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DEVELOPMENT OF A DIRECT EVAPORATOR FOR THE ORGANIC RANKINE CYCLE

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Abstract

Research and development is currently underway to design an Organic Rankine Cycle (ORC) system with the evaporator placed directly in the hot exhaust stream produced by a gas turbine (GT). ORCs can be used to generate electricity from heat that would otherwise be wasted, thus producing carbon-free energy. In conventional ORC configurations, an intermediate oil loop is used to separate the hot gas from the flammable working fluid. The goal of this research effort is to improve cycle efficiency and cost by eliminating the pumps, heat exchangers and all other added cost and complexity of the additional heat transfer loop by developing an evaporator that resides in the waste heat stream. Direct evaporation – although simpler and less expensive to implement than indirect evaporation of the working fluid – has historically been avoided due to a number of technical challenges imposed by the limitations of the working fluid. The high temperature of the hot exhaust gas may cause decomposition of the organic working fluid and safety is a major concern due to the high flammability of some of these working fluids. The research team has addressed these challenges and developed a new direct evaporator design that can reduce the ORC system cost by up to 15%, enabling the rapid adoption of ORCs for waste heat recovery. The ORC system is intended to integrate with the GT either as a retrofit or to be marketed as a single package, thus maintaining the manufacturer's warranty.

Introduction

Waste heat from turbines and engines used in industrial applications along with waste heat from industrial processes are exceptionally abundant sources of energy. If even a fraction of this waste heat could be economically converted to useful electricity, it would have a tangible and very positive impact on the economic health, energy consumption, and carbon emissions in the U.S. manufacturing sector. Land-based gas turbines are used in a broad range of applications to produce both shaft and electrical power. Most commonly known for generating electricity either as peaking units or as base load units, they are also used to directly drive pumps, compressors or other machinery requiring shaft power. Simple cycle gas turbines have the advantage of a short startup time relative to coal-fired and nuclear units, however, they incur a significant penalty on their efficiency. Large frame gas turbines usually are combined with bottoming steam-based Rankine cycles to increase the overall efficiency of the system and thereby improve their cost performance. Small-frame gas turbines with exhaust temperatures around 500°C could in principle benefit from steam bottoming cycles, but rarely use them in practice because of the high capital cost of the steam system. Particularly for base load small frame gas turbines, akin to those used in pipeline applications, an increase in efficiency is highly desirable.

The following sub-sections of this paper describe issues pertinent to the selection of an ORC working fluid, along with thermodynamic and design considerations of the direct evaporator. The FMEA (Failure Modes & Effect Analysis) and HAZOP (Hazards & Operability Analysis) safety studies performed to mitigate risks are described, followed by a discussion of the flammability analysis of the direct evaporator. Due to the proprietary nature of the design, no details will be disclosed relative to the actual working fluid selected or the design details of the direct evaporator. Rather, the methodology used to develop the ORC direct evaporator design will be discussed.

The Organic Rankine Cycle

The ORC is a vapor power cycle that operates using the same principles as the steam Rankine cycle, except that a fluid with a lower boiling point (and higher molecular mass) is used. An organic working fluid is evaporated, instead of boiling water to create steam, to run through a turbine to generate electricity. This enables the operation of the cycle at a much lower temperatures than a steam Rankine cycle. Thus, the ORC can utilize the energy from low temperature waste heat sources to produce electricity.

The Rankine cycle is comprised of four main components: evaporator or boiler, turbine or expander, condenser and pump. Depending on the working fluid, a recuperator may be advantageous, depending on the residual enthalpy of the fluid as it exits the expander. In ORC systems the heat source is coupled to the boiler to evaporate the working fluid before it is expanded in the turbine. ORCs are a viable option to recover the exhaust waste heat, using the ambient air as a heat sink. Typically, the heat of the exhaust stream is transferred indirectly to the ORC by means of an intermediate thermal oil loop. The direct evaporator eliminates the need for an oil loop by transferring heat to the working fluid with just one heat exchanger unit placed directly in the exhaust gas stream. Figure 1 compares the indirect vs. direct evaporation arrangement.

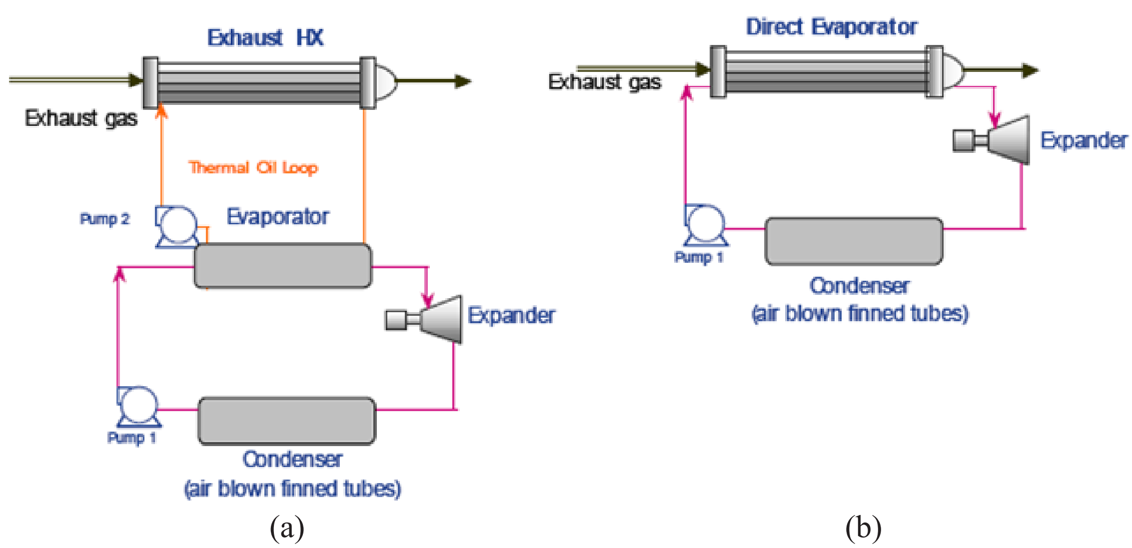

Figure 1. ORC with: (a) Indirect evaporation vs. (b) Direct evaporation.

The efficiency of an ORC depends both on the initial temperature of the waste heat and the level of irreversibility introduced as that heat is transferred to the cycle fluid, then from the cycle fluid to the sink. Figure 2 compares the maximum attainable Carnot efficiency with that of an endoreversible process. The endoreversible process is a much more accurate measure of heat engine efficiency in that the two processes of heat transfer are *not* treated as reversible [1]. An ambient air temperature of 18°C is used in the calculation. The Turbine Exhaust Gas (TEG) is available at temperatures between 400 and 550°C. However, the temperature to which the working fluid may be heated is limited by the chemical stability of the fluid. Although, in practice typical ORC efficiencies are around 10 to 20%, by integrating an ORC with a GT engine, total system efficiency can be increased by roughly 20% to 30%. Real-world GT efficiencies in the 25 MW power range of interest are between 35% and 40%, with 60-65% of fuel energy wasted as heat. If the ORC can harness 10% to 20% of the wasted heat energy (i.e., of the 65%), the total system efficiency increases to ~45%.

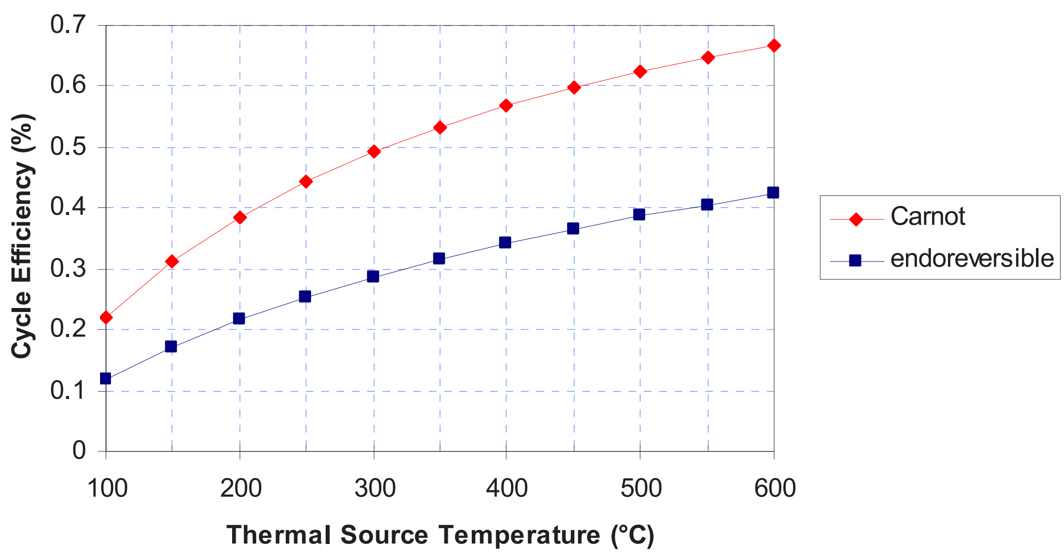

Figure 2. Comparison of Carnot and endoreversible cycle efficiencies.

The losses and productive output of the cycle can be represented graphically in an exergy diagram, in which the useful power output may be compared against the theoretical entitlement (shown in Figure 3 for an ORC heated by the exhaust stream from a GE PGT-25 gas turbine). A cycle that minimizes exergy destruction is sought.

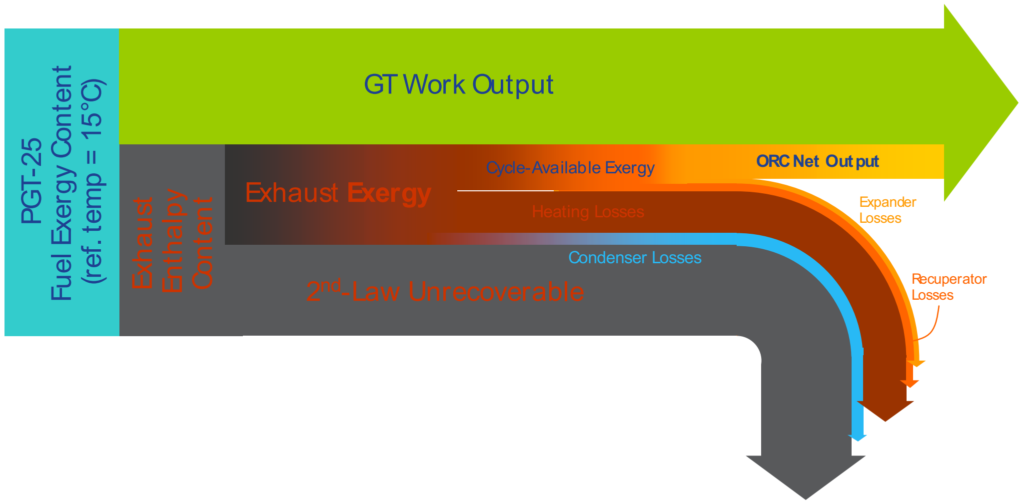

Figure 3. Exergy diagram for a PGT-25 gas turbine with ORC bottoming cycle.

Working Fluid Selection

ORC systems offer a wide range of parameters for optimization with the most obvious being the selection of working fluid. The working fluid selection dictates the operating pressures on the condenser and evaporator side, expander design, need for a recuperator, etc. The operating pressures are strongly dependent upon the available heat source and sink temperatures. For different combinations of heat source temperature range and heat sink temperature range, there would likely be a different optimal fluid. To simplify the optimization process, the initial down selection process focuses on cycle performance, with other considerations introduced later in the process.

The selection of the optimal working fluid is the end result of a systematic comparison of over 40 different fluids on the basis of their suitability for use in an ORC cycle. Fluids were compared on the basis of chemical stability, flammability, toxicity, performance under the boundary conditions of the gas turbine exhaust application, and environmental risk in the event of a leak. Other considerations that factor into working fluid selection include corrosiveness and tendency to foul. Cost was not considered as a distinguishing factor among fluids, since the pressure level, component selection, operating temperature and other attributes, independently from fluid choice, most influence cost. The candidate fluids fall under five broad chemical groups:

1. Simple aliphatic hydrocarbons, such as butane, pentane, and hexane – these chemicals are attractive because their near-ambient boiling points enable condensation near atmospheric pressure
2. Fluorinated (or otherwise halogenated) hydrocarbons (including most refrigerants), attractive because of their efficient expansion behavior and lack of need for a recuperator
3. Aldehydes & ketones – variations on simple hydrocarbons which can be chosen so as to combine the benefits of hydrocarbons and refrigerants
4. Silicones, with extremely high chemical stability at elevated temperatures to guarantee continued performance over the lifetime of the machinery

5. Aromatic hydrocarbons, combining high stability with good expansion properties, but generally boiling well above ambient temperatures.

Perfluorocarbons, chlorofluorocarbons and hydrochlorofluorocarbons have very attractive properties for the ORC, but unfortunately have an extremely high greenhouse warming potential and therefore were not considered. The down selection of working fluids was based primarily on performance in an ORC subject to the constraints identified above. Further selection was guided by consideration of the stability of the chemical at high temperature, health hazards, and potential to cause environmental harm. The qualities that tend to increase working fluid performance are as follows:

- A high stability and critical point such that the fluid may be boiled at relatively high temperature, allowing the recovery as work of a relatively high fraction of the embodied heat energy (enthalpy) of the fluid. The use of fluid blends versus a single fluid presents concerns over unmixing.
- Vertical to positive slope of the vapor curve on T-s diagram to eliminate need for superheating, increase efficiency and lower condenser cost. A tendency of the expanding vapor to remain close to saturation, without need for superheating. If the vapor is close to saturation as it is discharged from the turbine, its temperature will not differ greatly from the condensation temperature, and irreversible transfers of heat (within a recuperator) from the vapor to the cooler liquid returning from the pump will not be required. Any such irreversibility decreases cycle efficiency.
- Sufficiently high volatility to boil at or above ambient temperature, meaning that the condenser can be operated at or above atmospheric pressure. A lower-than-atmospheric (i.e., vacuum) condenser is undesirable, since such systems incur additional cost and complexity to prevent in-leakage of ambient air. Fluids with low vapor pressures at ambient temperatures require the use of sub-atmospheric condensers or costly, cascaded cycles. Condensers that operate at pressures below atmospheric are unacceptable in ORCs because the ingress of air and moisture through unavoidable minute leaks catalyzes degradation reactions in the working fluid [2].

Other desirable characteristics of the working fluid include:

- High thermal conductivity in the vapor phase to maximize heat transfer
- High autoignition temperature, preferably above TEG temperature
- High specific heat ratio
- Low environmental impact and toxicity
- Low overall system pressure to reduce component cost
- Minimal reactivity with air or materials of construction
- Low flammability rating and transport hazard class
- Low freezing point, as this affects operability in cold climates.

Thermodynamic Considerations

The performance of a particular working fluid, even once the source and sink temperatures for the ORC have been specified, is not uniquely determined. A principal variable strongly affecting performance is the pressure at which the working fluid boils. For each fluid, given a particular initial heat source flow and temperature, the electrical output of the ORC will be maximized for a particular pressure level. Here, a single source and sink temperature are specified.

To perform a comparison of fluids, the following five criteria were imposed on the computer simulations of ORC systems:

1. Fixed initial heat source temperature
2. Fixed log-mean temperature difference (LMTD), rather than fixed minimum temperature difference (the distinction is explained below), in evaporator and condenser
3. Fixed expander technology and expander adiabatic efficiency
4. Fixed pump efficiency
5. Use of an additional fixed-LMTD heat exchanger (recuperator), if its inclusion would be beneficial in the particular case, to transfer heat from the fluid vapor as it is discharged from the expander to the fluid in the liquid phase as it returns from the pump.

By using the criterion of a fixed LMTD, rather than a fixed minimum temperature difference between the two flows in each heat exchanger, we eliminate one possible source of variability between fluids. Under given conditions of flow rate and flow inlet temperatures, the effectiveness of a heat exchanger is limited by the requirement that the temperature of the heated fluid may at no point exceed that of the cooled TEG. For this reason, strategies that guarantee more nearly parallel temperature profiles for the warmed and cooled fluid within the exchanger can permit a lower overall LMTD than would be possible if the temperature profiles of either flow were strongly "kinked," as when, at certain low pressures, the process of boiling at constant temperature absorbs roughly the same amount of heat as it took to steadily increase the temperature of the liquid phase from ambient level to the point of boiling. A lower overall LMTD implies lower irreversibility in the transfer of heat, and consequently a more efficient cycle. If the point of minimum approach (in a boiler, this generally occurs at the onset of boiling in the liquid) is the limiting factor in the design of the heat exchanger, strategies such as supercritical heating, or mixing two working fluids together to produce a binary fluid that boils at progressively increasing temperature, can alleviate the limitation and increase the cycle efficiency. But, if source temperatures are sufficiently high, and sink temperatures sufficiently low in relation to the cycle fluid temperature (conditions which hold for our own application), the point of minimum temperature approach will *not* limit the cycle performance, regardless of the strategy used (i.e., supercritical boiling, binary fluid mixtures). In this case, it is only the heat exchanger's size that controls its effect on the cycle performance, and the implied size changes roughly in proportion to the LMTD of the exchanger. Since we wish to compare the different fluids on the basis of similar equipment size and cost, we have constrained LMTD to be constant across all fluid simulations in order to eliminate it as a source of performance variation. The difference in temperature between the two fluids at the point of closest temperature approach therefore varies slightly between different fluid trials. In practice, this "minimum ΔT" will not measure less than a certain value, so if in any case the chosen LMTD would have forced a minimum ΔT of less than 10°C, the LTMD was increased until a 10°C minimum ΔT was reached. A ΔT of 10°C at the pinch point is fairly typical for large industrial heat exchangers.

Direct Evaporator Design

A successful design of the direct evaporator needs to satisfy the required duty, i.e., the amount of heat to be transferred per unit time given the inlet temperatures and mass flows, and meet certain constrains specific to the working fluid and application. For extraction of heat from a low-pressure gas by a high-pressure fluid, finned-tube heat exchangers are employed because of their suitable characteristics of low pressure loss on the gas side along with high surface area ratio between the fins, where the heat transfer coefficient is low, and the tube inside, where the heat transfer coefficients of the fluid are typically about two orders of magnitude larger, leading to a high overall heat transfer coefficient with a relatively compact volume.

Optimizing the heat exchanger design demands a compromise between size, i.e. capital-intensive heat exchange area, and tolerable pressure losses in each of the fluids streams. In this case, however, specific constraints require a distinctive approach in regard to dimensions, geometry and layout. The primary constraints imposed to the heat exchangers of the direct evaporator by the working fluid are:

- Limiting working fluid maximum temperature to avoid excessive working fluid degradation
- Ensuring safety in the event of working fluid leak
- Observing fin surface temperature lower limit
- Maintaining TEG temperature above dew point temperature for nitric acid formation (otherwise, can't use carbon steel tubes).
- Limiting backpressure from the ORC to within allowable limits to avoid choking the GT

The most severe design constraint is the upper limit imposed upon fluid temperature above which decomposition is accelerated. As the highest fluid temperature is found in the boundary layer of the fluid close to the wall of an externally heated duct, the inside wall temperature of all heat exchanger pipes must remain below this temperature limit at all times. The thermal stability of the fluid determines the lifetime of the working fluid, affecting life-cycle cost, and has safety implications if undesirable chemical decomposition products are generated.

The dehydrogenation reaction results in hydrogen evolution that, since hydrogen in non-condensable, dramatically reduces expansion pressure ratio, maximum output power and efficiency. Longer-chain hydrocarbons may form, which can leave a gummy or coke type of residue that is deleterious to system components (especially the pump and heat exchanger). Undesired reaction products, including non-condensables, should be periodically or continuously removed from the heat transfer loop. Avoiding oxygen ingress into some working fluid is critical, since experiments conducted at INL show that decomposition products (measured in solution) increase five-fold upon a bulk temperature increase from 300°C to 350°C, whereas solid product deposition is three times higher. Also, avoiding materials of construction or contaminants that contain catalysts that can promote working fluid degradation is recommended.

Leak Ignition

Placing a heat exchanger operating with a flammable hydrocarbon working fluid directly in the hot exhaust gas stream presents potential safety risks. In order to mitigate risks, FMEA and HAZOP safety studies were performed. The most serious risks anticipated from heating the working fluid in direct proximity to a hot gas turbine exhaust were examined. Potential causes of tube breaches that would initiate a leak include thermal fatigue, mechanical vibration, corrosion and manufacturing defects.

1. Thermal Fatigue

Following a cold start of the direct evaporator, metal temperatures increase over a range of hundreds of degrees C. Differential thermal expansion in the various materials used in the construction of the evaporator can put large stresses on the material interfaces, especially on welded joints between the working fluid tubes and the frame. Over the life of the evaporator unit, repeated cycles of startup and shutdown can eventually aggravate small imperfections in the weld to open cracks through which working fluid under high pressure escapes from the tube into the hot TEG. A large leak would be noticed immediately from the measurable loss of working fluid, while the smallest leak could persist for weeks or months before it is recognized and repaired.

2. Mechanical Vibration

The boiling process within the tubes, as well as the aerodynamic buffeting experienced by the tube banks during steady-state exhaust flow, contribute to vibration that can eventually fatigue and weaken the tube joints. Excessive strain of fatigued members could potentially open cracks in the tube material or welded joints, allowing a release of working fluid into the hot exhaust flow. This phenomena must be addressed during the design of the direct evaporator.

3. Corrosion

Although substantially depleted of oxygen, the residual oxygen content, as well as the water content, of the exhaust flow from the gas turbine have a non-negligible potential to corrode the carbon steel of the direct evaporator fluid tubes over time. The risk of corrosion is already significantly reduced by observing a minimum exhaust temperature to prevent so-called “acid gas” exhaust components from precipitating out of the gaseous phase and corroding metal surfaces. The concern arising from corrosion of the evaporator tubes is that it may ultimately open pinhole leaks in the tube wall, or simply weaken the wall sufficiently such that thermal or mechanical stresses could induce rupture. Routine inspection of all system components is recommended.

4. Manufacturing Defects

Defects in the piping material or welded seams, if not discovered through pressure tests during commissioning, remain as potential nucleation points for cracks throughout the lifetime of the evaporator.

Various more serious effects could result from leaks in any of the above scenarios, including ignition of the fluid causing hot spots and gradual weakening of the structure, as well as the possibility that leaks would feed larger cells of combustible gas, which could explode suddenly causing catastrophic failure. The estimated magnitude of these risks was necessarily quite provisional, as no research had yet been performed on the detailed mechanism for each of the failure mechanisms. However, reports on steam boiler technology provide examples of rupture mechanisms originating from corrosive interactions with the tube steel. For many boiler applications, leaks are described in the boiler literature as an inevitable symptom of ageing.

As shown in Figure 4, oxygen, heat and fuel are the three elements necessary for a fire to occur. Autoignition occurs when sufficient self-heating by chemical reactions takes place to accelerate the rates of reactions to produce full-scale combustion. Combustion is the sequence of exothermic chemical reactions that occurs between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species. Combustion feeds a fire with heat, enabling the process to continue. In the proposed ORC design, oxygen, heat (from the TEG) and fuel (i.e., the working fluid) are present creating the potential for a fire in the direct evaporator.

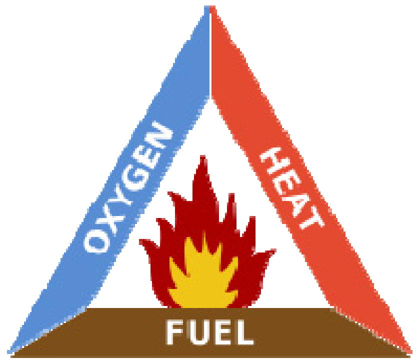

Figure 4. Fire triangle (courtesy of Wikimedia Commons).

The reaction rate depends on the mean species concentration of the mixture and the local mean temperature. The concentration field and the progress of chemical reaction are affected by the topology of the turbulent flow field [3]. Ignition processes are usually very complex and involve many intricate physical and chemical steps [4]. These steps take a finite amount of time and the period between the start of injection and the start of combustion is referred to as *ignition delay time.* The ignition delay time is a latent period in the combustion process, during which the temperature remains nearly constant [5]. The delay time is comprised of a physical delay and a chemical delay component. The physical delay is due to the finite rate of mixing of injected working fluid with hot exhaust gas and is the time needed for the flammable gas mixture to reach the autoignition temperature. The chemical delay is due to pre-combustion reactions of the combustible gas mixture that lead to autoignition. In reality, both the physical and chemical processes are occurring simultaneously and cannot be decoupled. Therefore, the actual autoignition delay time in a flowing system is difficult to determine, as it will be affected by the [6]:

- Time taken for fuel and TEG to mix,
- Time for the fuel temperature to rise to that of the TEG, and
- Chemical kinetic time for the autoignition reactions to initiate.

Computational fluid dynamic (CFD) analyses were performed to assess the flammability of the selected working fluid in the hot exhaust gas stream stemming from a potential pinhole leak in the evaporator. The primary concern here is the potential for leaked working fluid to become trapped in the recirculation regions aft of the finned tubes. The stabilization of a flame in the eddy region behind a bluff body in a high velocity gas stream is a well known phenomenon used to anchor the flame in the combustors of jet engines [7]. A flame stabilized in this manner can spread throughout the entire flammable mixture. The residence time of gases in the recirculation zone behind a bluff body dictate whether the flame will propagate or extinguish. The scenario of concern is that fluid released a small leak in a finned tube could ignite, burn undetected for a long time, and potentially degrade surrounding materials or ignite secondary fires. A highly conservative mixed-is-burned approach was implemented for the combustion. As a worst case scenario, the CFD analysis was performed assuming a zero ignition delay time wherein the working fluid burns as soon as it is released from the breached tube.

Summary

A modification of the conventional ORC system using direct evaporation technology has been outlined. Issues surrounding the selection of an ORC working fluid have been outlined. The conditions and constraints imposed on the thermodynamic analysis and heat exchanger design have been discussed. Safety risks recognized during the FMEA/HAZOP are given, along with mitigation strategies. Leak ignition processes are identified and the methodology employed in the flammability analysis is provided.

By identifying a safe means of detecting and handling leaks in general, all the particular leak scenarios, including corrosion, thermal or mechanical strain failure, can be simultaneously addressed. A safety mechanism that could anticipate and "disarm" leaks, allowing no opportunity for ignition or explosion, would conclusively mitigate all conceivable leak scenarios at once. In line with this approach, subsequent analyses and experiments have focused on setting safe limits on the range of velocities and temperature of hot exhaust within which no amount of leaked working fluid could ignite. Specifically, even at exhaust temperatures as high as 600°C and flow rates as low as one-third of the normal operating level, any leaked fluid would be expelled from the system before it had the chance to ignite. A prototype is being constructed for testing at GE GRC's testbed located in Niskayuna, NY. During the prototype testing, leak tests are planned to confirm the retirement of fire risks, test detectors and safety chain under real-life conditions.
Specific recommendations to minimize the potential for a deflagration in the direct evaporator unit include:

1. Do not allow flammable/explosive concentrations of working fluid-TEG mixtures to stagnate. It is advisable to sweep such mixtures through the system. A minimum TEG velocity should be observed.
2. Purge the oxygen out of the ORC with an inert gas upon system startup.
3. Incorporate hydrocarbon sensors in appropriate locations to detect leaks. If a leak is detected, a system to divert the hot gas to bypass stack should be activated and the working fluid system depressurized. Since the working fluid is heavier than air, any escaped liquid or vapor will tend to settle in low areas or travel some distance along the ground or surface towards ignition sources.

The direct evaporator design shows promise for future ORC systems due to its simplicity and lower cost. Overall efficiency can be increased by eliminating the losses associated with the oil loop. The direct evaporator concept is probably best suited for lower temperature heat sources, where there is no need to protect the working fluid from overheating and autoignition is not a concern.

Acknowledgments

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References

1. Callen, H.B., *Thermodynamics and an Introduction to Thermostatistics*. Vol. 2nd Edition. 1985: John Wiley & Sons, Inc.
2. Doty, F.D. and S. Shevgoor. *A Dual-Source Organic Rankine Cycle (DORC) for Improved Efficiency in Conversion of Dual Low- and Mid-Grade Heat Sources*. in *ASME 2009 3rd International Conference on Energy Sustainability, July 19-23, 2009*. 2009. San Francisco, CA.
3. Bergeron, C.A. and W.L.H. Hallett, *Ignition Characteristics of Liquid Hydrocarbon Fuels as Single Droplets.* The Canadian Journal of Chemical Engineering, 1989. **67**: p. p. 142-149.
4. Agarwal, A., and Assanis, D.N., *Multi-Dimensional Modeling of Natural Gas Autoignition using Detailed Chemical Kinetics.* Combust. Sci. and Tech., 2001. **Vol. 163**: p. p. 177-210.
5. Golovitchev, V.I. and J. Chomiak, *Evaluation of Ignition Improvers for Methane Autoignition.* Combust. Sci. and Tech., 1998. **135**: p. p. 31-47.
6. Goy, C.J., A.J. Moran, and G.O. Thomas, *Autoignition Characteristics of Gaseous Fuels at Representative Gas Turbine Conditions*, Rolls Royce.
7. Longwell, J.P., E.E. Frost, and M.A. Weiss, *Flame Stability in Bluff Body Recirculation Zones.* Industrial and Engineering Chemistry, 1953. **45**(8): p. p. 1629-1633.