



THERMOELECTRIC EFFECT, ITS BACKGROUND AND SCOPE IN DAIRY: REVIEW

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Abstract

Non-conventional cooling systems have found wide range of applications to meet the energy requirements of the present and future. This paper presents a review of thermoelectric cooling/ heating systems and their applicability in various sectors. It explores the fundamentals of thermoelectric cooling/ heating and its applications. The efficiency of thermoelectric materials and its scope for improvement is also discussed.

Introduction

The applications of thermoelectric coolers are increasing with an ever increasing demand of cooling in every sector for the past forty years. The TE coolers convert electrical energy into a temperature gradient which is also known as Peltier effect. Although the physical principles upon which modern thermoelectric coolers function actually discovered in early 1800s but commercial thermoelectric modules were made available in the year 1960.

In 1821, the first important discovery relating to thermoelectricity occurred by German scientist Thomas Seebeck who found that an electric current would flow continuously in a closed circuit made up of two dissimilar metals, provided that the junctions of the metals were maintained at two different temperatures. Without actually comprehending the scientific basis for the discovery, Seebeck, falsely assumed that flowing heat produced the same effect as flowing electric current. Later, in 1834, while investigating the Seebeck Effect, a French watchmaker and part-time physicist, Jean Peltier found that there was an opposite phenomenon where by thermal energy could be absorbed at one dissimilar metal junction and discharged at the other junction when an electric current flows within the closed circuit. Afterwards, William Thomson described a relationship between Seebeck and Peltier Effect without any practical application. After studying some of the earlier thermoelectric work, Russian scientists in 1930s, inspired the development of practical thermoelectric modules based on modern semiconductor technology by replacing dissimilar metals with doped semiconductor material used in early experiments. The Seebeck, Peltier and Thomson effects, together with several other phenomena, form the basis of functional thermoelectric modules. Its applications are found in military, aerospace, telecommunication, electronic systems, laser diodes and medical sector. Recently TE coolers are also finding applications for cooling in high powered components such as microprocessors in both manufacturing test processes and user conditions. High cooling capacity TE coolers, in combination of air cooling or liquid cooling techniques, are being pursued to extend the conventional air cooling limits for high power dissipating microprocessors (Bierschenk and Johnson, 2004; Bierschenk and Gilley, 2006; Chein and Huang, 2004; Hasan and Toh, 2007; Ikeda et al., 2006; Anon, 2006; Phelan et al., 2002; Sauciuc et al., 2003; Simons et al., 2005; Solbrekken et al., 2003; Taylor and Solbrekken, 2006). Compact in size and silent in operation, the TE cooler is easy to be integrated into a system in comparison with the vapour compression cooling technology (Phelan et al., 2002 and Zhang, 2010). With time the cost of production of the TE cooler has decreased and the scope for the consumer market has widened significantly. The variety of TE products is quite large and is ever increasing with the imaginations of design engineers for heating and cooling applications. The reliability of the TE coolers is very high, but the efficiency remains limited (Riffat and Ma, 2003).

Thermoelectric cooling systems are analogous to conventional refrigeration systems. A conventional cooling system includes an evaporator, a compressor, and a condenser. In the evaporator the pressurized refrigerant goes through expansion, boiling and then evaporation. When the phase changes from liquid to gas heat energy is absorbed. Then the compressor recompresses the gas into a liquid and the condenser expels the gas to the ambient surroundings. A TE cooling system has similar subassemblies. However, TE cooling is specifically the abstraction of heat from electronic components. Over the past four decades, improvement in the conversion efficiency has been marginal. The challenge has been the improvement in the performance of the thermocouple materials, which could lead to a breakthrough in terms of the efficiency of the TE device (Riffat and Ma, 2003).

An increasing surge in the demand of refrigeration has been noticed e.g. air-conditioning, food preservation, vaccine storages, medical services, and cooling of electronic devices, led to an increase in the consumption of electricity which is a contributing factor for global warming and climate change (Xi et al., 2007). TE refrigeration is a beneficial alternative as it can use waste electricity for further cooling applications and meeting our present energy challenges (Tritt and Subramaniam, 2006). Further, these are entirely solid-state devices and absence of moving parts makes them rugged, reliable, and quiet. In addition to this, these use no ozone depleting chlorofluorocarbons, potentially offering a more environmental friendly alternative to conventional refrigeration (Awasthi and Mali, 2012). Therefore, TE refrigeration is greatly needed (Sofrata, 1996), particularly for developing countries where long life and low maintenance are needed (Godfrey, 2010; Riffat, and Ma, 2003). TE coolers can be analyzed by



Joule heat, which is called heat rejection (Q_h), from TEC hot side larger than the heat absorption (Q_c), into TEC cold side (Jugsujinda et al, 2011).

Basic principles

Seebeck effect

A voltage is generated when a temperature differential is established between the hot and cold ends of the semiconductor material. This voltage is called the Seebeck voltage. The phenomenon is known as seebeck effect in which seebeck voltage is directly proportional to the temperature differential (Fig.1) (Rajput, 2009).

$$\Delta V = \alpha_{ab} \times \Delta T \tag{1}$$

Where, $\alpha_{ab} = (\alpha_a - \alpha_b)$ = Seebeck coefficient for materials A and B (or P and N) of materials

A and B

ΔT = Temperature difference between the junctions A and B.

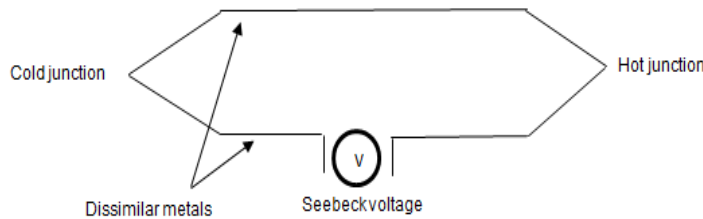


Figure 1 Temperature gradient causing seebeck voltage in circuit (Seebeck effect)

The effect is reversible in nature. The thermoelectricity has power generation application based on the Seebeck effect. If heat supplied at the one junction causes an electric current to flow in the circuit and electrical power is delivered. When a large number of such thermocouples are connected electrically in series a module is formed.

Peltier effect

The Seebeck effect and the Peltier effect are both inverse of each other. Peltier effect involves the passage of an electric current through a thermocouple produces heating or cooling i.e. conversion of electrical energy into temperature gradient by TE devices (Peltier, 1834) This is also called as Peltier cooling (Fig.2) (Lee, 2013).

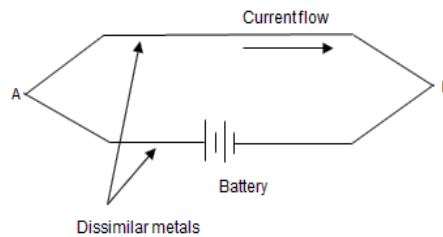


Figure 2 Current flow causing temperature gradient between points A and B (Peltier effect)

At the junction between the two dissimilar metals the heat evolved or absorbed in unit time is proportional to the current (Rajput, 2009) and is given by:

$$Q_p = \Pi_{ab} \times I \tag{2}$$

Where, Q_p = heat evolved or absorbed in unit time, watts

$\Pi_{ab} = (\pi_a - \pi_b)$ = Peltier coefficient

I = Direct current, amperes



The application of this effect was limited until the development of semiconductor materials. With semiconductor materials opened a wide variety of practical TER applications opened up. TER is achieved when a DC is passed through one or more pairs of N and P-type semiconductor materials. In the cooling mode, DC passes from the N to P-type semiconductor material. The temperature TC of the interconnecting conductor decreases and heat absorption occurs from the environment. This heat absorption from the environment (cooling) occurs when electrons pass from a low energy level in the P-type material through the interconnecting conductor to a higher energy level in the N-type material. The absorbed heat is transferred through these semiconductor materials by electron transport to the other end of the junction TH and liberated as the electrons return to a lower energy level in the P-type material. This phenomenon is called the Peltier effect.

The Peltier effect is controlled by the Peltier coefficient, defined as the product of Seebeck coefficient of the semiconductor material and the absolute temperature. The Peltier coefficient relates to a cooling effect as current passes from the N-type material to the P-type material, and a heating effect when current passes from the P-type material to an N-type material. Reversing the direction of the current reverses the temperature of the hot and cold ends. Ideally, the amount of heat absorbed at the cold end and the heat dissipated at the hot end are dependent on the product of the Peltier coefficient and the current flowing through the semiconductor material. Practically the net amount of heat absorbed at the cold end due to the Peltier effect is reduced by two sources, conducted heat and Joule heat. Due to the temperature differential between the cold and hot ends of the semiconductor material, heat will be conducted through the semiconductor material from the hot to cold end. As the current is increased, the temperature differential, and thus the conducted heat, increases because the Peltier cooling effect increases (Riffat and Ma, 2003).

Thomson effect

In 1854, William Thomson discovered that if a temperature difference exists between any two points of a current-carrying conductor, heat is either absorbed or liberated depending on the direction of the current and the material (Fig. 3).

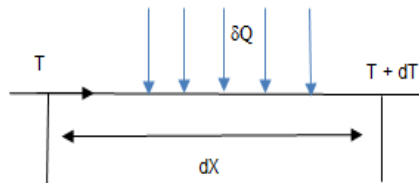


Figure 3 Heat absorbed due to temperature difference across a conductor (Thomson effect)

This is called the Thomson effect (Thomson, 1854 and Lee, 2013). The rate of heat transfer is as follows:

$$\delta Q/dx = \tau I (dt/dx) \tag{3}$$

Where, $\delta Q/dx$ = Thomson heat transfer

τ = Thomson coefficient

I = flow of the current through the conductor

dt/dx = temperature gradient along the conductor

The following two relations connecting these three coefficients were obtained (α , π , τ) by applying the first and second laws of thermodynamics to a simple TE circuit:

$$\Pi_{ab} = \alpha_{ab} \times T \tag{4}$$

$$\tau_a - \tau_b = T \times d\alpha_{ab} / dT \tag{5}$$

From the above equations it may be noted that the Thomson effect has been defined for a single conductor, the seebeck and peltier coefficients refer to a junction between two materials.

Using both the equations:

$$Q_p = \alpha_{ab} \times I \times T \tag{6}$$



This equation indicates that to get a high value of cooling or heating, α_{ab} should be high, otherwise large current would be required (Rajput, 2009).

Huang et al., (2005) considered heat conduction, Joule heat, Thomson heat, convection, and radiation to analyse a TEC and discuss the influence of the Thomson effect on temperature distribution. Results showed that Thomson heat could reduce the effect of Joule heat and enhance the performance of a TEC so that the methods to improve the performance of a TEC were not only using a larger figure of merit, but also considering the influence of the Thomson effect.

Joule effect

When the electric current flows through a conductor, there is a dissipation of electrical energy (Rajput, 2009). According to joule it is related as:

$$Q_J = I^2 R \quad (7)$$

Where, I = Current resistance

R = Electrical resistance

The joulean effect is irreversible in nature

Conduction effect

When the ends of any elements are maintained at differential temperatures, there is heat transfer from the heat end to the cold end (Rajput, 2009) and is related by:

$$Q_{\text{cond}} = U (T_h - T_c) \quad (8)$$

Where, U = Overall conductance

T_h = temperature at hot end, and

T_c = temperature at cold end

If there is only one conductor of cross-sectional area A , conductivity k and length L , the overall conductance U is given by:

$$U = kA/L \quad (9)$$

This effect is irreversible in nature

Cooling and heating due to TE effect is given by Peltier effect:

$$Q_c = \alpha_{ab} I T_c \quad (10)$$

$$Q_h = \alpha_{ab} I T_h \quad (11)$$

For the cold junction:

$$Q_c + \frac{1}{2} I^2 R + U (T_h - T_c) = \alpha_{ab} I T_c \quad (12)$$

For the hot junction:

$$Q_h + U (T_h - T_c) = \alpha_{ab} I T_h + \frac{1}{2} I^2 R \quad (13)$$

Thermoelectric materials and its properties

High-efficiency thermoelectric materials are important for power-generation devices that are designed to convert waste heat into electrical energy. They can also be used in solid-state refrigeration devices. The conversion of waste heat into electrical energy may play an important role in our current challenge to develop alternative energy technologies to reduce our dependence on fossil fuels and reduce greenhouse gas emissions.

A number of different systems of potential TE materials are currently under investigation by various research groups around the world, and many of these materials are discussed in this article. These range from thin film super lattice material to large single crystal or polycrystalline bulk materials, and from semi-conductors and semi-metals to oxide materials.

According to slack, the chemical characteristics of materials must be considered while selecting good thermoelectric



material. For good performance of thermoelectric system, the candidate needs to be narrow band gap semiconductor with high mobility carriers, while the thermal conductivity has to be low. Since thermoelectric performance depends upon seebeck coefficient and electrical conductivity as shown in eqn 14 which further depends upon doping level and chemical composition, has to be optimized for good results. The conductivity of complex materials can often be modified by chemical substitutions. Understanding these various effects, and optimizing strategies can be exceedingly a different problem, because in complex materials there are often many possible degrees of freedom. Therefore, “phonon-glass, electron-crystal” (PGEC) was suggested as best thermoelectric material which exhibit the electrical properties of crystalline material as well as thermal properties of an amorphous and glass like material. This material is typically a narrow band gap semiconductor ($E_g \approx 10 \text{ kB T}$ or $\approx 0.25 \text{ eV}$ at 300K). Also the mobility of carriers must remain high, ($\mu \approx 2000 \text{ cm}^2/\text{Vs}$) while thermal conductivity must be minimized. However, material has always been a design problem due to its structural complexity. The electronegativity difference, $\Delta\chi$ required to maintain a high mobility should be preferably less than 0.5 per bond on average (using Allred scale). The heavy metal or metalloid set (p-band electrons) of the periodic table such as Bi, Sb, Se, Te, Ge, Sn, etc are few examples of structural elements which have small electronegativity differences and compounds formed by these elements are of narrow band gap semiconductors.

Recent advancement in thermoelectric materials

Complex chalcogenides

One of the important reason which limits the application of thermoelectric technology at low temperature is lack of mechanism that can provide high thermo-power at low temperatures. To combat with this problem, several promising materials including phonon drag, heavy fermion materials, kondo systems and materials which exhibit face transition as well as quasi one dimensional materials have been developed. Results on a new system grown by the Kanatzidis at Michigan State University exhibit very promising low temperature thermoelectric properties and have yielded some of the highest ZT values achieved below $T \approx 250 \text{ K}$ (Chung et al., 2000). These materials are CsBi₄Te₆ based materials with $ZT \approx 0.8$ at $T \approx 220 \text{ K}$. Another family of low dimensional semi-conductors or semimetals, called pentatellurides (HfTe₅ and ZrTe₅), also have been proven as potential low temperature thermoelectric materials for exhibiting thermo power at relatively broader range at low temperature i.e. $T < 250 \text{ K}$ (Littleton et al., 2001). Another group f complex chalcogenides that are of interest are the Tl₂SnTe₅ and Tl₂GeTe₅ systems that were identified as potential thermoelectric materials by Sharp et al., (1999). Although these materials exhibit very low total thermal conductivity ($\approx 0.5 \text{ W/m-K}$), $ZT \approx 0.6$ at $T \approx 300 \text{ K}$, its use is limited due to extreme toxicity of oxides of Tl, however compounds or derivatives without Tl are other possible alternatives.

Thermoelectric Oxide Materials (NaxCo2O4)

The new developed air and water-stable refractory metal oxides as thermoelectric materials has numerous advantages over existing high temperature TE materials, especially for power generation applications. These are easier to prepare and more rugged than conventional materials and are expected to have a wider range of operating environments. According to Terasaki et al., (1997), the NaxCo₂O₄ class compounds has displayed surprisingly very effective thermoelectric properties.

Zinc Antimonides (β -Zn₄Sb₃)

The Jet Propulsion Laboratory re-investigated β -Zn₄Sb₃ material for its thermoelectric applications and found that it is temperature independent between 300 K and 650 K (Caillet et al., 1997). This compound forms a full range of solid solution with the isostructural compound Cd₄Sb₃ and further to obtain reduced lattice thermal conductivity, mixed crystals for Zn_{4-x}Cd_xSb₃ can be obtained, but these crystals appear to be even less temperature stable than β -Zn₄Sb₃ itself. Optimization of these materials is difficult due its restricted compositional variations possible.

Half-Heusler Alloys

Another group of potential thermoelectric materials are the half-Heusler alloys (Poon, 2000). These are intermetallic compounds with general formula MNiSn where M is a group 4 transition metal ($M = \text{Zr, Hf, Ti}$). The high negative thermo power ($-40 \mu\text{VK}^{-1}$) and low electrical resistivity values (01-8 m Ω) of half-heulser alloys make it a potential thermoelectric material. Effect of Sb doping on the Sn site (TiNiSn_{1-x}Sb_x) has also been investigated which resulted in a relatively large power factor of 0.2-1.0 W/mK at room temperature for small concentration of Sb. These values are comparable to that of Bi₂Te₃ alloys. At high temperature ($\approx 700 \text{ K}$), the power factor is much larger making these materials very attractive for potential power generation considerations. Unfortunately, thermal conductivity is relativity high so the efforts are being made to reduce the thermal conductivity while maintaining the high power factor.

Skutterudites

Skutterudites are the next class of materials that received a lot of attention due to its ability to greatly vary lattice thermal conductivity. These materials are members of open structure or cage-like family of compounds. When atoms are filled into the interstitial voids or cages of these materials, the lattice thermal conductivity can be substantially reduced compared with that of



unfilled skutterudites. These compounds exhibit electrical properties ranging from that of low-temperature superconductors to narrow gap semiconductors (Nolas et al., 1999).

Clathrates

Another group of TE materials that gain interest are clathrates (Sr8Ga16Ge30) (Nolas et al., 2001, Nolas et al., 2000). Like skutterudites, these materials are also cage-like structures that allows “ratling” mechanism to alter the thermal conductivity.

Thin film materials

Thin film materials offer exciting applications in the field of small scale electronics and opto-electronics where small heat loads or low level of power generation are required. The “nano-engineered material” is an example of thin film material which would offer high coefficient of performance in solid state refrigeration as well as allow high cooling power density. Besides these materials are extremely fast acting, as compared to existing TE materials.

Although large extent of TE materials have been investigated, there is certainly much more work is required for the development of high efficiency thermoelectric materials and devices which could address large scale refrigeration (home refrigerator) or power generation (automotive or industrial) requirements.

Design of a thermoelectric device

Composition of thermoelectric module

Semiconductors are the most important part of the TE module. More than one pair of semiconductors are usually assembled together to form a TE Device (module). Semiconductors are called a thermo-element in each module, and a pair of Thermo elements is called a thermocouple. A typical TE device is composed of two ceramic substrates that serve as a foundation and electrical insulation for P-type and N-type Bismuth Telluride thermo elements that are connected electrically in series and thermally in parallel between the ceramics (Fig.4). The specifications of the TE devices may vary with the application of the device and the variation is from 3 mm square by 4 mm thick to 60 mm square by 5 mm thick, with the maximum heat-pumping rate ranging from 1 to 125 W. The maximum temperature difference of 700C between the hot and cold side can be acquired. The number of thermocouples in the device may vary from 3 to 127. For large temperature differentials multistage (cascade) series TE devices are designed and they meet requirements up to 1300C. The lowest practically achievable temperature is about 1000C (Riffat and Ma, 2003).

The TE chilling machine consists of a TE cooling module. The cold side of the module is set inside the chiller and the hot side is set outside whereas in case of heating applications, hot side is set inside the heater and cold side is set outside. A fin type heat exchanger is tied with the hot side in order to release heat more efficiently. In the module, the electric current flows from the N-type element to the P-type element at the cold junction, whilst the current flows from the P-type element to the N-type element at the hot junction, the heat goes to the outside at the same time.

Heat exchangers and cooling fans are used to improve the efficiency of the module. The finned surface (i.e. heat sink) was used to enhance and increase the rate of heat transfer from the hot surface of the TE module so the heat will be discarded outside of the refrigerator. In order to maintain the efficiency of the thermal module, cooling fan was used to reject the heat from hot side of the module to the ambient surroundings (Abdul wahab et al., 2009).

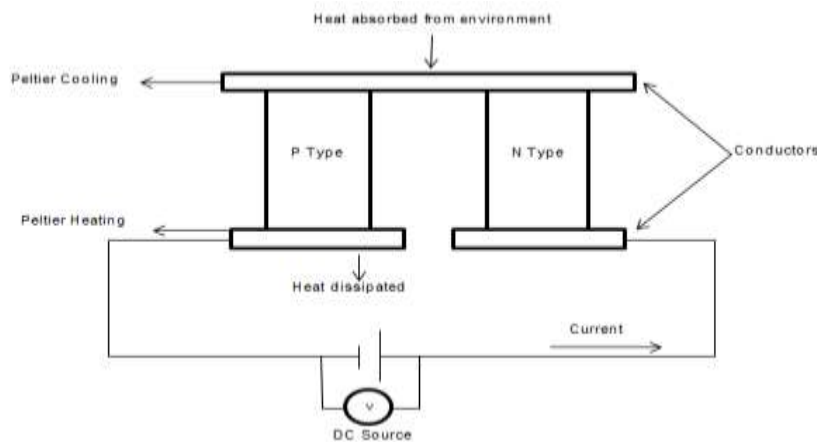


Figure 4 Schematic diagram of a thermoelectric module depicting Peltier cooling and heating

Possible power sources

In designing a portable TE refrigeration system driven by solar cells the important aspects to be considered are weight and



cost of the unit. The objective is to keep the system light, for easy handling and less expensive, so that it can be affordable for larger strata. The two most necessary components to achieve TE refrigeration are TE cooling module and electric power supply. The other two components viz. solar cells and storage battery backup can be adjusted as they make the apparatus bulky and can also contribute in the increased cost of the whole setup. The approach of power source can be kept flexible and to meet the requirements the following operation mode should be one of good choices to be considered. Here, daytime use and night time use are treated in different ways: if the requirement is only for daytime use the system without a storage battery mainly solar cells plus TE refrigerator, is just apt and meets the requirement. For night time use the system without solar cells, i.e. solar battery, rectifier and TE refrigerator, is only used at night when the owner is usually at rest and AC electric power is available. The advantage is that the amount of solar cells required is minimal and the weight consideration is also relatively less. Only on overcast or rainy days can the storage battery be considered for outdoor use, and the battery could still be charged by AC rectifier beforehand (Dai et al, 2003).

The solar cell-driven TE coolers have various applications such as (Hara et al. 1998) installed it at the front of a headgear to cool the forehead for outside personal cooling device, and Mei et al. (1993) studied a solar-assisted automobile TE air conditioner. Lately, Bansal and Martin (2000) compared the relative performance among the vapour-compression refrigeration system, the solar cell-driven TE cooler, and the absorption refrigerators. Recently, global increasing demand for air conditioning for buildings led to production of more electricity and consequently more release of CO₂ all over the world. A recent report of Xi et al. (2007) indicated that the energy consumption for air-conditioning systems is estimated to 45% of the whole households and commercial buildings. It is recognized that the TE coolers and the solar cells combined system can be used for the air conditioning applications, and the technology actually meets the demand for energy conservation and environment protection (Chein and Chen, 2005).

The studies conducted on solar cell driven TE coolers showed that cooling the solar cell is an important factor to improve the performance of our TE module because it can easily raise the output power of solar cell. It is found that the steady state temperature of the solar cell is decreased by increasing the flow rate of the cooling water. Furthermore the solar cell leads to waste heat generation and therefore to enhance the efficiency TE cooler can also be utilized for water heating. In this way, the demands for both air conditioning as well as water heating can be accomplished without consuming any electricity provided from the external source (Cheng et al., 2011).

Figure of Merit and Coefficient of Performance

The figure of merit, ZT determines the potential of a TE material and its application:

$$ZT = \alpha^2 \sigma T / \kappa = \alpha^2 T / \rho \kappa \quad (14)$$

Where, α = Seebeck coefficient,

σ = electrical conductivity,

ρ = electrical resistivity,

κ = Total thermal conductivity ($\kappa = \kappa_L + \kappa_E$, the lattice and electronic contributions, respectively).

The TE material is found to be better with the value of $ZT \approx 1$. The value of ZT can be increased either by decreasing the value of κ_L or by increasing the value of α or σ . However, σ is tied to the electronic thermal conductivity, κ_E , through the Wiedemann–Franz relationship, and the ratio is essentially constant at a given temperature. The objective of the on-going research efforts is to find new materials that can raise the efficiency of the current flow or be capable of operating at a wider range of temperatures, especially at lower temperatures ($T \leq 250$ K) and higher temperatures ($T \geq 400$ K). Over the past 30 years, alloys based on the Bi₂Te₃ system [(Bi_{1-x}Sb_x)₂(Te_{1-x}Se_x)₃] and the Si_{1-y}Gey system have been studied extensively and optimization for TE refrigeration applications has been done. Extensive investigation on traditional TE materials has been done and there is very little scope for improvement in those materials. However, new classes of compounds are investigated and nanostructures of TE materials are analyzed for further improvement (Tritt and Subramaniam, 2006).

TE performance depends on a) temperature of the cold and hot sides b) thermal and electrical conductivities of the device materials c) contact resistance between the TE device and heat source/heat sink d) thermal resistance of the heat sink.

Usually, for single-stage TE module, the maximum COP under the optimum current (I_ϕ) is determined by the temperature of the hot side and cold side as well as the figure of merit of TE material:

$$I_\phi = \frac{(\alpha_p - \alpha_n)(T_h - T_c)}{R[(1 + ZT_m)^{1/2} - 1]} \quad (15)$$

The equation for COP is as follows (Atik and Yildiz, 2012):



$$\text{COP} = \frac{Q_c}{P} = \frac{T_1[(1+ZT_m)^{1/2} - T_2/T_1]}{(T_2 - T_1)[(1+ZT_m)^{1/2} + 1]} \quad (16)$$

Where, Q_c = Cooling power absorbed at the TE cooler cold side

P = Electrical power generated

$T_m = (T_h + T_c)/2$

A simplified way of determining the voltage and the heat load are given by:

$$Q_c = (\alpha_p - \alpha_n)IT_c - K(T_h - T_c) - 1/2I^2R \quad (17)$$

$$V = 2N \left[\alpha(T_h - T_c) \frac{IRL}{A} \right] \quad (18)$$

Where V is the voltage and Q_c is the heat load, N is the number of couples, and L is the element height.

A typical AC unit has a COP ~ 3. TE coolers usually have COP < 1 and 0.4 to 0.7 is a typical range.

For a fixed hot side temperature and the value of the figure of merit, the maximum COP typically decreases with a decrease in the cold side temperature, i.e. an increase in the temperature difference between the hot and cold side. As it is known, multistage modules are often used for extending operating temperature range of the TE cooling. However, some research results have indicated multistage modules may be used to improve the COP of TEC (Anatychuk et al., 1996; Lindler, 1998; Chen et al., 2002). Therefore, the application of multistage TE modules can be developed as another approach to improve the COP of TE modules (Yu and Wang, 2009).

TE devices are solid state devices. They have several advantages over the other competitive refrigeration techniques as follows: (Karimi et al., 2011; Yu and Wang, 2009; Chen et al., 2012; Liu and Wen, 2011).

- a) The energy conversion by thermoelectricity is reliable.
- b) As there are no moving or mechanical parts there is practically no noise or vibration in the setup.
- c) The portability of a TE chiller would be more as it is relatively smaller in size and lesser in weight as compared to other refrigeration apparatuses such as vapour compression apparatus.
- d) They pose no threat to the environment as no refrigerant gas such as CFC etc. is used during the refrigeration. Because of the absence of any refrigerant gas the problem of replenishment also does not arise.
- e) The operational life of a TE module is around 100,000 h of steady state operation.
- f) The TE device can be used both for cooling as well as heating. By changing the polarity of the DC power supply the heating cycle can be reversed and the heat is pumped in the other direction.
- g) The TE refrigeration is also a precise technology as it can maintain a temperature control to 0.1°C.
- h) Operating in extreme environment is a big limitation for conventional refrigeration. The TE devices on the other hand can operate in harsh environment and are relatively insensitive to the external heat as compared to conventional refrigeration.
- i) TE devices are not position-dependent.
- j) It is the most direct utilization of electricity for heat removal. Because of its direct conversion between electrical and thermal energies, thermal management is more efficient than other electronic cooling devices.
- k) In addition, it can be manufactured from millimeter to micrometer scales or even made inside the electronic component, so that this solves the problem of limited installation space inside electric equipment in practical application.

The three main categories in which these applications can be segmented according to their functioning are namely cooling units, power generation systems and thermal energy sensors.

TE devices have certain disadvantages and inconvenience too as discussed further. It has lesser efficiency as compared to the vapour compression system i.e. its COP is lower than as compared to other mechanical cooling devices and it gets lower in wide temperature range applications (Gao and Rowe, 2006; Atik and Yildiz, 2012; Yu and Wang, 2009). One approach to improve the COP of TE modules is to develop new materials. Over the past years, the research on improving the performance of TE materials has been developed continuously and progress has been made (Riffat and Ma, 2003). In addition to the improvement of the TE material,



efforts have also been made to increase the TEC performance by improving the module design, fabrication and optimization of the TE cooling system (Yamanashi, 1996; Huang et al., 2000; Omer et al., 2001; Xuan, 2003; Chein and Chen, 2005; Chen et al., 2005; Cheng and Shih, 2006; Lineykin and Ben-Yaakov, 2007; Yu and Wang, 2009). The cost of these systems is not viable and is more than other refrigeration systems (Gao and Rowe, 2006; Atik and Yildiz, 2012).

Common problems related to Te refrigeration

Maintaining a specific load

The design of heat sink is a critical aspect of a good thermoelectric system. The heat sink must be able to reject heat load from the system. If the heat load is not rejected from the system, the temperature of the entire system will rise and the load temperature will increase. Increasing the current to maintain specific load temperature results in a reduced efficiency. Most thermoelectric companies custom design system depending in the desired application.

Condensation

A common problem with TE cooling is that condensation may occur causing corrosion and eroding the TE's inherent reliability. Condensation occurs when the dew point is reached. The dew point is the temperature to which air must be cooled at constant pressure for the water vapor to start to condense. Condensation occurs because the air loses the ability to carry the water vapor that condenses. As the air temperature decreases its water vapor carrying capacity decreases. Since TE coolers can cool to low and even below ambient temperatures, condensation is a problem. The most common sealant employed is silicon rubber (Nagy, 1997). Research has been performed to determine the most effective sealing agent used to protect the chip from water.

Applications of Te technology

The conventional cooling systems are bulky in nature and cannot be used for new technologies as the primary consideration for any device especially in the household is mainly portability. Hence TEC are gaining popularity as they are light weight and relatively more convenient to use, especially for niche applications. The TE cooling is applied as a cooling solution for heat producing devices to maintain their efficiency and normal operation. A TE cooler conducts the heat from the device and keeps the temperature of the device as close to ambient temperature. These devices also proven to be very beneficial in the cases of lesser cooling requirements such as portable coolers. Other sectors such as military where energy cost is not an issue utilize the TE cooler for cooling purposes. Where larger cooling requirements are concerned the application of TE refrigeration is limited due to a relatively low COP and higher energy requirement and hence higher cost. The COP of a present TE refrigerator is typically (< 0.5) when operating at temperature difference (ΔT) of 200 °C. As the environmental concerns are increasing and so are the energy costs and demands it is predicted that TE coolers and air conditioners will become competitive in world market. Also the environmental treaties have banned chlorofluorocarbons therefore reduced manufacturing costs of TE devices have been opening up new markets. Some of the examples where TE cooling is incorporated are discussed below:

The range of applications for TE effect is wide and need for thermoelectricity is growing with time in every area. In military sector the TE cooler are used for cooling their electronic equipment's, cooled personnel garment, portable refrigerators, cooling infrared sensors and cooling laser diodes. In aerospace also the TE cooler for electronics is a beneficial alternative to conventional cooling systems. There is a wide range of consumer products in the market such as recreational vehicle refrigerators, mobile home refrigerators, car refrigerators, portable picnic coolers, wine coolers, beer keg coolers, water-coolers, motorcycle helmet refrigerators, insulin coolers (portable), residential water coolers/purifiers and beverage can coolers. There is a big scope for convenient cooling solutions in laboratories and scientific equipment's as cooling. Some of the applications include photomultiplier tube housing coolers, laser diode coolers, charge-coupled device cooler, change induced device coolers, integrated circuit coolers, tube coolers, laboratory cold plates, stir coolers, cold chambers, immersion coolers, ice point reference baths, microtome stage cooler and electrophoresis cell coolers. Industry widely uses the TEC for NEMA enclosures, harsh environment protection for critical components, PC computer microprocessors, microprocessor and PCs in numerical control and robotics, stabilizing ink temperature in printers and copiers. A large market will open for the automotive industry. This is because the compatibility of many TE devices with automotive voltage, makes them especially suitable for small cooling jobs in that industry. In restaurants the cream dispensers, whipped cream dispensers, butter dispensers, individual portion dispensers utilize the TE cooling. Other applications such as pharmaceutical refrigerators-portable and stationary, hotel room refrigerators, automobile mini-refrigerators, automobile seat cooler, aircraft drinking water cooler, coach coolers, marine cooler, van coolers and refrigerators, trucks coolers and refrigerators, car air conditioners, DNA cyclers, diagnostic medical equipment, hot/cold therapy pads come under TEC (Riffat and Ma, 2003; Karimi et al., 2011; Chen et al., 2012; Huang et al., 2000; Yu and Wang, 2009). Table 1 lists some typical applications of thermoelectric technology in varied fields.

Table 1 Applications of thermoelectric technology



Sr. No.	Industrial/ Commercial	Medical/ Laboratory	Consumer	Military/ Aerospace
1.	Dew point hygrometers	Temperature controlled therapy pads	Picnic box coolers and heaters	Electronic equipment cooling
2.	Osmometers	Protein coolers	Air conditioned motorcycle helmets	Photo scanning equipment cooling
3.	Electronic enclosure coolers	DNA amplifiers	Small refrigerators	Military avionics
4.	Dehumidifiers	Blood analysers		Infrared detectors
5.	CCD housing and cameras	Constant temperature baths		Black body references
6.	Integrated circuit coolers	Cold chambers		Space telescope cameras
7.	Laser diodes	Water proofing stations		Light wave transmitters
8.	Graphic films			

Source: Soo et al., 1997

Scope of Te cooling in dairy

In almost all developed dairying countries, production of milk is confined to rural areas, while demand is mostly in urban areas. Hence milk has to be collected and transported from production points in the milk shed areas to processing and distribution points in the cities. In milk collection-cum-chilling centres the milk is graded for acceptance/rejection, weighed, sampled for testing, cooled and stored at a low temperature until dispatch to the processing dairy.

Milk already contains some microorganisms when the milking process is done. The number of microorganisms keeps on increasing during the handling of the milk. The ideal temperature range for the growth of the microorganisms is found to be between 200C and 400C. Bacterial growth is invariably accompanied by deterioration in market quality due to development of off-flavors, acidity etc. The various effects caused by bacterial growth, protein decomposition and enzymatic production are souring, gassiness, aroma production, proteolysis, ropiness and sweet curdling (Sukumar de, 2008).

The time taken for transportation of milk to the collection/chilling centres from the household is the most sensitive area for contamination of milk. As discussed above, it leads to degradation of milk as a result of microbial growth (Fig. 5).

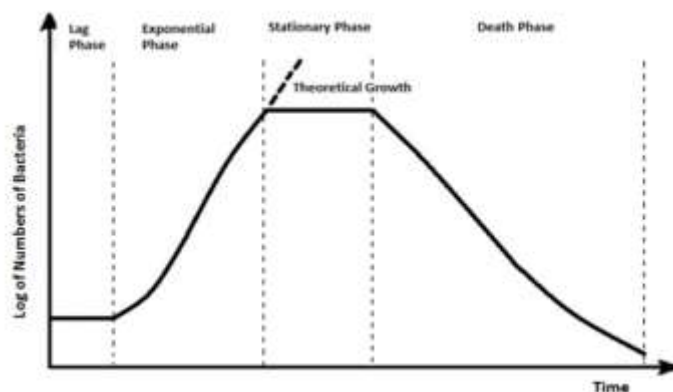


Figure 5 Microbial Growth Curve (Logarithmic Bacterial growth v/s Time) (Anon, 2013)



It is seen from table 1 that 10 °C is a critical temperature for milk. Freshly drawn milk should, therefore, be cooled to 4 °C or below immediately and also held at that temperature till processed.

Gould R E, (1961) designed a small thermoelectric powered wall mounted refrigerator for dairy products. Elfving (1963) invented thermoelectric heat pumps and more particularly to thermoelectric cooled system. Pries A, (1986) provided a compact cooling appliance powered by electricity convenient for use in an automobile and effective to cool beverages in standard beverage containers to a desired low temperature. Hlavacek R A, (1996) devised an individual liquid container used for cooling or keeping milk or coffee cool. Park et al., (2003) designed and patented a cooling and heating apparatus using a thermoelectric module in which the thermoelectric module, a heat emitting member and a heat conducting block are integrated into a single unit, to improve the performance and durability of the thermoelectric module. Qian et al., (2009) invented a yogurt maker which is able to automatically prepare yogurt by distributing transformation culture into milk following the gradual warming, incubation and natural cooling processes; fermentation time is automatically set according to the load production and environment temperature; afterwards, maintain yogurt with cold temperature for extended periods of time. Glaros et al., (2011) devised a compact merchandiser cooler for chilling food and beverage containers. It is customized with branding information related to the food and beverage containers to be chilled within the compact merchandiser cooler. Lu Q, (2012) embodied a TE cooling system for food and beverages.

TE refrigeration is a convenient option to bring down the temperature of the milk to a desirable 4 °C at domestic level, before the milk leaves for collection centres. The bacterial growth factor as seen from the Table 2 can be controlled to 1.05 and hence the degradation of the milk and spoilage can be easily avoided. For the chilling of milk, TE refrigeration is acquired with the help of TE modules which are integrated in the design of the milk collecting utensil. With the help of a battery powered source the chilling of milk can be acquired as soon as the milking process is done. This way the temperature of the milk falls down drastically in a short interval of time, hence avoiding milk deterioration and eliminating the need for bulky piping and mechanical compressors as used in vapor-cycle cooling systems.

Table 2 Bacterial growth factor for milk at different temperature

Milk held for 18 hours at temperature (°C)	Bacterial growth factor*
0	1.00
5	1.05
10	1.80
15	10.00
20	200.00
25	1,20,000.00

Note: *Multiply initial count with this factor to get the final count

Source: (Sukumar de, 2008)

A prototype of TE cooling headgear powered by solar cell was constructed to cool the forehead. Amorphous flexible paper solar cells were mounted on a baseball cap. A TE element is mounted under the root of the brim to cool the forehead by the cold side of the element. A multi-pin fin is then attached at the hot side of the TE element. This headgear can achieve required temperature difference between ambient and cooling temperature (4–5 °C) for thermal comfort (Hara et al., 1998).

A prototype of TE ‘‘cryo-concentration cell’’ is developed for obtaining concentrated orange juice, which use Peltier effect as an alternative to the traditional methods of cryo-concentration using the conventional refrigeration cycles based on gases such as NH₃ (Sanz-Bobi et al., 1996; Riffat and Ma, 2003).

Suppliers of Te modules in India

The detail list of suppliers dealing with thermoelectric modules in India is given in Table 3.

Table 3 Suppliers list of TE modules

Sr. No.	Supplier	Address	Contact Details



1	C S Park	Near Sai Baba Temple, Eastern Street, Door No. 7B-11-23, District West Godavari, Eluru-534001, Andhra Pradesh.	080430-53432
2	Rajguru Electronics	259 Shanti Sadan, 3 rd Floor, Office No. 23, Lamington Road, Mumbai-400004, Maharashtra.	083768-05835
3	Teewave Powertech Pvt. Ltd.	167/ A, I.D.A. Phase II, Cherlapally, Hyderabad-500051, Telangana.	080494-72978 narasimham@teewave.co.in
4	Nippon India	No. 237/8, Solan Link Industrial Estate, Building 2, Link Road, Malad West, Mumbai-400064, Maharashtra.	022-40620000 info@nipponindia.com sales@nipponindia.com
5	Pulse Digital Devices	A-7, G D Plaza Complex, Opposite Autoneeds, Mehrauli Road, Gurgaon-122001, Haryana.	080430-43355
6	Macnet Technology	No. 18, Shree Ganesh Bhuvan, Kalpana Building, Floor No. 357, Lamington Road, Grant Road, Mumbai-400007, Maharashtra.	083778-06754 info@vegarobokit.com
7	Salecha Electronics, Inc.	212-A, Bajaj House, 97, Nehru Place, Delhi-110019.	098710-66440 sales@salechagroup.com

Conclusion

TE technology has found application in wide variety of areas since the last 40 years. The TE devices can act as coolers, heat pumps, power generators, or thermal energy sensors and are used in almost all the fields such as military, aerospace, instrument, biology, medicine, industrial or commercial products. The major challenge faced in TE cooling is lower COP especially in large capacity systems. However, as the energy costs are elevating and environmental regulations regarding the manufacture and release of CFCs have become more firm with time, the scope of TE effect has revived, especially in the developing countries or the third world where the energy is not surplus. Milk being a perishable commodity has a wide scope of TE effect application. TE chilling of milk can be done at the farm level to inhibit any enzymatic or microbial change in quality of the milk. The TEC can reduce the temperature of the milk to 40C to attain stability in terms of bacterial count. Research in the field of thermoelectricity and experimentation with different materials is required to improve the COP of the TE cooler. Advancements have taken place and various prototypes in different fields utilizing thermoelectricity have been made besides other conventional refrigeration applications. In the coming years thermoelectricity has a lot of potential to create energy saving and effective solutions for the industry and commercially as well.

NOMENCLATURE

The following abbreviations are used:

TE = Thermoelectric

TEC = Thermoelectric cooler

TER = Thermoelectric refrigeration



COP = Coefficient of Performance

ZT = Figure of merit

CFC = Chlorofluorocarbon

DC = Direct current

AC = Alternating current

NH₃ = Ammonia

Bi₂Te₃ = Bismuth Telluride

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