten salts have been used as heat transfer fluids in solar towers in a number of concentrated power plants around the world. Their use in solar towers has been quite established though at the same time it makes the electricity generated from such solar towers expensive. Further, since solar plants are operated intermittently, keeping the salts in molten state is a big engineering and economic challenge. However, salts offer an added advantage of being used as a thermal energy storage (TES) medium as well [111-116].

Molten metals

Some of the known metals such as liquid sodium used as heat transfer medium in nuclear industry have also been proposed to be used as a heat transfer fluid for solar application for high temperatures beyond 550°C [117,118]. Liquid sodium has a fairly low melting point, very high boiling point, very high thermal conductivity and fairly high heat capacity. However, sodium as metal as well as liquid sodium, is extremely reactive with water and this makes its use in solar application difficult [119].

Another variant, a eutectic sodium-potassium alloy NaK, has been reported to be used to overcome this problem. Nak has very lower melting point of -12°C which makes it suitable to be used for all practical purpose in CSP applications [120]. Though, NaK has boiling point lower than sodium, lower specific heat capacity and inferior heat transport properties than sodium, owing to the fact that it has subzero melting point, it has been considered as an excellent high temperature heat transfer fluid. Eutectic NaK has a composition of 77.8% potassium by weight and 22.2% sodium by weight and has -12°C melting point. The NaK mixture which has 46% potassium can have a melting point of 20°C and has higher thermal conductivity and specific heat capacity than eutectic NaK. But the inherent danger of reactivity with water remains with NaK as well and thus restricts its use in solar CSP applications. It has been experimentally tried in an experimental solar tower in Spain and there was a huge fire reported causing lot of damage to the system [121]. Another eutectic mixture, Lead-Bismuth (44.5-55.5%) having very high boiling point of above 1500°C, owing to its inherent properties of being non-reactive with water and air, is also being applied in R and D stage in CSP application. Similarly, binary eutectic mixtures of liquid metals like Cadmium-Bismuth, Tin-Bismuth, Bismuth-Zinc, Calcium-Copper etc are other combinations which are being studied under combinatorial material chemistry and synthesis for their usefulness in CSP applications with respect to safety of use, corrosion, pump ability, operation and maintenance issues etc [122].

The choice of heat transfer fluid for high temperature solar applications depend on a number of important factors such as the concentrated solar power technology being employed, the operating temperatures and pressures in the system; all of which governs the cost and performance of the electricity generation. Table 5 below gives an indicative list of the same:

Several authors have carried out comparison studies of some of the in-use as well as promising novel heat transfer fluids including the compatibility studies of these heat transfer fluids with the metallurgies of the system. A comparison of the various properties of some commonly used thermo fluids, solar salts and oil used in high temperature solar collectors is given in Table 6 below [123].

Fluidized solid particles

A very new and novel concept of high temperature resistant HTF in the form of a dense suspension of solid silicon carbide particles in mean diameter of ~ 64 micron range approximating to 30-40% by weight and remaining being air 60-70%; has been recently reported from studies carried out by a European consortium [124]. The dense suspension is circulated upward in a specially designed vertical absorbing tubes located inside a single cavity created in a receiver of alkaline-earth silicate exposed to highly concentrated solar flux reaching a temperature as high as 750°C. The solid particles of silicon carbide has heat capacity as good as the conventional synthetic oil based HTFs but can withstand high temperature without degradation. Heat transfer coefficients as high as 500 W/m^{2}K has been reported to be achieved in this experimental study at very low mean particle velocities in the range of 2.5 cm/s. It has been concluded in this study that the particle volume fraction in the suspension and suspension velocity are the important influencing factors for achieving good heat transfer rates but the same are also some of the engineering challenges to be overcome to make this concept workable on a larger and commercial basis [125].

Conclusions

Solar thermal energy is a technology for harnessing solar energy for thermal applications such as heating-cooling, hot water, industrial heat, power generation etc. Solar thermal collectors are defined by the USA Energy Information Administration as low-, medium-, or high-temperature collectors. The heat from the sun falls on the solar collector which is coated with special solar selective coatings so as to absorb the maximum solar radiations' heat. The heat absorbed on the collector surfaces is then transferred to a heat transfer fluid, generally known as thermo-fluids, diligent choice of which plays a very vital role in determining the overall efficiency of solar energy utilization. The choice of heat transfer fluids for a given solar energy collector depends primarily on the working temperature of the fluid.

In the low temperature solar collectors where traditionally refrigerants like HCFC (R123) and HFC (R245fa) were used rather

	Unit	Sodium salt	Sodium potassium salt	Potassium salt	Salt Hitec XL	Salt Hitec	Salt grade Hitec Solar salt	Solar grade HTF (oil)
Melting point	°C	97.82	-12.6	63.2	120	142	240	15
Boiling point or maximum operating temperature	°C	881.4	785	756.5	500	538	567 (bp 593)	400
Density	Kg/m^3	820	749	715	1640	1762	1794	1056
Specific heat capacity	KJ/KG.K	1.256	0.937	0.782	1.9	1.56	1.214	2.5
Viscosity	Pa.s	0.00015	0.00018	0.00017	0.0063	0.003	0.0022	0.0002
Thermal conductivity	W/m.K	119.3	26.2	30.7	Na	0.363	0.536	0.093
Prandtl number		0.0016	0.0063	0.0043		12.89	4.98	5.38

Table 6: Comparison of the various properties of commonly used thermo fluids used in high temperature solar collectors.

extensively, hydrocarbons such as butane (R600) and isobutene (R600a) known to be more environment friendly, non-toxic, chemically stable and highly soluble in conventional mineral oil, have been increasingly used in several applications. For solar cooling and refrigeration purposes, several researchers have reported increased use of absorption/adsorption cycle as the preferred route. Another new research interest has been seen in utilizing PCMs in conjunction with solar energy systems such as PV-ST-PCM wherein the heat of PV panels is absorbed in PCMs which then transfers this heat for solar thermal applications like building space heating, water heating etc. For slightly higher temperature range for water heating applications, direct water, water-ethylene glycol mixtures and water based nano-fluids are increasingly finding place.

The use of medium temperature solar collectors though has extremely large potential as industrial and commercial heat source is rather relatively less explored and applied. For temperatures beyond 100 °C and up to about 150°C, water-glycol mixtures are used wherein propylene-glycols are increasingly replacing traditional ethylene glycol. Another new class of glycol which is more thermally stable and environmentally safe, trimethylene glycol, manufactured by way of bio-processing, is also reportedly being utilized. For the higher side of medium temperature solar collectors, hydrocarbon oils, mostly aromatic or naphthenic in nature are used. Sometimes, semi-synthetic oils, mixture of mineral based hydrocarbons and chemicals are also used for certain high end applications.

High temperature solar collectors are mostly used for power generation and allied uses. These collectors use more stable paraffinic hydrocarbon oils to some extent and eutectic mixture of synthetic compounds, in most cases for upto 400°C. For temperature ranges beyond 400°C, molten salts - mixture of sodium and potassium salts in varying proportions have been used. This category of solar collectors is poised to grow very fast and its growth is majorly hampered by the choice of a suitable thermo-fluid that can withstand higher temperatures for extended period of time. Realizing the important of efficiency increase with every 10° rise of working temperature of the thermo fluids, extensive research is being carried out in synthesizing suitable chemicals that can withstand temperatures beyond 400°C and so far fluid up to 470°C has been reportedly developed in a US lab. To achieve higher system efficiencies, direct steam generation technologies are also being adopted. In few cases, direct heating of air is also being reported to achieve very high temperatures of above 800°C.

For high temperatures solar collectors, another route being adopted by researchers is that of nano-fluids, which are a colloidal mixture of base fluid containing nano-sized particles such as oxide ceramics, nitride ceramics, carbide ceramics, metals, semiconductors, carbon nanotubes and composite materials such as alloyed nanoparticles etc and have predominant characteristics because of nanoparticles' small size and high surface area. Magnetic nanofluids (MNF) as a special class of nanofluids exhibiting both magnetic and fluid properties with a possibility of controlling flow and heat transfer process via an external magnetic field are also being studied. All most all the researchers have reported nano-fluids to exhibit significantly higher thermal features such as thermal conductivity, convective heat transfer coefficient and boiling critical heat flux. Known metals such as liquid sodium or a eutectic mixture of sodium-potassium alloy NaK, that can be used in molten state as thermo fluids, is also reported being used as heat transfer fluid for solar application for high temperatures beyond 550°C. Dense suspension of solid silicon carbide particles also are reported to be used experimentally for high temperatures CSP application such as solar tower, owing to high temperature stability and heat capacity.

For concentrated solar power applications, a very major need at present is for a workable and user friendly heat transfer fluid that can be operated and maintained easily at low temperatures and is environmentally benign. The available CSP technologies of parabolic troughs are capable of reaching temperatures beyond 400°C but such temperatures are not achieved as the heat transfer fluid, which is synthetic in nature, though very convenient to use becomes prone to thermal degradation beyond 400°C. On the other hand, the molten salts that are used in solar towers can sustain higher temperatures of 650°C or so, becomes very inconvenient to operate and maintain below 250°C which is quite a high freezing point for any working fluid. Hence, any incremental developments of heat transfer fluid with operating temperatures beyond 400°C and ease of maintenance can be a path breaking innovation in CSP technology, per se, and has the potential to place concentrated solar power amongst the most bankable and reliable renewable energy option.

With the available state-of-the-art technologies in heat transfer fluids for concentrated solar power (CSP) plants, which is the solar energy technology of immense importance and need in today's world for generating reliable and despatchable renewable energy, an ideal heat transfer fluid is one which operates as a Thermally Stable, Easily Pump able, having Negligible Vapour Pressure, Fully Compatible, Non-Corrosive, Single Phase Liquid at all operating temperatures having some of the important physical properties as given in Table 6 below.

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