INCREASING THE EFFICIENCY OF CRYOGENIC AUTOMOBILE POWER SYSTEMS USING THERMOELECTRIC GENERATORS

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New non-polluting cryogenic vehicles operating on liquid nitrogen have been developed in the US and in Ukraine. Recent discovery of the low-temperature thermoelectric material $CsBi_4Te_6$ motivates evaluation of thermoelectric generators for automotive cryogenic power systems. By recovering some of the cryogenic fuel's latent heat of liquefaction by conduction through storage-tank-embedded thermoelectric elements, a supply of energy can be created to power a vehicle's on-board electrical systems.

The maximum energy conversion efficiency of a proposed cryogenic thermoelectric generator assembly embedded within a fuel storage tank approaches 15 %. To determine power production potential per unit area of storage tank, heat flow through the thermoelectric generator was calculated using a one-dimensional thermal model. We determined that thermoelectric generators are viable for power generation in cryogenic automobiles, and these generators can increase a vehicle's total performance, making the thermoelectric generators a worthwhile addition.

1. INTRODUCTION

In the last twelve years, new non-polluting cryogenic vehicles operating on liquid nitrogen (LN2), which convert ambient thermal energy to mechanical work, were developed in the US at the University of North Texas (UNT) (Plummer *et al.*, 1999; Plummer *et al.*, 2000) and the University of Washington (UW) (Williams *et al.*, 1997; Knowlen *et al.*, 1999) and in Ukraine at Kharkov National Automobile and Highway University (KNAHU) (Bondarenko *et al.*, 2004a; Turenko *et al.*, 2005). Some of these vehicles are shown in Figure. 1.

A motivation for developing such vehicles is to enable an environmentally friendly means of transportation that does not use batteries or hydrocarbon fuel. The cryogenic propulsion systems in these vehicles consist of a pneumatic engine, an air-to-gaseous-nitrogen heat exchanger, and a cryogenic tank. The function of the tank is to provide both LN2 fuel storage and primary evaporation. The maximum specific energy of nitrogen as a working fluid is estimated at 770 kJ/kg for a temperature difference between ambient air at 300 K and LN2 at 77 K (Plummer *et al.*, 1999). Using free thermal energy from the environment, the LN2 is heated to release its stored energy and produce compressed gas to run the pneumatic engine. An advantage of LN2 as an automobile fuel is the availability of abundant gaseous nitrogen in the atmosphere. When consumed for transportation, LN2 is environmentally benign. Like hydrogen fuel, LN2 is an energy carrier, not a source. So, energy must be invested to liquefy atmospheric nitrogen. However, this energy can be produced in a large stationary power plant with efficiency far exceeding internal combustion engines, and the effluent can be scrubbed or captured to mitigate pollution and greenhouse gasses. Moreover, the energy for liquefaction can also be obtained from alternative and non-polluting sources, such as solar and wind, which provide the opportunity to create self-contained "green" regions that produce and utilize LN2 for pollution-free transport applications.

The critical constraint for cryogenic vehicles is fuel economy, which must be optimized to minimize the volume of LN2 onboard. Special attention is given to achieving maximum efficiency in all parts of the cryogenic power system (Bogomolov *et al.*, 2004). The typical function of a LN2 Dewar is prolonged storage of cryogenic liquid by minimizing heat leak paths from the ambient into the liquid. For cryogenic vehicles, the storage tank serves two functions: 1) prolonged fuel storage when the vehicle is not in use (like a Dewar) and 2) rapid evaporation of the liquid to produce high-pressure gaseous nitrogen to drive the vehicle when it is in use (Bondarenko *et al.*, 2004b). From this later function arises the classical thermodynamic arrangement of heat moving along a temperature gradient from hot to cold; this configuration can be adapted for supplementary energy generation.

Thermoelectric generators topping organic working fluid Rankine cycles will add to the overall energy of the system and thereby raise cycle efficiency (Miller *et al.* 2009). The potential for automotive high temperature waste heat recovery using thermoelectric generators in diesel vehicles has been described (Crane, 2003). Here, we evaluate placing a thermoelectric generator within the wall of a LN2 storage tank on a cryogenic vehicle to recover part of the nitrogen's latent heat of liquefaction as electricity. As we will demonstrate, this configuration presents a sufficient temperature gradient for useful thermoelectric generator applications. The recent creation of thermoelectric materials with high figure of merit at cryogenic temperatures further motivates analysis of this energy recovery technology for practical cryogenic automobiles. Moreover, the presence of cryogenic liquid in a storage tank onboard the vehicle provides new synergistic opportunities. For example, generated electrical energy can be stored in the magnetic field of a high-temperature superconductor submerged in the tank, instead of as chemical energy stored in a battery as in conventional automobiles.

2. THEORY AND BACKGROUND

The thermoelectric material figure of merit, Z [1/K], is defined as follows (Rowe, 1999):

$$Z = \frac{\alpha^2}{k\,\rho}, \tag{1}$$

where α is the Seebeck coefficient [V/K], k is the thermal conductivity of the material [W/m K], and ρ is the electrical resistivity of the material [Ohm·m].

Both p- and n-type semiconductor materials are used in making thermoelectric generators, and the properties of each are sometimes sufficiently different to warrant considering each material in estimating an overall figure of merit using the following equation (Rowe, 1999):

$$Z = \frac{\left(\alpha_p - \alpha_n\right)^2}{\left[(k_p\,\rho_p)^{\frac{1}{2}} + (k_n\,\rho_n)^{\frac{1}{2}}\right]^2}, \tag{2}$$

where the subscripts p and n correspond to the p-type and n-type materials respectively.

These parameters arise from the geometry of p- and n-type legs of thermoelectric generators arranged in series, as shown in Figure 2. The efficiency of a thermoelectric generator is given by (Rowe, 1999)

$$\eta = \frac{(T_h - T_c)}{T_h}\frac{(M-1)}{\left(M + \frac{T_c}{T_h}\right)}, \tag{3}$$

where the M factor is obtained by calculating

$$M = (1 + ZT_{mean})^{\frac{1}{2}}, \tag{4}$$

and T_{mean} is the mean temperature of the material, derived from temperatures T_h and T_c of hot and cold ends of the thermoelectric material respectively.

A candidate thermoelectric material with high figure of merit at cryogenic temperatures has been identified: $CsBi_4Te_6$ (Chung *et al.*, 2000; Chung *et al.*, 2004; Lykke *et al.*, 2006). For our analysis, this material was selected on the basis of producing the most energy per unit mass of cryogen vaporized. The $CsBi_4Te_6$ compound is a very recent discovery and can achieve as much as a 40 % improvement in energy conversion efficiency over more traditional Bismuth Telluride compounds

(Chung *et al.*, 2004; Kulbachinskii *et al.*, 2001), which were previously the best cryogenic thermoelectric materials available. The temperature-dependent figures of merit for both materials are shown in Figure 3 (Chung *et al.*, 2004).

For estimation of the maximum performance of a thermoelectric generator placed within the walls of an automotive cryogenic tank, we used 300 K for T_h and 80 K for T_c. We also used a high value of ZT for $CsBi_4Te_6$, 0.75, which corresponds to the assembly's mean temperature value, 190 K. For these conditions, we calculate a maximum energy conversion efficiency of 14.9%. This value is the percentage of heat flowing into the generator's hot surface which gets converted to electricity. To estimate the maximum electricity generation, heat flow through the thermoelectric element was next calculated.

3. METHOD FOR ESTIMATING HEAT FLOW

The proposed thermoelectric assembly schematic, shown in Figure 2, provides a basis for estimating heat transfer through the generator. The thermoelectric generator consists of two branches, one n-type and one p-type, which are selected to be 3 mm in length. Manufacturing limitations on conventional thermoelectric generators prevent the entire space from being filled with generator material, and a packing fraction (PF) of 0.4 to 0.6 is typical. We use PF = 0.5 for heat transfer calculations. The remaining open space is under vacuum, as in a Dewar, to restrict undesirable heat transfer around the thermoelectric generator. Heat transfer though this void space occurs by radiation, and we estimate its magnitude at less than 0.2% of the conduction through the thermoelectric legs. So, radiation is ignored.

The legs of thermoelectric material are sandwiched within two thin copper layers, which provide electrical contact. Electrical insulation between the copper and cryogenic tank walls is provided by layers of Polytetrafluoroethylene (PTFE), a material chosen for its mechanical, electrical, and thermal stability from ambient to cryogenic temperatures. PTFE lines the inner and outer walls of the cryogenic storage tank. The inner tank wall contacts stored LN2 while the outer tank wall contacts the ambient environment.

A one-dimensional heat transfer model was applied to the thermoelectric generator assembly to estimate maximum heat flux for a set of material properties and realistic assembly dimensions presented in Table 1. Cryogenic tank wall thicknesses were selected to withstand an internal pressure up to 3.5 MPa (500 psi). One-dimensional Cartesian heat transfer was assumed because the tank radius is large enough to neglect surface curvature local to the thermoelectric assembly.

For the cryogenic tank inner wall, which is in direct contact with liquid nitrogen, heat transfer to the liquid is assumed to occur via nucleate boiling. This assumption is justified because the calculated burn-out heat flux is about 135 times greater than the heat flux through the inner evaporator wall, and this wall is always at similar temperature to the liquid. The convective heat transfer coefficient is estimated from classic nucleate pool boiling correlation (Rosenow, 1952) on an upward-facing heated plate,

$$h_{tank} = \frac{k_l\, Ja^2}{C_{nb}^3 Pr_l^m \left[\frac{\sigma}{(\rho_l - \rho_v)g}\right]^{\frac{1}{2}}}, \tag{5}$$

where k_l, Ja, Pr, σ are respectively the liquid's thermal conductivity, Jackob number, Prandlt number, and surface tension; ρ_l and ρ_v are respectively the liquid and vapor densities; and g is the gravitational constant. The coefficient C_{nb} arises from experimental data and C_{nb} = 0.004 is suggested (Mirza, 1990) as value at the top of the range for smooth surfaces and the bottom of the range for rough surfaces. The exponent m also normally arises from experimental data, but an appropriate value could not be found in the literature for boiling nitrogen. Experimentally correlated m values range from 2 to 4.1 (Mills, 1999a). We therefore select m = 3, which is in the center of the range of available values for other boiling liquids. The approach gives a convective heat transfer coefficient on the inner cryogenic tank wall of 4890 W/(m^{2}K), which compares favorably to 8520 W/(m^{2}K), a representative heat transfer coefficient calculated for boiling water at ambient pressure (Holman, 1976).

To estimate the natural convection heat transfer coefficient between the cryogenic tank's outside surface and ambient, a shape- and size-independent correlation (Mills, 1999a) for a cooled plate facing downward is used,

$$h_{ambient} = 0.14 \left(\frac{\rho_{\mathrm{air}}\, \Delta\rho\, C_{p,air}\, g}{\mu_{\mathrm{air}}} \right)^{\frac{1}{3}} k_{air}^{\frac{2}{3}}, \tag{6}$$

where ρ_{air}, $C_{p,air}$, μ_{air}, and k_{air} are the density, specific heat, viscosity, and thermal conductivity respectively of air evaluated at ambient conditions (300 K and 1 atm), and $\Delta\rho$ is the air density difference between ambient and the temperature of the tank's outside surface. Importantly, this approach assumes 1) natural convection only with no forced convection, in other word the tank and car are not moving; 2) no liquid condensate or ice build-up on the tank's outer surface; 3) the tank is elevated far enough off the ground that no obstructions interfere with the convection process; and 4) radiation heat transfer between the tank surface and the ground is negligible. Forced convection and radiation to the ground would tend to increase $h_{ambient}$ while convection obstructions and ice build-up would tend to lower it. Equation 6 gives a convective heat transfer coefficient on the outer cryogenic tank wall of 9.4 W/(m^{2}K), which is within the generally accepted range of 3 – 25 W/(m^{2}K) typical for this process (Mills, 1999b).

4. RESULTS AND DISCUSSION

Table 2 gives thermal resistances for each element within the thermoelectric generator assembly calculated in the arrangement proposed. The greatest resistances to heat transfer occur at the outer wall, within the layers of PTFE insulation, and across the thermoelectric generator. Resistances in the metal layers are so comparatively small that they can be neglected.

The calculated energy conversion efficiency is 14.9% and the heat flux entering the hot side of the thermoelectric generator is 1477 W/m^2. Therefore, the electrical energy generated per square meter of cryogenic storage tank is 220 W/m^2. The voltage/current balance can be adjusted, depending on the needs of the electrical system, by wiring multiple thermoelectric generator couples in parallel (to increase voltage) or in series (to increase current). Since heat absorption from the environment will take place only where the liquid is available for evaporation, it is not economical to line the entire cryogenic storage tank with thermoelectric generators. Instead, the generators should be placed at the bottom of the tank where gravity ensures liquid will always be present provided some fuel remains. Dividing heat flux by thermoelectric length gives a volume-specific power of 73 kW/m^3, and dividing this power by the density of $CsBi_4Te_6$ (7088 kg/m^3 per Chung *et al.*, 2004) gives a mass-specific power of 10.34 W/kg.

This performance analysis is optimistic because it fixes the temperatures on the hot and cold sides of the thermoelectric material at 300 K and 80 K respectively. In reality, these temperatures will each adjust, as governed by the thermal circuit made up of the thermoelectric assembly, to become closer to the mean assembly temperature. The corresponding reduction in temperature gradient will drop the thermoelectric generator efficiency. The constrained temperature model used in these calculations exaggerates the benefit of low PF and short thermoelectric generators. By reducing these two geometric parameters for this model, the total mass of thermoelectric assemblies in the wall of the cryogenic tank drops, but efficiency is unaffected. Moreover, by reducing the generator length (thereby reducing the thermal resistance presented by the thermoelectric material), more heat flux is allowed through the generator, which appears to increase the total electrical work output because efficiency is unaffected using the fixed temperature model. In reality, reducing the thermoelectric generator length would also reduce the resistance to heat conduction through the thermoelectric generator assembly, which would decrease the temperature gradient supported by the generator. Reduced temperature gradient across the thermoelectric generator drops its efficiency. We therefore expect these competing effects to yield an optimization problem resulting in calculable thermoelectric generator lengths that give maximum power point, maximum volume-specific power, and maximum mass-specific power (but not necessarily at the same length).

While the development of low-temperature thermoelectrics embedded in storage tank walls will lead to increased total efficiency of power system for cryogenic vehicles, the necessary presence of LN2 fuel motivates further areas of study. For example, generator performance could be further enhanced by judicious application of permanent or induced magnetic fields to capitalize on the Ettinghausen effect (Rowe, 1995). Also, it is well-known that thermoelectric generators produce high electric currents, which can be harnessed for energy storage in superconducting magnetic energy storage (SMES) systems. SMES based on high-temperature superconductors could be kept at operating temperatures via immersion in the cryogenic fuel tank. These systems possess sufficient specific power and might be used on hybrid-electric cryogenic vehicles for propulsion (Bogomolov *et al.*, 2003; Kudryavtsev *et al.*, 2002).

5. CONCLUSIONS

Due to the appearance of a new thermoelectric compound $CsBi_4Te_6$, which is effective at cryogenic temperatures, efficiency improvement of LN2 evaporators for cryogenic automobiles can be achieved. By lining the vehicle's cryogenic storage tank with thermoelectric generators, up to 14.9% of the heat flux necessary for fuel evaporation that was simply lost before can be directly converted to useful energy to power the automobile's electrical systems. Using published parameters for $CsBi_4Te_6$ and a one-dimensional heat transfer model for a practical thermoelectric generator assembly, a volume-specific power of 73 kW/m^3 and a mass-specific power of 10.34 W/kg were calculated for cryogenic vehicle applications.

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Figure 1. Experimental Cryogenic Vehicles Operating on LN2: UNT (left) and KNAHU (right).

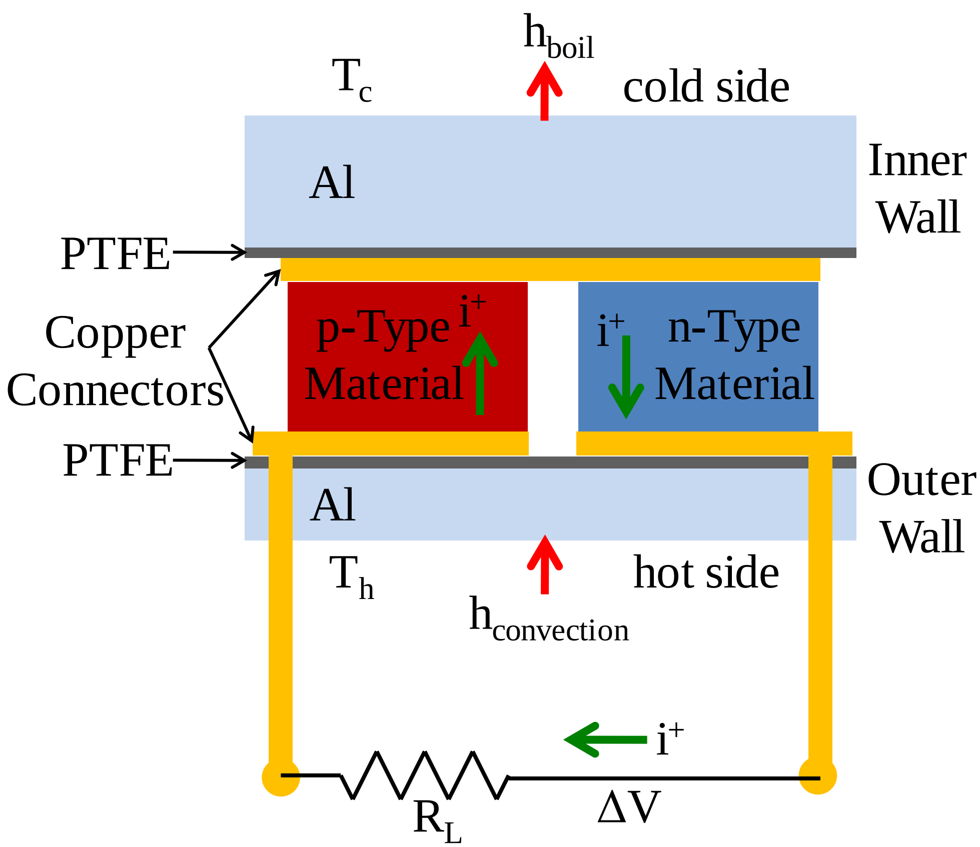

Figure 2. Basic Elements of the Proposed Thermoelectric Generator Assembly

M. J. Traum, I. N. Kudryavtsev, M. C. Plummer, "Increasing the Efficiency of Cryogenic Automobile Power Systems Using Thermoelectric Generators," *Proceedings of the Conference on Physical and Technical Problems in Energetics and Their Solutions*, V. N. Karazin Kharkiv National University, Kharkiv, Ukraine, November 15 – 16, 2011, pp. 33-37.

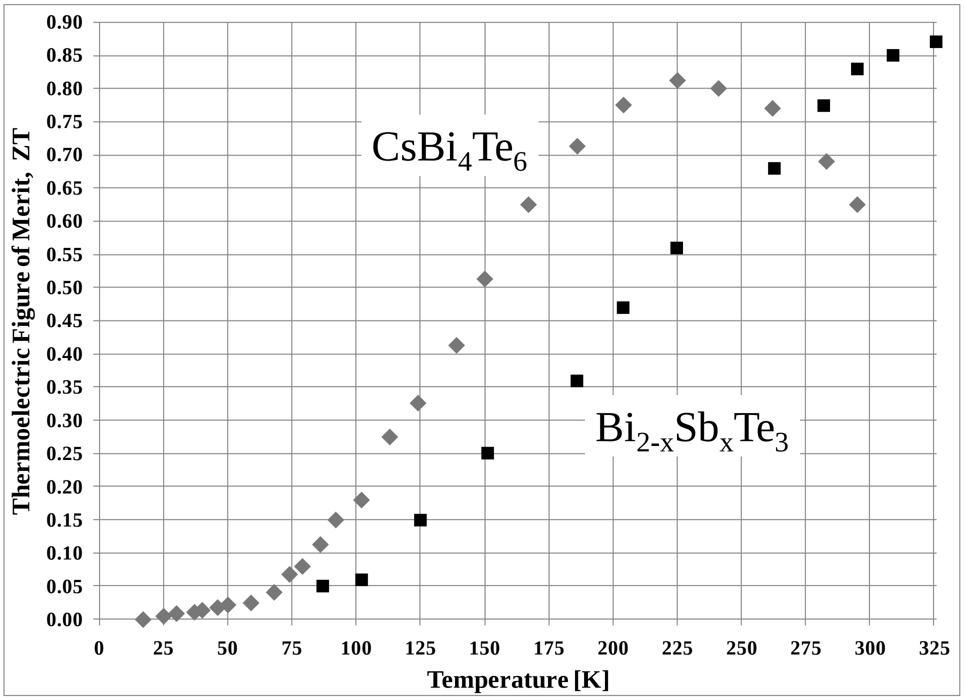

Figure 3. ZT Values of $CsBi_4Te_6$ and $Bi_{2-x}Sb_xTe_3$ (Chung *et al*., 2004)

Table 1: Properties of Component Materials
(Cheng *et al*., 2004; Lide, 2006; Medvedev *et al*., 1987

Material	Thickness	Thermal Conductivity
Units	**mm**	**W/(m K)**
Aluminum		
Inside (80 K)	6	432
Outside (300 K)	3	237
Copper		
Inside (80 K)	1	557
Outside (300 K)	1	401
Teflon		
Inside (80 K)	5	0.25
Outside (300 K)	5	0.28
$CsBi_4Te_6$	3	1.48

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Table 2: Thermal Resistances of Elements in the Thermoelectric Generator Assembly.

Outer Wall Convection	**Outer Wall Al Conduction**	**Hot Side PTFE Conduction**
[m^2K/W]	**[m^2K/W]**	**[m^2K/W]**
1.07E-01	1.27E-05	1.80E-02
Hot Side Copper Conduction	**Thermoelectric Generator**	**Cold Side Copper Conduction**
[m^2K/W]	**[m^2K/W]**	**[m^2K/W]**
2.49E-06	1.01E-02	1.80E-06
Cold Side PTFE Conduction	**Inner Wall Al Conduction**	**Inner Wall Convection**
[m^2K/W]	**[m^2K/W]**	**[m^2K/W]**
1.99E-02	1.39E-05	2.05E-04

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