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Highly Efficient Magnetocaloric Natural Gas Liquefaction

Final Report

March 2020

Jamie Holladay
John Barclay
Corey Archipley
Kerry Meinhardt
Greg Whyatt
Edwin Thomsen

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99352

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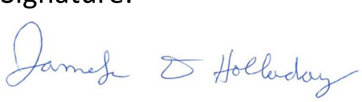

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I Accomplishments

I.1 Synopsis of Accomplishments

Over the twelve-month project the following achievements were accomplished:

- Liquefication of methane as primary component of natural gas was accomplished with a magnetocaloric liquefier (MCL) prototype. This was the first time an MCL was used to liquefy methane.
- Improved MCL designs were completed.
- Cooling to 135 K from room temperature was achieved for the first time in a single MCL stage with dual four-layer regenerators.
- Techno-economic analysis for a multi-stage 5 tonne/day magnetocaloric liquefier was completed. The detailed thermodynamic analysis of this MCL design showed a figure of merit (FOM) of 0.6 was achievable. This is almost a 2x improvement over current state of the art.
- Cost of an efficient 5 tonne/day LNG multi-stage liquefier was projected to be $5.3 MM for a low-risk, twelve magnet design with controllable heat transfer subsystems for each stage. With 6-layers in a single, multi-layer, dual regenerators with a new lower pressure-drop flow geometry, and has controllable diversion flow of heat transfer fluid between adjacent layers reduces the number of magnets from 12 to 2, and allows an increase in operating frequency from ~0.4 Hz to ~1 Hz, the capital cost decreases by ~40% to ~$3.1 MM for the 5 tonne/day MCL.
- Market study of U.S. merchant LNG demand by energy sector was completed showing that at beginning of 2019, total use was ~2.5 million gallons/day primarily in three sectors that was filled by ~20 small companies in the merchant LNG supply business producing ~2.3 million gpd. These data exclude LNG produced at dedicated peak shaving and export plants.
- Business case for MCL technology based on LNG market study was completed showing the high FOM feature of MCL reduces cost of plant power, and lower capital cost reduces debt repayment and plant depreciation operating expenses. However, today's demand for U.S. merchant LNG in most sectors is satisfied with conventional technology. Further, with today's extremely low natural gas (NG) feedstock costs (e.g., ~$1.8/MMBtu), the cost of fuel for NG gensets and for LNG feedstock is already very low. Therefore, possible new merchant LNG liquefier plant developers anticipating demand growth in the transportation, industrial, and electricity generation sectors do not obtain sufficient cost benefits to adopt new, commercially unproven MCL technology.
- Other market factors such as remoteness from existing NG pipelines, or unfilled or unsatisfied applications such as boil-off gas re-liquefaction in LNG vessels, or policy factors such as some form of emissions-related fees may make lower capital costs and higher FOM of MCL technology attractive for new small-scale (~50 tonne/day) LNG plants. Two potentially attractive niche markets for MCL technology were identified: i) re-liquefaction of boil-off gas from large LNG transport vessels where severe transport conditions are problematic for conventional technology; and ii) providing LNG in distributed-scale plants that eliminate road transport costs to meet diverse, smaller-scale, distributed LNG bunkering fuel demands. By eliminating significant cryogenic tanker delivery costs and create an attractive cost-savings benefit with small-scale MCL plants.

II Milestones

Program Milestones are presented in Table 1. All milestones are completed.

Table 1. Milestones

Type	*Description*	*Months*	*Status*
Milestone	MCL system modifications completed	3	Complete
Milestone / Deliverable	NG liquefaction demonstrated at 1-10 gpd and memo report documenting performance	6	Complete
Milestone / Deliverable	Techno-economic analysis complete. Report on ability to achieve a projected FOM of 60% or more and a projected capital cost ~ of current technology	8	Complete
Milestone / Deliverable	Business case complete. Report on ability to identify a minimum of one scenario and build a business case for the MCL technology showing it will have a lower operating cost of 25% or more at an equivalent capital cost compared to current technology	12	Complete

III Background

Most LNG plants are very large scale and use conventional gas cycle refrigeration technologies such as the Linde-Cascade cycle, the turbo-Brayton cycle and the mixed refrigerant cycle for plants to produce LNG. The maximum efficiency as measured by the figure of merit (FOM) of these liquefiers is ~35% at best. As capacities are reduced from hundreds of metric tons/day to tens of metric tons/day, the FOM decreases toward ~20-25%. The Department of Energy (DOE) program managers responsible for the Technology Commercialization Fund (TCF) sought liquefaction technologies which could simultaneously increase thermodynamic efficiency and reduce capital costs of smaller-scale LNG production. The Fuel Cell Technology Office of DOE has been supporting development of magnetocaloric liquefaction (MCL) technology for much more efficient and less costly production of LH_2 over the past several years. After a competitive solicitation, the Pacific Northwest National Laboratory (PNNL) was selected to leverage its knowledge of and experience with magnetic refrigeration to investigate application of MCL technology to produce small-scale quantities of LNG.

The MCL utilizes a dual active magnetic regenerator (AMR) system which uses an alternating magnetic field and magnetocaloric materials to transfer heat between reservoirs (Figure 1). The magnetic material in a high-performance regenerator is adiabatically placed in a high magnetic field. The conservation of total entropy in this adiabatic process requires the magnetic regenerators to increase in temperature to compensate for the increased order (lower entropy) among the material's magnetic moments.

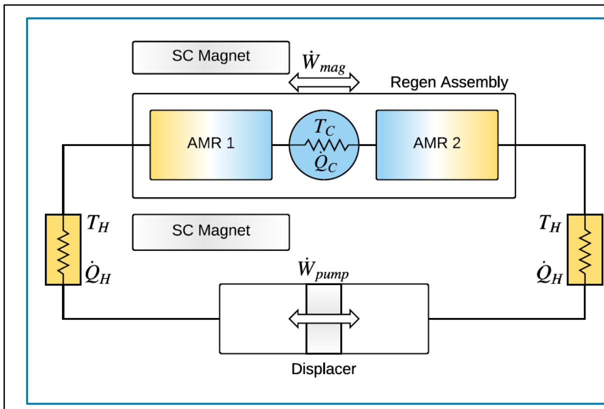

Figure 1. Schematic of magnetocaloric system. (Teyber R, et al. 2019)

The increased thermal energy is transferred to a heat sink by the cold-to-hot flow of heat transfer fluid (HTF). In this project we used compressed He as our HTF. After the cold-to-hot heat transfer fluid flow is completed, the magnetic material is adiabatically removed from the high magnetic field resulting in a decrease in regenerator temperature to compensate for decreased order among magnetic moments of the magnetic materials. During a hot-to-cold flow of the heat transfer fluid at constant low magnetic field, the colder magnetic regenerator accepts heat from the thermal load from cooling the hydrogen process stream. The active magnetic regenerative cycle is repeated at the operating frequency. The principle of operation is schematically shown in Figure 1. The current MCL test stand is shown in Figure 2.

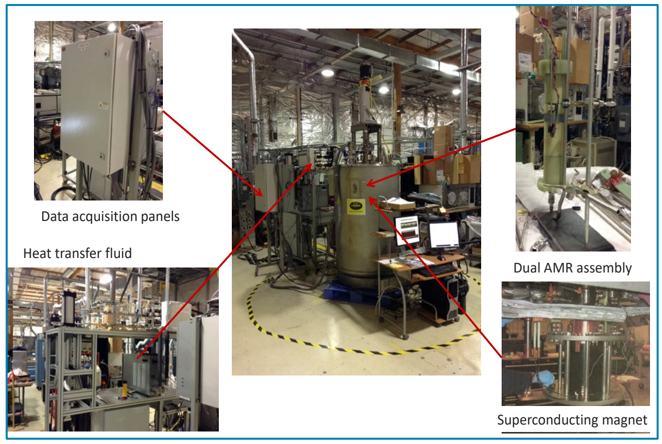

Figure 2. Magnetocaloric test system at PNNL. This shows the key parts: AMR assembly, superconducting magnet, Dewar, HTF, and controls/data acquisition

Some of the keys to high performance include: use of ferromagnetic materials with a high adiabatic temperature change and second order phase change (Holladay 2018a), exploitation of second order phase change in the by-pass configuration (Holladay 2018a), minimization of force balance issues (Teyber 2017), high frequency operation (Holladay 2018b), multiple materials with Curie temperatures that span the operational temperature range (Teyber 2019 and Meinhardt 2019) and use of diversion flow to control the internal flow within the materials layers (Holladay 2018b and Holladay 2017). Here only the need for multiple materials and diversion flow will be reviewed. Please see the references for the full description of the past work PNNL has done in these areas. As can be seen in Figure 3, the adiabatic temperature change is greatest near the Curie temperature and is proportional to the magnetic field change. Therefore, we designed the system to include a large magnetic field change and to use 4-5 materials. The final set of material used in this work are shown in Table 2.

Table 2. Magnetocaloric Materials Used

Material	Cure T (K)	~T Span (K)
Gd	293	280-240
$Gd_{0.30}Tb_{0.70}$	253	240-200
$Gd_{0.32}Dy_{0.68}$	213	200-160
$Gd_{0.33}Ho_{0.67}$	183	160-120

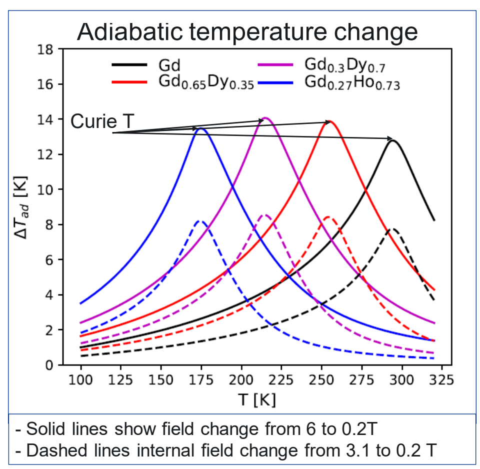

Figure 3. Adiabatic temperature change as function of material and field. Note: for wide temperature performance multiple materials are required

It is important to recognize that the heat load and thermodynamic work of the colder layer is dumped to the next warmest layer. The next layer's heat load would be the thermal energy to cool across the span, the work for this layer, plus the thermal energy from the adjacent colder layer. For example, if $Gd_{0.33}Ho_{0.67}$ had a heat load and work of "a", then the $Gd_{0.32}Dy_{0.68}$ would have a heat load "b" to cool from 200-160 K and its thermodynamic work, plus "a" for a total of "a+b". Then $Gd_{0.3}Tb_{0.7}$ would have a heat load to cool "c" from 240-200 K and its thermodynamic work, plus "a" and "b" for a total of "a+b+c". Thus, each layer will have a different heat load and work such that each layer's thermal loads getting progressively larger with each warmer layer (i.e. $Gd_{0.33}Ho_{0.67}$ being the smallest and Gd the largest loads). Ideally, because each layer has different heat and work inputs, both the mass of refrigerant in each layer and the heat transfer fluid flow through each layer has to be different. This sequential refrigeration can easily be accomplished by having each refrigerant in a single regenerator as a separate stage with its own superconducting magnet, HTF flow, etc. (left side of Figure 4). Unfortunately, this low-risk approach has the disadvantage of higher expense because of more magnets and separate HTF circulators. To minimize the number of magnets and HTF circulators, PNNL invented an approach of using tapered, layers of magnetic refrigerants in a single regenerator with a spacer between each layer (right side of Figure 4). To provide the correct HTF flows for each layer, we created controllable diversion flow valves between each set of adjacent layers to adjust the correct HTF flow through each layer (Holladay 2017). This approach required dual regenerators where one was magnetized and the other was demagnetized during the two blow steps of the AMR cycle. The extra complexity of using this more elegant multi-layer design requires careful understanding of choosing the correct refrigerant masses for each layer and the correct amounts of diversion flow between layers for proper operations. Before we begin this TCF project, the record temperature span in a multi-layer regenerator was ~80 K and during this project we increased that to ~150 K (and we learned much more about this type of MCL design.

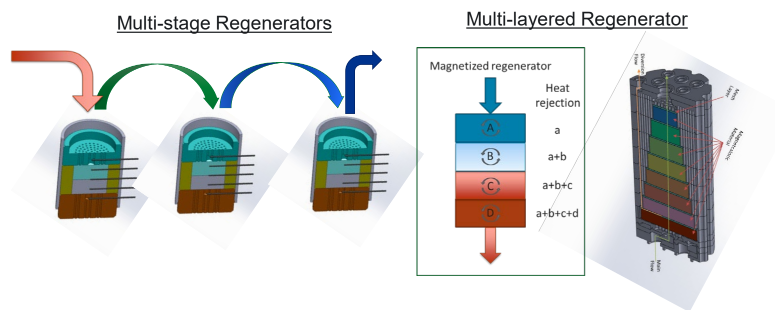

Figure 4. Options for using multiple materials: multi-stage device or multi-layered device

The work in this project is divided into technical and commercialization sections. For the technical work, we modified the MCL system for methane liquefaction, tested several iterations of AMR designs, liquefied methane with the best system and performed a techno-economic analysis (TEA). For the commercialization scope, we completed a merchant LNG market study and based on those results, created a business case for recommended near-term application for MCL technology. The report is organized by task for each section.

IV Technical Summary

Task 1. Design and Build 280 K to 120 K prototype. The initial plan was to modify the first stage (280 K to ~120 K) of a dual stage magnetocaloric gas liquefaction (MCL) that was built for our Fuel Cell Technologies Office (FCTO) hydrogen liquefaction MCHL project. For this to be successful, we needed to add a heat exchanger where the methane (used to simulate natural gas) would be liquefied and we needed to upgrade the system's balance-of-plant.

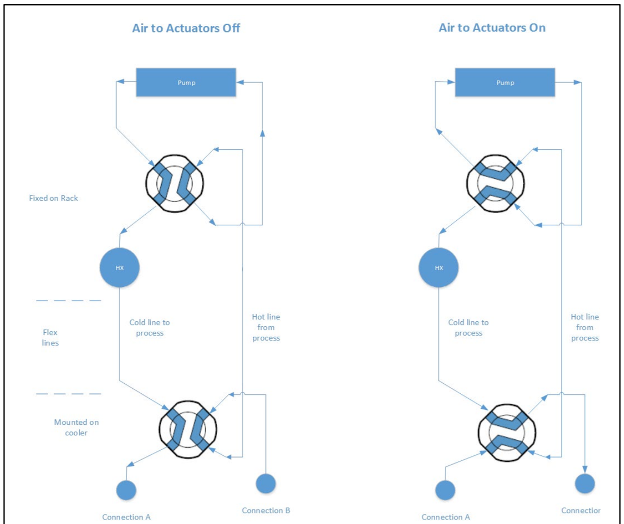

Figure 5. New Valve Configuration to Increase Performance

To improve the performance of the system, we upgraded the MCL heat transfer fluid (HTF) system from 200 psi to 400 psi operation. This change doubles the possible mass flow rate of the helium HTF which approximately doubles the amount of heat transferred to and from the magnetic regenerators during the blow steps of the AMR cycle which increases the cooling power of the refrigerants. A new linear actuator driven, reciprocating, positive displacement pump was procured and installed. The valves and sensors were upgraded for the higher pressure. Analysis of the HTF system indicated that the reversing flow in the lines delivering helium from the HTF subsystem to the hot end of the regenerators in the magnetocaloric refrigerator there was regenerative heat transfer within the lines that was reduced the ability to transfer heat in the magnetic refrigerants. This effect can be greatly reduced by installing two 4-way cross over valves (see Figure 5). The readily available valves are rated for 1500 psig and have air-actuated positioners. One is installed on the moving portion of the system and another on the stationary support rack of the HTF subsystem. The same air supply was split between the two valves. This modification created one hotter helium line return to the pump and one cooler helium line supply going to the AMR regenerators plus a pneumatic line to drive the actuator. The hotter and cooler helium streams pass each other in the same valve body but with minimal thermal exchange compared to that from the back and forth flow we previously had through the common supply-return lines going to the regenerators. We implemented this improved HTF subsystem and successfully used it during the TCF experiments.

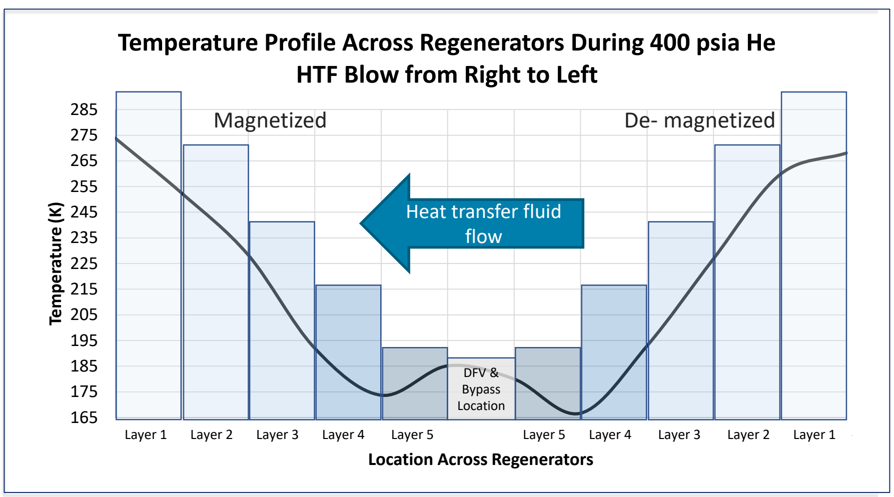

Figure 6. MCL Performance to Achieve 165K Temperature. Data generated as part of the FCTO MCHL Project

As part of the magnetocaloric hydrogen liquefier (MCHL) project at PNNL funded by the FCTO, we designed, fabricated, and tested the 285-120 K stage of the MCL for hydrogen liquefaction. To achieve this temperature span, multiple (~5) different ferromagnetic refrigerants are required. Because we only have one 7 T superconducting solenoidal magnet available, a multi-layer, reciprocating, dual-regenerator stage was chosen instead of a multi-stage design. The first prototype was designed and built to cool from room temperature to 140-120 K with ~20 K to ~40 K per layer. Because the required mass of refrigerants increases from cold to hot temperatures, the layered regenerators are tapered from cold to hot temperatures within the regenerators. The different layers in the regenerators require different helium mass flow for their respective AMR cycles so hot-end inlet He flow rate has to be sequentially reduced in the demagnetized regenerator and sequentially increased in the magnetized regenerator to achieve the correct HTF flow rates during the hot to cold and cold to hot blows. To control this function, we added valves for each diversion flow channel. These pneumatically controlled diversion flow valves between adjacent layers were used to adjust the proper HTF flows. Each diversion flow from the hot-to-cold blow was sent to the corresponding layers for the cold-to-hot blow. To assemble the dual regenerators required a set of cryogenic seals for 400 psia Helium gas (to vacuum) in each flow channel between the regenerators. The controllable diversion flow valves, made from Inconel, were located in the space between the dual regenerators. The ~3/8” diameter tubes on either end of each valve were sealed to another polished Inconel sleeve epoxied into machined grooves in the G-10 end flange of each regenerator with a tiny circular coiled spring inside a circular thin cup-shaped Teflon wall about 1/32” thick. These two walls of Teflon seal against the Inconel sleeve and the Inconel tube of the valve. The Teflon walls are energized either by the spring at low He pressure of by the He gas at higher pressures. These seals worked quite well at room temperature but proved very problematic as the MCL apparatus cooled down toward our target temperature of ~120 K. These energetic seals started to leak into the high-vacuum stainless-steel chamber that isolates the cold regenerators from wall of the chamber near room temperature at ~200 K. The helium gas in the vacuum created sufficient heat leak into the coldest layers in the regenerators to limit their ultimate cold temperature to 165 K. Figure 6 shows the performance of the five-layer dual-regenerator MCL. The left side of this figure shows the refrigerants that are inside the magnetic field and heated by the magnetocaloric effects of each layer with cold-to-hot helium flow that is dumping heat to the heat sink at ~275 K. The right side of the figure shows the refrigerants outside the magnetic field which are all cooled by their magnetocaloric effect which cools the

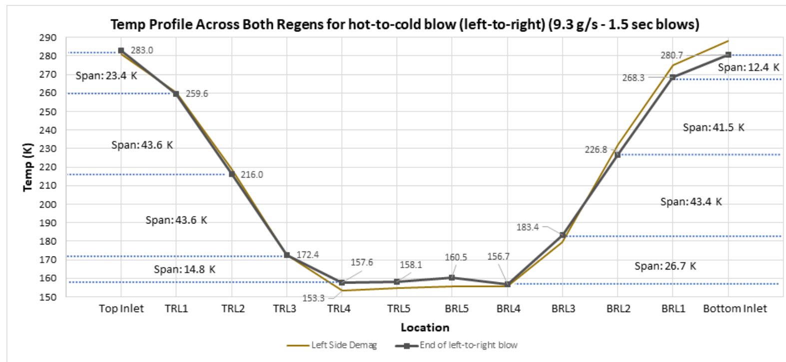

Figure 7. Temperature profile of a four-layer AMR achieving 153 K

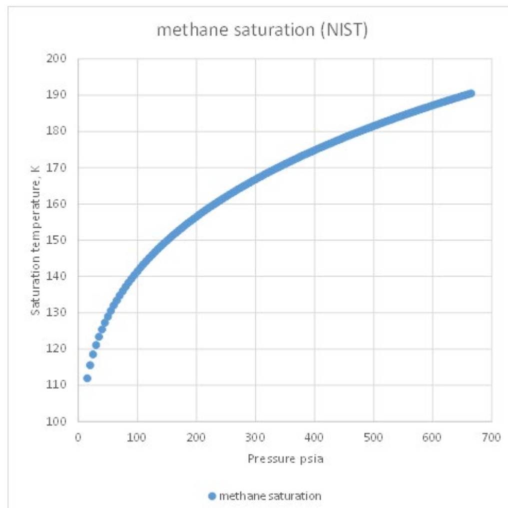

Figure 8. Methane saturation. This curve shows 200 psia methane will liquefy at ~157K

helium HTF in a hot-to-cold blow which cools the process stream. The spring-energized Teflon seal only leaked below 200 K and was reversible as the regenerators warmed up. After discussing these results, we concluded a better version of this type of seal was required. A new improved energized seal was acquired from Eriks Corp. The old seals used PTFE (polytetrafluoroethylene) with a 316 stainless steel, coil spring. At lower temperatures the spring had insufficient pressure to maintain the seal load. The new seals use a PCTFE (polychlorotrifluoroethylene) as the sealing material and the helical spring made from a cobalt-based alloy. We tested the new seals in a test fixture with one of the diversion-flow valves up to 400 psia helium at room temperature. No leak rate was detected. Then the whole assembly was submerged in liquid nitrogen to test the cold performance. The leak rate was still at zero after the valve cooled to the liquid nitrogen temperature. We also tested the PTFE with stainless steel seals in the same way and confirmed the PTFE version of these spring energized seals failed at low temperature. The new seals at both ends of the diversion flow valves were tested again after assembly of the valves with the regenerators. Unfortunately, one of the Inconel sleeves on the top regenerator epoxied into the G-10 flange into which the seals are inserted was slightly oversized and still leaked. One sleeve was ~0.001" larger in diameter than the rest which reduced the pressure on the PCTFE cup. It is clear that very high tolerances are needed for these seals and it is one of the issues with this type of seals. We also found that a fraction of the helium leak is through the epoxy joint between the G-10 and the Inconel sleeve. We believe this was caused by a seam between glass weave and epoxy for the G-10 material used to fabricate the end flanges for regenerators. We concluded that we'll only use the higher quality G-10-CR in the future for regenerator housing parts. Rather than to continue to resolve the frustrating differential contraction problems, we decided to increase the capacity of the turbo-vacuum pump on the evacuated chamber around the dual regenerators to help reduce the external parasitic heat leaks.

One way to mitigate the risk of seal failures on the diversion flow valves is to eliminate them if possible. We know that no diversion flow valves are required for 2-layered regenerators, and multiple valves will definitely be required for 8-layered regenerators. We hypothesized that we might be able to achieve larger temperature spans with tapered masses per layer but without any diversion flow with 4-5 layers in each regenerator. To test this hypothesis, we built a tapered, multi-layer AMR without diversion flow valves. The G-10 regenerator housings can be loaded with 1-5 layers of the ferromagnetic refrigerants (see Table 2) and total mass flow rate of the 400 psia helium HTF can be varied from 0 to ~8 gram/second during the experiments. With four refrigerants the layered AMR cooled to 165 K as shown in Figure 7. Each layer should cool by ~40 K below its respective Curie temperature. The measured temperatures show that the heat flows among the various layers inhibits that operation. E.g. Gd should operate between ~285-290 K and ~245-250 K which would allow the $Gd_{0.30}Tb_{0.70}$ layer to operate below its Curie temperature of 253 K. The results were analyzed with an improved phenomenological model that solves the circular references for performance of each layer for the HTF flow rate the layer receives. This analysis shows that the uppermost layer is under blown (too little helium flow), the second layer is about right, and the third and fourth layers are over blown (too much helium flow).

A graph of the liquid methane saturation temperature vs. pressure in Figure 8 shows 200 psi methane will liquefy at ~157 K. We designed and built an improved multilayer AMR with a better understanding the effects of no diversion flow valves and mass of each layer. We expected the improved AMR's would be able to achieve a lower temperature, but at the sacrifice of high efficiency. However, results from tests of these prototypes are validating the aspect ratio models and aid us in better understanding the limitations of diversion flow valves (i.e. do we need one valve for every layer, or a valve per every 2 layers or possibly every 3 layers?). We also learned that the regenerator housings need to be fabricated with G-10 CR, a superior fiberglass epoxy composite with much more uniform mechanical and transport properties than

G-10. It was previously developed by NIST to avoid the type of material failures we've experienced at cryogenic temperatures.

We built a new 4-layer prototype without any diversion flows (a limiting case) that was tested with ~8 gram/s flow rates of 400 psia helium and successfully cooled to 135 K (Figure 9). This is a record low temperature reached from near room temperature with a multi-layer active magnetic regenerative regenerator.

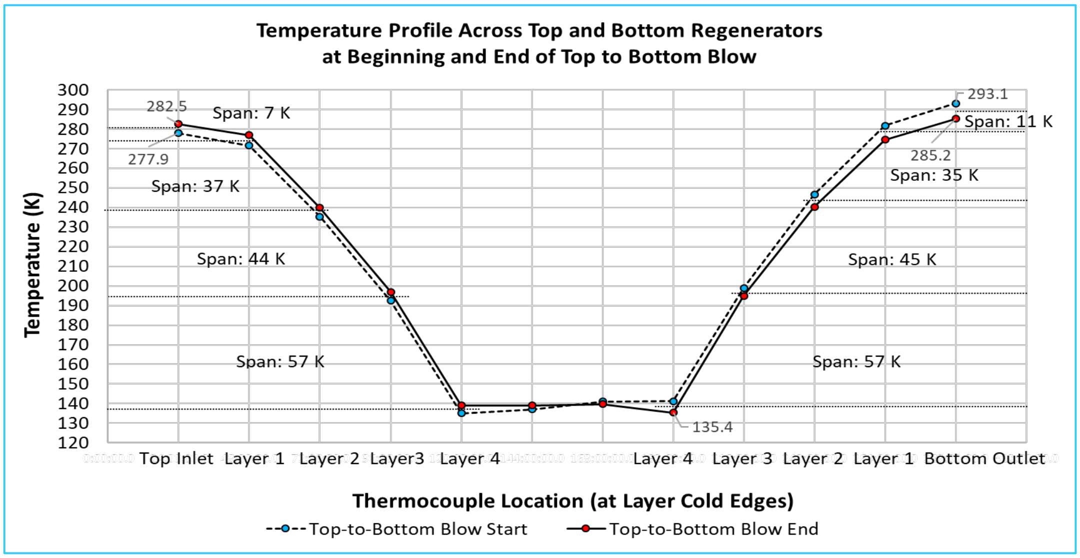

Figure 9. Temperature profile of a four-layer AMR achieving 135 K

Task 2. Liquefy Methane

We already had a coiled-fin tube condensing heat exchanger identical to one built for a propane liquefaction experiment about 2 years ago. The exchanger shown in the middle of Figure 10 was integrated into the cold helium HTF flow region between the dual 4-layer regenerator design that reached 135 K. The coiled-fin tube heat exchanger was tightly wound around a ~100 cm^3 stainless steel vessel to collect liquefied methane. The schematic of the integrated for the methane liquefaction experiment is shown in the left side of Figure 10. As can be seen, the device had two regenerators with each regenerator using four layers of ferromagnetic refrigerants reported in Table 2. The coiled-fin tube heat exchanger was successfully used for liquefaction in a propane liquefaction with only Gd refrigerants in dual regenerators. (Barclay 2019). It was located between the AMRs. The liquefaction rate of methane, initially at room temperature, was tested at three different pressures listed in Table 3 below.

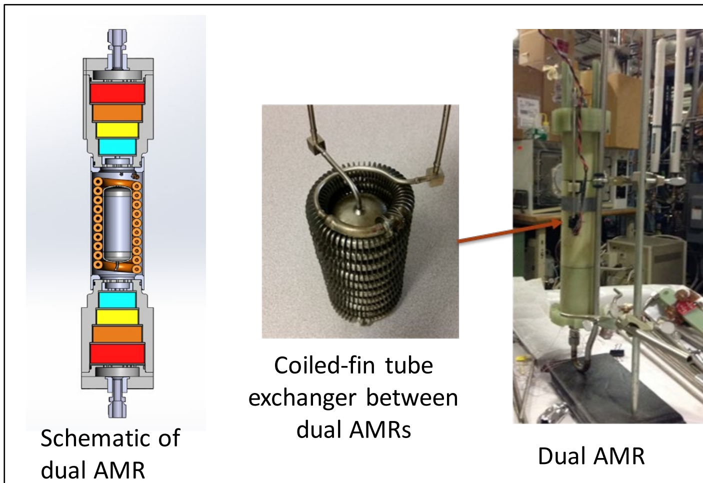

Figure 10. Magnetocaloric Methane Liquefaction system

The liquefier was run at 0.167 Hz with 2 second blow steps and 1 sec magnetize and demagnetize steps. These parameters were used to limit the pressure drop for helium flow through the regenerators during blow stages and reduce magnetic flux-change induced heating in the magnet windings during magnetization /demagnetization steps of the cycle.

Table 3. Methane Liquefaction test conditions

Test	CH_4 Pressure (psia)	CH_4 Saturation Temp (K)	Cycle Frequency (Hz)	Blow Period (s)	Mag/Demag Period (s) (no helium flow)	Helium Heat Transfer Fluid Flow Rate (g/s)
1	256	162.6	0.1667	2	1	3
2	228	159.7	0.1667	2	1	3
3	195	155.9	0.1667	2	1	3

Other operational conditions and details include:

- HTF flow: Helium at 400 psia and at a flow rate of 3 g/s was used as the heat transfer fluid, because previous tests had shown these to be the optimum flow conditions for this device.
- Temperatures of the helium heat transfer fluid were recorded every 0.1 s at the inlet of each regenerator and at each layer junction. The methane process stream temperatures were recorded every 0.1 s at the condensing heat exchanger (CHEX) inlet and at the CHEX vessel top.
- Each test was started with the dual-regenerator device and CHEX at room temperature requiring a cooldown period of ~1 hour prior to liquefaction conditions being met.
- The procedure for introducing the methane from its lecture bottle into the CHEX for tests 1 and 2 was to wait until methane saturations temperatures were met in the CHEX inlet to introduce methane flow into the CHEX (the CHEX has no outlet). However, test 3 was conducted with the methane valve to the CHEX open at startup. Either method relied on condensation of methane into liquid within the CHEX vessel to drive the methane flow rate into the vessel. Hence, the methane flow rate into the vessel is the liquefaction rate.

The methane liquefaction results are summarized in Table 4 below. The average temperature of the cold helium during the hot-to-cold blows of the cycle correlated closely with the saturation temperature of methane at the pressures set by the regulator on the methane supply lecture bottle as liquefaction took place. The table shows the liquefaction flow rate and calculated cooling power for each test. These cooling powers were derived from the enthalpy difference between room temperature methane and liquid methane at the given conditions and the methane flow rate measured with a calibrated Alicat mass flow meter at the outlet of the lecture bottle into the AMR prototype.

Table 4. Liquefaction flow rates and cooling power

CH_4 Pressure (psia)	CH_4 Saturation Temp (K)	CH_4 Liquefaction Rate (g/s)	Cooling Power (W)
256	162.6	0.023	15.8
228	159.7	0.0129	8.8
195	155.9	0.0098	6.75

Figures 11,12, and 13 show temperature versus time for each test beginning with the cooldown period, then the liquefaction period, and the final sub-cooling period (once the coiled fine tube heat exchanger vessel is full of liquid methane). They show that the liquefaction is very stable with the rates slightly slower than expected from the cooling power predicted from the performance model of the multi-layer regenerators. The cooling power from the rate of methane liquefaction allows determination of the external parasitic heat leaks into the cold region of the AMR prototype. The cooling power curve as a function of cold load temperature for this multi-layer design, magnetic field changes, and helium HTF flow rates can be obtained from the results for the three different pressures.

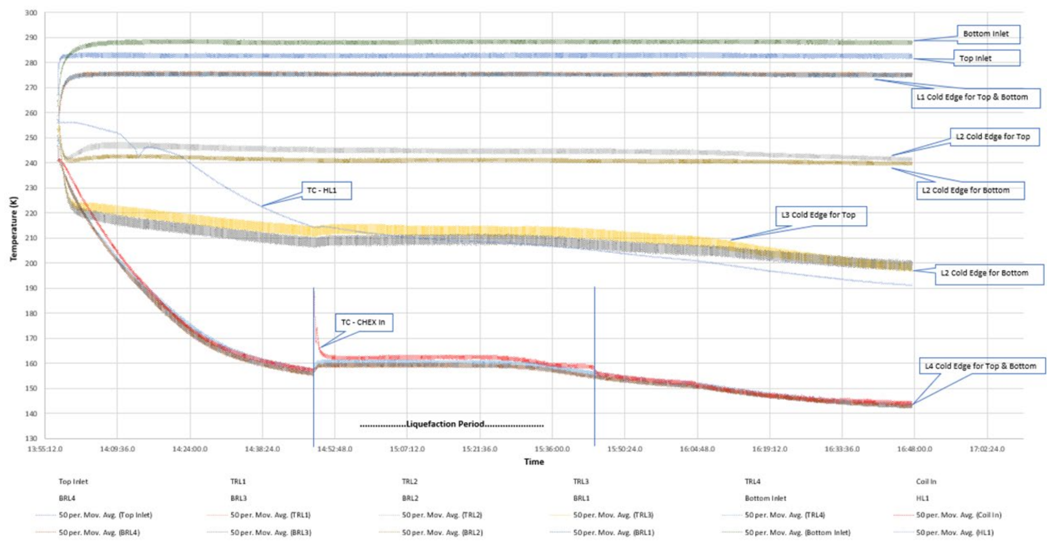

Figure 11. Temperature vs Time for methane liquefaction – CH_4 at 256 psia

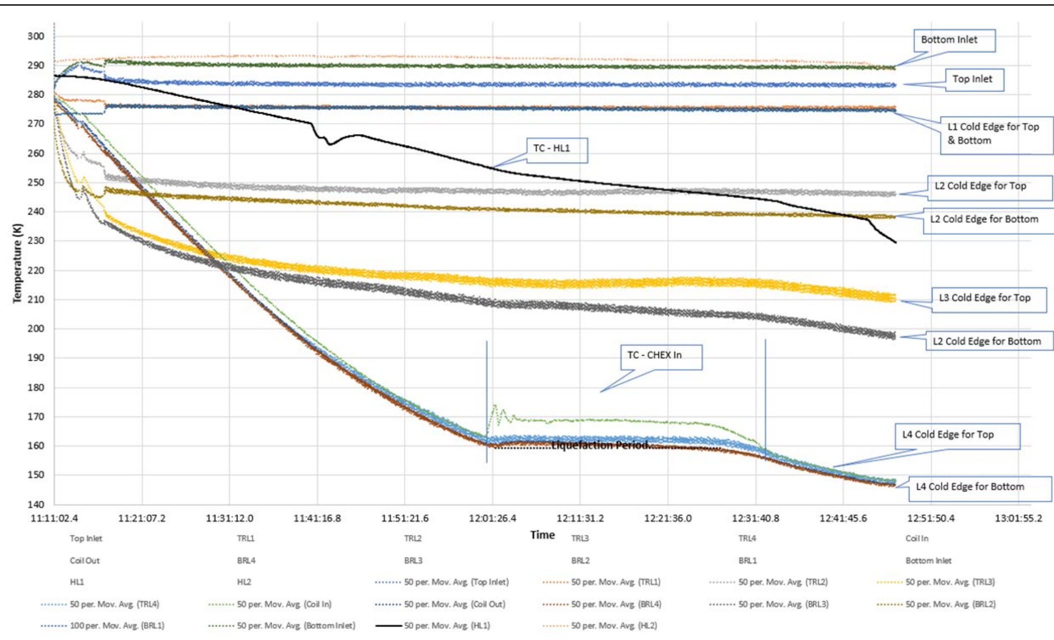

Figure 12. Temperature vs Time for methane liquefaction – CH_4 at 228 psia

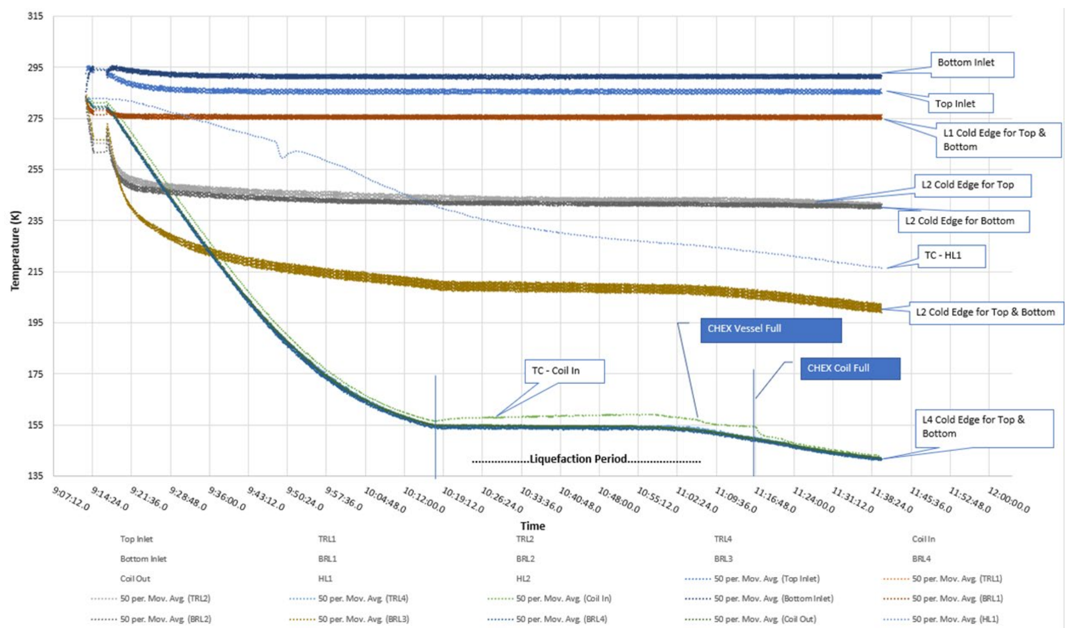

Figure 14. Temperature vs Time for methane liquefaction – CH_4 at 195 psia

Figures 14, 15, and 16 show temperature versus time for the CHEX inlet and cold edges of the regenerators as well as the accumulated liquid methane volume versus time. Similar to the previous sets of data, the rates increased with increased pressure because the cooling power of the 4-layer regenerators increase with increasing temperature. In Figures 14 and 15, the lecture bottle valve was kept closed until the AMR cooled to the saturation temperature of methane at the set pressure. In the third run at 195 psia, the lecture bottle valve was opened with no flow and everything at a quiescence state before the cool-down began. No methane flow occurs because there is no pressure difference between the condensing heat

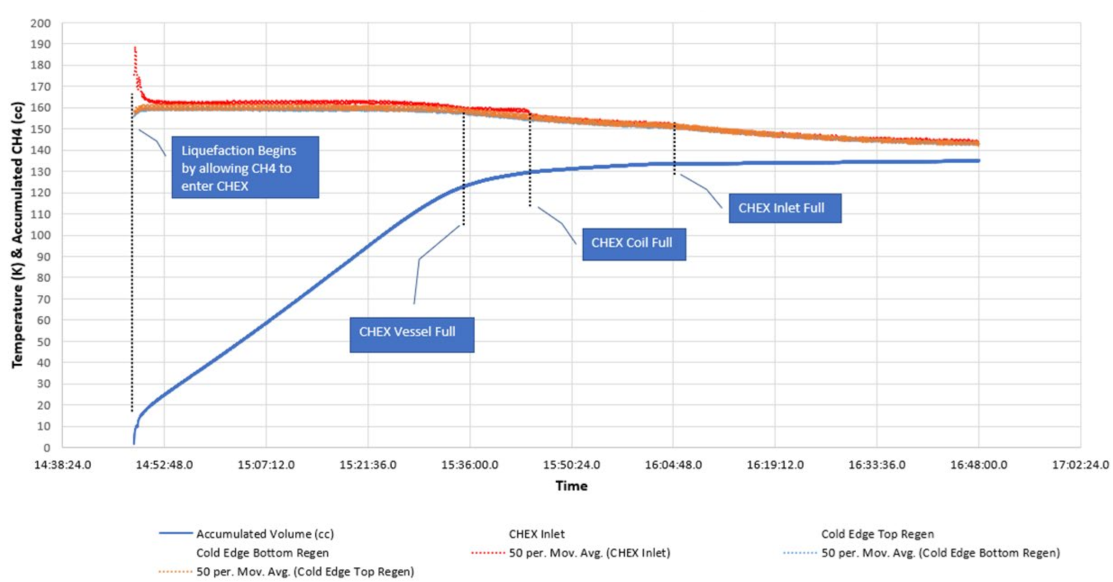

Figure 13. Temperature and LCH_4 accumulation vs time for methane liquefaction – CH_4 at 256

exchanger and the lecture bottle. Once condensation occurs for the set pressure of the methane, a cryopump is created by the reduction in pressure in the condensing heat exchanger by the ~600 times volume reduction upon liquefaction. The liquefaction rate remains almost constant until the small storage vessel is filled with liquid methane followed by filling the coiled tubing but at a smaller rate. When all cold storage volumes are filled, cryopumping stops and methane flow rate from the lecture bottle stops even though its valve is open.

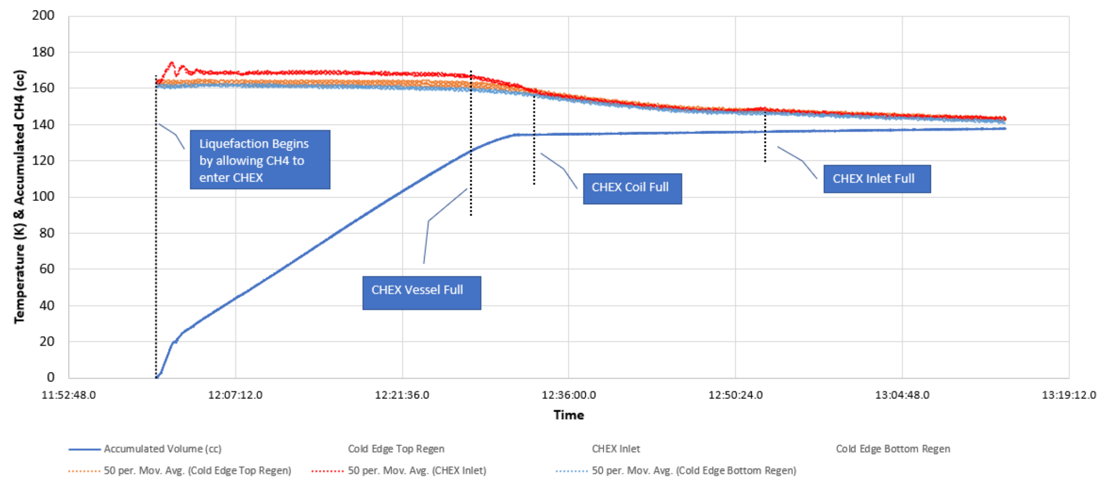

Figure 15. Temperature and LCH_4 accumulation vs time for methane liquefaction – CH_4 at 228 psia

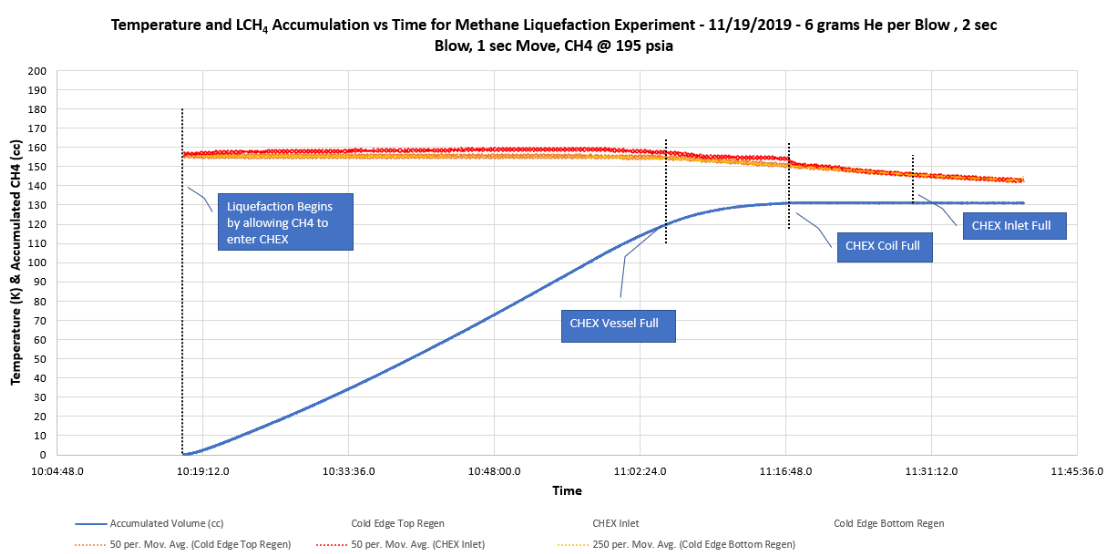

Figure 16. Temperature and LCH_4 accumulation vs time for methane liquefaction – CH_4 at 195 psia

Figures 17, 18, and 19 show detailed snapshots of temperature versus time for the cold edges of the regenerators, the CHEX inlet (Coil-in), and CHEX Vessel Top (Coil-out) as well as the methane flow rate during the liquefaction period for each run. The varied liquefaction rate revealed in the above charts reflects the fact that no cooling blow occurs while the regenerators are moving between magnetized and demagnetized states. Subsequently, the liquefaction rate varies in tandem with the blow/no-blow stages of the refrigeration cycle. A slight imbalance in temperatures between the top and bottom regenerator adds a secondary effect to the liquefaction rate where the top regenerator climbs above the saturation temperature of methane at the end of its cold blow stage causing a decrease liquefaction rate during this brief period of the stage.

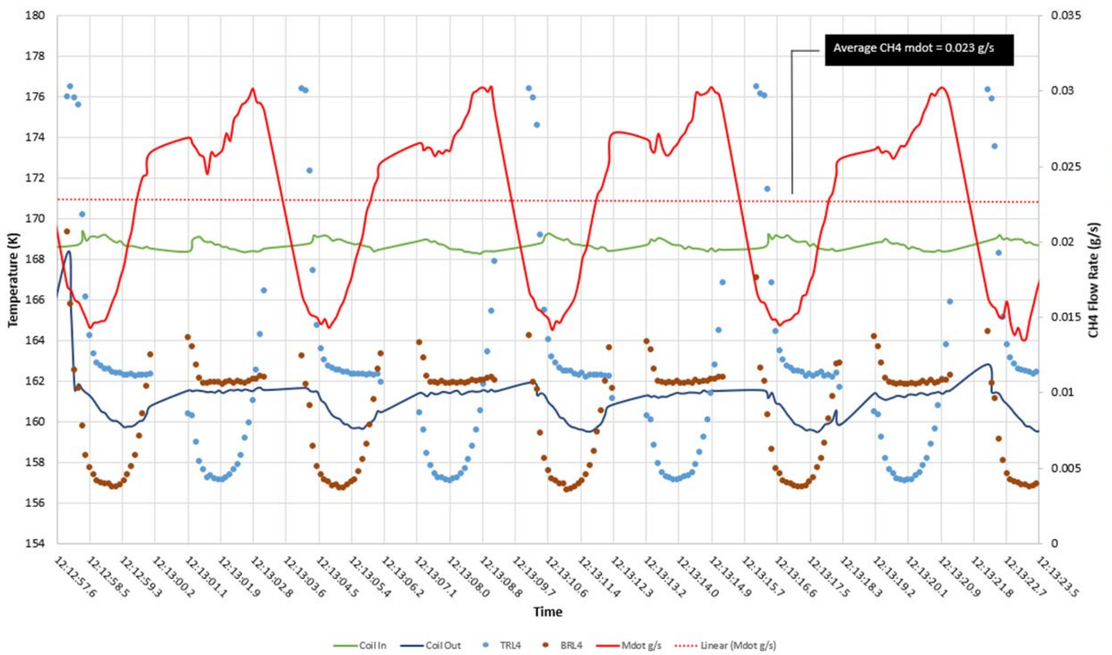

Figure 17. Temperature of cold ends and CH_4 flow rate vs time for methane liquefaction – CH_4 at 256 psia

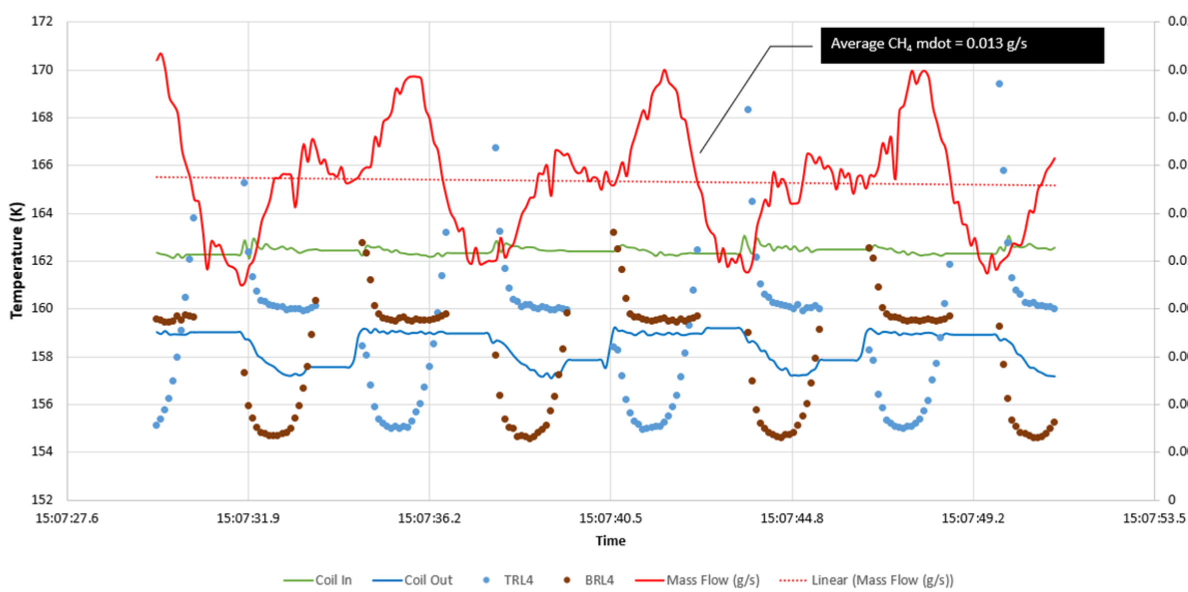

Figure 18. Temperature of cold ends and CH_4 flow rate vs time for methane liquefaction- CH_4 at 228 psia

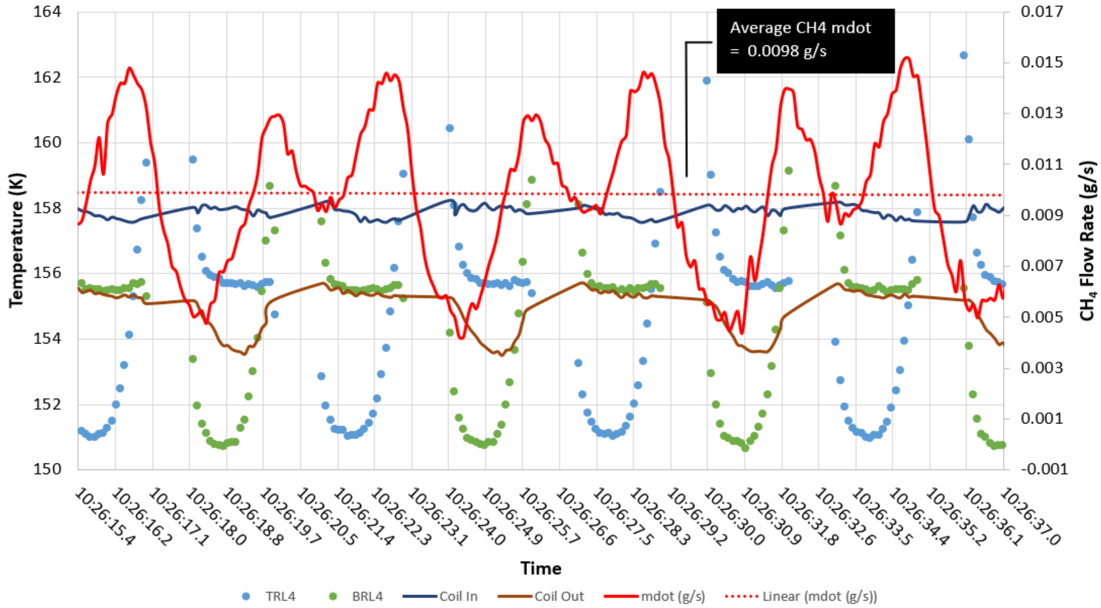

Figure 19. Temperature of cold ends and CH_4 flow rate vs time for methane liquefaction – CH_4 at 195 psia

Task 3. Techno-economic analysis

A techno-economic analysis was completed by Dr. John Barclay at Emerald Energy NW. A design basis of 50 tonne/day natural gas was used for the analysis. To perform a realistic very conservative cost analysis of a magnetocaloric liquefier for LNG, we chose a reciprocating active magnetic regenerative liquefier (AMRL) design that has been proven on a laboratory scale. The AMRL design is a 6-stage, serially coupled active magnetic regenerative refrigerator (AMRR) with a single refrigerant per stage shown in Figure 20. The active magnetic regenerator (AMR) cycle executed by an AMRR consists of four steps: hot-to-cold blow of heat transfer fluid (HTF) through a demagnetized regenerator; no HTF blow during magnetization; cold-to-hot HTF blow through a magnetized regenerator; and no HTF blow during demagnetization. Because cooling occurs once every four steps in an AMR cycle, four regenerators with sequential cooling steps in each stage are required to provide continuous cooling in its cold heat exchanger (CHEX)[1]. This combination is called a reciprocating QUAD configuration and is illustrated in Figure 21. Note the four identical regenerators sequentially execute the four steps of an AMR cycle. Further, use of three-way flow control valves enable use of a single HTF circulator per stage. The specific application used for the TEA design is a potentially important case of re-liquefying boil off gas (BOG) from LNG storage tanks. The minimum refrigeration power required for this application occurs when BOG is condensed before it warms above the dew point temperature of the LNG. The AMRR design selected for detailed analysis is a proven, low-risk multi-stage magnetic refrigerator with no process gas cooling as in a liquefier. In this case, no bypass fluid flow or process heat exchangers are required. The cold HTF flows from the hot-to-cold blows of four AMRs continuously pick up all thermal loads for each stage that includes the heat rejected from the adjacent colder stage. The detailed design basis specifications are as follows:

[1] Note: The acronym CHEX was used as Condensing Heat Exchanger in task 2 (see previous section above) and is used as Cold Heat Exchanger in task 3 (see this section)

- Compositions of the LNG and BOG are assumed to be pure methane
- Total rate of BOG re-liquefied per module is 5,000 kg/day (5 tonne/day)
- Pressure of LNG in tank is 15 psia
- Temperature of LNG at its dew point or bubble point at stated pressure is 112 K
- Six AMRR stages are used with a single magnetic refrigerant per stage
- Average temperature span of each AMRR stage is ~30 K
- Temperature span of AMRR is ~289 K to ~109 K
- High applied magnetic induction is 6.55 T
- Low applied magnetic induction is 0.15 T
- Frequency of AMR cycle in each stage/module is 0.4 Hz
- HTF compositions are mixtures of liquid propane/ethane/methane
- HTF pressure are 200 psia or 300 psia to maintain subcooled liquid conditions throughout each AMR cycle for the respective stage
- HTF properties are calculated at mean temperature of each stage
- Magnetic refrigerants are known characterized rare-earth metals, alloys, or intermetallic compounds.

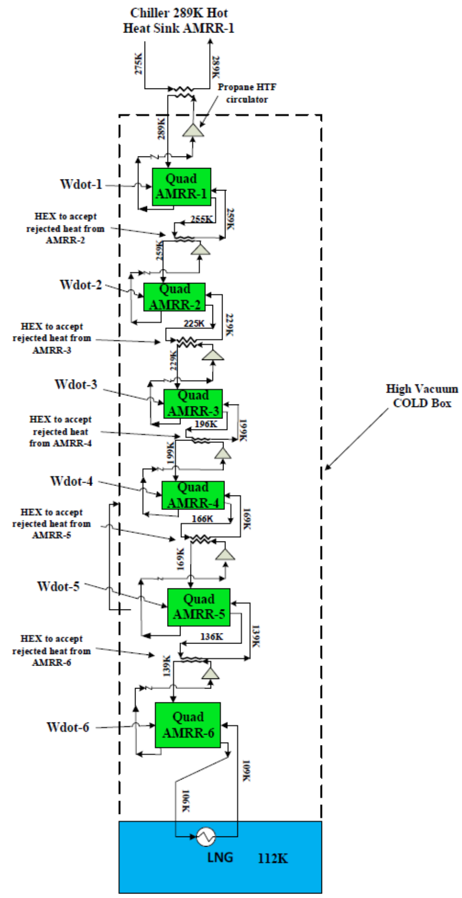

Figure 20. Block process flow diagram of a six stage serially coupled active magnetic regenerator refrigerator

The thermal loads for the CHEX of each stage illustrated in Fig. 20 were sequentially calculated from the coldest stage up to the warmest stage. The external parasitic and direct longitudinal conduction loads for each stage were included although they are dominated by rejected heat and HTF pump power from the adjacent colder stage except in the coldest stage. In this instance (for stage 6), the cold loads are dominated by the latent heat of condensation of the BOG back into the LNG reservoir. The thermal loads are used to determine energy flow, entropy flow, regenerator mass, and HTF flow of each AMRR stage.

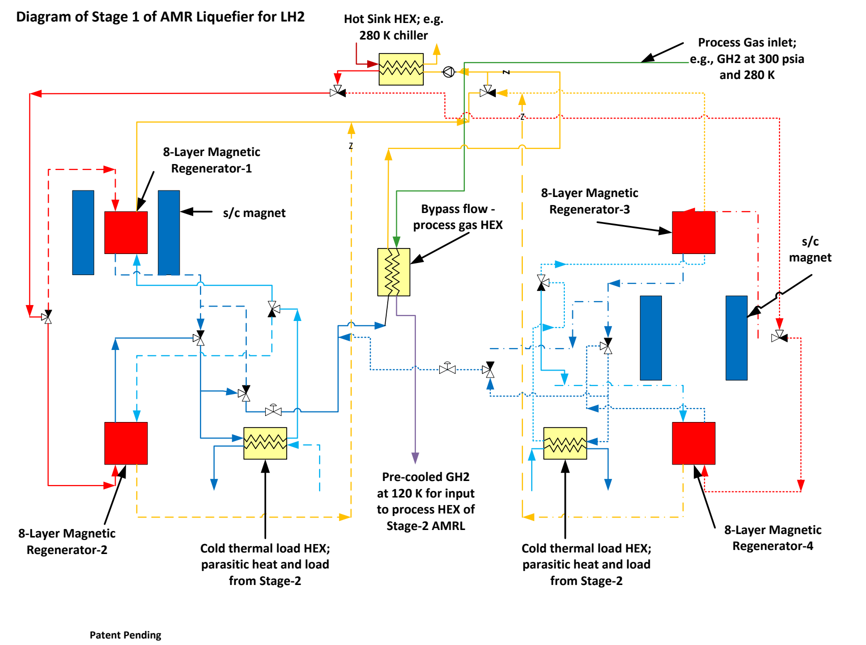

Figure 21. Diagram of major components of first stage in a reciprocating QUAD configuration multi-layer refrigerator

The initial design choice for BOG re-liquefaction was a 50 tonne/day AMRR. However, while it is possible to make this in a single 6-stage design, the irreversible entropy from pressure drops of the required large HTF flows through single, large spherical-particle regenerators was too large to achieve high thermodynamic efficiency in each stage. To overcome the low FOM, the 50 tonne/day BOG re-liquefaction plant was split into identical parallel AMRR modules with re-liquefaction capacity of 5 tonne/day (~3,131 gpd of LNG). Each module has reciprocating dual regenerators in a QUAD configuration for continuous cooling to the thermal loads which requires two identical magnets per stage.

The smaller module size significantly reduces sizes of the superconducting magnets, regenerators, pressure drop per module, and HTF circulators of each module. This module-size change increases the re-liquefier efficiency including the HTF pump power to FOM of 0.60. Obviously, 10 identical modules are required instead of 1 module to achieve the 50 tonne/day target for this TEA. The identical AMRR modules have high potential to be integrated in various ways such as putting several (6-8) magnets together in a common cold box. The detailed design of the integrated plant was beyond the scope of this TEA; however, this multiple parallel module approach yields a high achievable FOM for the larger plant. The estimated capital costs for 5 tonne/day were calculated in detail. The estimated cost of the 50 tonne/day BOG system was obtained by scaling the ratio of capacities to the 0.7 power (which is a standard value used in chemical engineering). In addition, this TEA analysis helped identify many design improvements that could enable individual module capacity to be increased to 10 or even 25 tonne per day while retaining the high FOM and simultaneously significantly reduce to the capital cost per unit capacity.

The specifics for how the costs of major components of the AMRR is considered proprietary. If the DOE desires the specifics, the TEA can be provided in a business sensitive report. As mentioned previously, this estimate is technically very conservative because it does not require layered regenerators nor controllable diversion flow valves for optimum operation. Rather it uses a separate stage for each of the six materials.

This requires two superconducting magnets for each of the six stages which increases the capital costs substantially. Proprietary models were used to calculate the heat loads for each stage, determine the mass of each refrigerant per regenerator, and thus the costs for each material. The material costs were indexed to account for processing to the desired form and regenerator installation. The size and the costs of the superconducting magnets were optimized using known techniques from magnet vendors. The HTF flows required were included as indicated above, other balance of plant and construction materials costs were included in the TEA. Table 5 below summarize the capital costs of AMRL designs that produce 5 and 50 metric ton/day of LNG from BOG. The 50 tonne/day re-liquefier is comprised of 10 identical 5.0 metric ton/day modules in parallel with 6 QUAD stages cooling from 289 K to ~109 K. The costs of the larger plant were scaled from the 5 tonne/day module by the liquefaction capacity to the 0.7 power that is commonly used in chemical engineering literature to estimate larger or smaller plant costs from a known value.

Table 5. Capital costs of each subsystem for the multi-stage AMRR for re-liquefaction of Boil-off gas

MCL subsystem	Cost-5 tonne/day BOG-LNG	Cost – 50 tonne /day BOG- LNG	% of total cost of 5 tonne/day module
Magnetic regenerator sub-system	$1,126,336	$5,645,051	21.2%
Regenerator housing assembly	$240,000	$1,202,849	4.5%
Superconducting magnet sub-system	$1,087,997	$5,452,904	20.5%
Conduction cooling of magnets	$220,000	$1,102,612	4.1%
Heat transfer fluid circulators	$210,000	$1,052,493	4.0%
Chiller, heat rejection HEX, interstage HEX, cold HEX	$1,080,000	$5,412,822	20.3%
Piping and valves	$162,000	$811,923	3.1%
Drive subsystem	$90,000	$451,069	1.7%
Structural subsystem and enclosures	$192,000	$962,279	3.6%
Instrumental/control subsystem	$900,000	$4,510,685	17.0%
Total	**$5,308,333**	**$26,604,688**	**100%**

The overall FOM calculated for the 6-stage, 5 tonne/day AMRL re-liquefier is 0.60. The constraints of the design to obtain this high FOM such as reducing the frequency from ~1 Hz to 0.4 Hz directly increase the mass of magnetic refrigerants required by over a factor of two. The larger regenerators require larger high-field magnets. These two AMRR components contribute almost 50% of the total cost of the AMRR. If the frequency is increased for this particular design basis, the FOM drops by almost 1/2 due primarily to irreversible entropy generation from pressure drops for HTF flows through the regenerators. This additional irreversible entropy is rejected at heat into the adjacent warmer stage. The increase in CHEX thermal loads increases the mass of refrigerant required to lift the load by the ~30 K per stage. Thus, increasing frequency without maintaining the FOM does not reduce the mass of refrigerants by the ratio of the frequencies. The process flow analysis done in the TEA shows that reducing the viscous dissipation of the HTF is a powerful way to reduce irreversible entropy generation within the regenerators and pump power simultaneously. This design challenge requires attention for optimization of the regenerator/HTF subsystem and maintain the high FOM while reducing three major components of the cost.

The detailed thermodynamic analysis of a **1-layer/stage, 6-stage design** spanning large temperatures such as ~289 K to ~109 K illustrates that it is one limit of AMR design space. A **6-layer/stage, 1-stage design** spanning the same temperatures is the other limit of AMR design space.

In the multi-stage design, each stage operates as a separately controllable unit with their own HTF flow circuit, so each stage requires no diversion flow of HTF. This design provides the simplicity of independent control of HTF mass flow rate, easy accommodation of variable process thermal loads and rejected thermal loads from the adjacent colder stages. The amount of bypass flow can be varied at each stage to match variable process loads such as found in many process streams. The multi-stage design uses a single refrigerant per regenerator and has readily measured thermal flows through the entire device. These advantages come at the complexity of many additional superconducting magnets.

Alternatively, a multi-layer design spanning the same temperature range minimizes the number of magnets. E.g., in the reciprocating, dual-regenerator case with 5 refrigerants, the number of s/c magnets is reduced from 10 to 2. However, the sizes of 2 multi-layer magnets are somewhat larger than those in the multi-stage design) but increases the complexity of the regenerators and correct flows in the combined single HTF subsystem. For high FOM designs, both controllable diversion flow rates of HTF between each layer and the ability to add or remove thermal loads to/from the cold or hot diversion flows after it leaves each layer in the demagnetized regenerator and before it enters the corresponding layer of the magnetized regenerator.

The new and important insight is that these two design limits must be thermodynamically similar because they transition continuously from one limit to the other limit. This emphasizes additional important development tasks that need to be completed such as:

- Develop hermetic diversion flow paths with controllable flow rates; and
- Develop means to add a thermal load to each diversion flow because bypass flow and parasitic heat leaks are not sufficient to effectively accomplish this requirement.

The TEA for a reciprocating, multistage AMRL for re-liquefying BOG from a large LNG vessel was completed. It used a MCL design that could be built today for a known application to estimate reachable liquefier capital cost. In comparison, the cost of a ~30,000 gpd LNG (~50 tonne/day) liquefier plant for pipeline natural gas feedstock using conventional liquefier technology (turbo-Brayton or Mixed refrigerant) is approximately \$20 MM. The cost of the specified **multi-stage** magnetic liquefier is ~20% higher than that. Use of a **multi-layer** MCL design incorporating changes to the regenerator geometry to reduce pressure drop of HTF flows and enable operation up to ~1 Hz, reduces the capital costs estimated in the TEA by ~40%, to ~ **\$3.1 MM for the 5 tonne/day liquefier and ~\$15.3 MM for the 50 tonne/day plant**. These values are well below those of comparable conventional LNG liquefiers. The increase in FOM by ~2 will reduce the power component of operating costs an AMRL to about ½ that of a conventional liquefier design. This is important because power costs are a major contributor to operating costs of liquefier plants. This is especially true for a BOG re-liquefier system. The cost analysis presented herein will become more precise when a complete Bill of Materials is available from a detailed, optimized mechanical design and firm quotations can be obtained from numerous vendors.

V Commercialization Summary:

An important aspect of the TCF is consideration of commercialization of the MCL technology for production of LNG. The commercialization tasks are below.

Task 1. Merchant LNG Market refinement.

The United States (U.S.) presently uses ~100 quads of energy per year (~105.5 exajoules in 2018) at a cost of ~$2 trillion U.S. dollars. The uses are segmented into five energy-use sectors: transportation; industrial; residential; commercial and electric power generation. In 2018 natural gas (NG) provided about 1/3 of the total U.S. sources of energy for these use sectors. By liquefying pipeline natural gas (PNG) at atmospheric pressure, the volumetric energy density (MJ/m^3) increases by ~625 times which makes its storage, transport, and delivery as liquid natural gas (LNG) an important element of NG energy supply chains for several U.S. end-use sectors.

The U.S. global and domestic LNG industry has been transformed over the last decade after precision drilling and fracturing technologies gave economical access to large shale deposits containing many decades of NG supply (and oil) at present use rates. Conversion of shale gas (also referred to as non-conventional NG) into LNG for inexpensive transport to global customers has become a large and rapidly growing international business that benefits the U.S. economy in multiple ways. The large supply of shale gas injected into the extensive U.S. pipeline network has kept PNG prices low (typically ~$2.50/MMBtu at well-known market hubs and even below that recently). However, the domestic and global LNG energy supply business models are distinct from one another because big consortia of mega-scale businesses are required to successfully execute global LNG export projects using U.S. shale gas feedstock. It is no surprise that such large consortia aren't very interested in domestic LNG projects that are ~100 times smaller, i.e., it isn't cost-effective for huge energy companies to use their resources to do small projects. Consequently, there are numerous smaller robust businesses focused on various parts of the domestic energy supply and end-use chain for PNG and LNG. During an extensive search of relevant literature, we found substantial energy supply chain data on the existing and steadily expanding global LNG energy business arena in which the U.S. is a major participant. The liquefaction capacity of LNG plants developed at export ports is several millions of gallons of LNG/day. Such huge plants require multi-billion-dollar investments and need decade-long operational perspectives to create fundable successful projects. Detailed assessment of all types of risks is a key task during the comprehensive feasibility phase of such mega-scale projects. It is no surprise that new-technology risks are avoided in such projects! A new liquefaction technology, no matter how efficient or cost-effective it may be, must commercially demonstrate such impressive performance for a decade or more before it will be considered in mega-scale LNG projects. Therefore, to explore the impact of evolving development of highly efficient and lower capital cost liquefaction technology, EENW focused this LNG market assessment report on micro-, small-, and mid-scale LNG domestic U.S. markets that are potentially impacted by significantly better liquefaction technology. The primary objective of this market study was to quantitatively identify existing LNG end-use demand and present merchant LNG supply which will provide a good basis to develop a business case for potential applications of magnetocaloric liquefier technology.

The U.S. merchant LNG demand estimates at the beginning of 2019 are summarized by energy sector in Table 6. These data were obtained from reliable sources such as the Energy Information Administration web site and corroborated by comparing those data to data from published reports from companies, energy institutes, professional organizations, and private communication. The industrial and transportation sectors are further segmented in subsectors such as for marine vessel fuel, heavy duty vehicular fuel, and rail fuel. No attempt was made to estimate the growth rate of LNG used among the various sectors to maintain a set of demand data that is already established.

Table 6. Summary of Merchant U.S. LNG Demand by End-Use Sector as of the fall of 2019

Merchant LNG Demand by End Use Sector in US as of the fall of 2019	
Sector	**Estimated LNG use (GPD)**
Residential	0
Commercial	0
Industrial	790,000
Electrical power generation	910,000
Transportation	850,000
TOTAL	**2,550,000**

Making LNG from NG typically increases its market value ($/MMBtu) by ~4-5 times the local feedstock value of PNG[1]. (N.B. The cost of NG feedstock/gallon of LNG purchased at Henry Hub prices is only $0.16!). LNG provides thermal capacitance because it can be cost-effectively stored and transported in cryogenic tankers. When LNG is re-gasified, the LNG converts back into the gaseous state to satisfy most end-users. The safe use of PNG/LNG is well established via compliance with an array of codes and standards (e.g., NFPA, ASME, API) that are enforceable by federal (FERC), state (utility commissions), and local (fire marshals) rules and regulations.

A list of available merchant LNG suppliers producing 1000's of gallons of LNG per day was compiled and is presented in Table 7. These entries are from EENW's experience in small-scale LNG production and from the public literature, published reports for clients from reputable marketing study groups, individual company web sites, professional society news briefs, LNG marketing newsletters, stock market investment searches, USPTO patent publications, and private communication with contacts engaged in the merchant LNG business. The web site of each company was accessed to confirm (to the extent possible) what their LNG production rates were as of early 2019. The list includes a few utilities who have presented arguments to their utility commissions that guarantee rate-base customers in the utilities' area will have priority and only excess LNG will be sold to merchant customers. In most cases, the original peak shaver liquefaction plant has been upgraded to increase both LNG production rate and storage plus tanker transfer infrastructure. Most of the merchant plants in Table 7 are relatively new plants given their lifetime is 25-30 years or longer.

1 There are several "hubs" in the extensive natural gas pipeline network where several pipelines are interconnected, and gas is bought and sold among different entities who purchase PNG from one another for use around the U.S. The transfer price changes continuously as transactions are negotiated. Henry Hub in Louisiana is a well-known hub used by New York Mercantile Exchange (NYMEX) for NG transactions. Recent prices were just under $2/MMBtu.

Table 7. Merchant LNG suppliers in the U.S. as of fall of 2019

Compiled from multiple sources and validated by cross referencing plus some direct communication		
Vendor Name	**Location**	**Potential LNG production capacity (GPD)**
Applied LNG-1 (2 trains)	Needles, AZ	172,000
Applied LNG-2	Midlothian, TX	86,000
Clean Energy-1	Boron, CA	160,000
Clean Energy-2	Willis, TX	100,000
Distrigas (now Exelon; a portion of LNG capability is sold for non-peak shaving use)	Everett, MA	100,000
Eagle LNG (Ferus Group)	Maxville, FL	87,000
Elba Island LNG (some LNG for non-export uses)	Savannah, GA	100,000
ExxonMobil (gas processing plant)	Shute Creek, WY	60,000
Ferus LNG	Edmonton, Alberta	100,000
FortisBC (peak shaving with most for LNG fuel)	Vancouver, BC	450,000
Intermountain Gas (peak shaving and LNG fuel; amt shown is for merchant customers) [MDU Resource Gp]	Nampa, ID	20,000
JAX LNG (Pivotal LNG and NorthStar Midstream JV)	Jacksonville, FL	120,000
Kinetrex Energy (2 plants-Citizens Energy Group)	Indianapolis, IN	200,000
Merit Energy Painter Processing Plant (downstream of Chevron gas processing plant)	Evanston, WY	35,000
Memphis LGW (Utility allowed to sell LNG as fuel)	Capleville, TN	30,000
New Fortress Energy LNG plant (2 in the US; LNG for export in PA; LNG for local use and export to Caribbean) [Fortress Investment Gp]	Miami, FL and Bradford County, PA	100,000
NiCHe LNG (Dominion Energy)	Towanda-, PA	50,000
North Dakota LNG (became Alkane Midstream in 2019)	Tioga, ND	76,000
NuBlu Energy	Port Allen, LA	30,000
Pivotal LNG (Southern Gas Co/Southern Co)-1	Tussville, AL	60,000
Puget Energy -2021 (600,000 gpd in 2021)	Tacoma, WA	
Passyunk Energy Center (120,000 gpd in 2021)	Philadelphia, PA	
Spectrum LNG	Ehrenberg, AZ	60,000
Stabilis Energy (Prometheus Energy)	George West, TX	120,000
TOTAL		**2,316,000**

Task 2. Business Case for Active Magnetic Regenerative Liquefiers and Refrigerators.

To explore the impact of evolving development of highly efficient and lower capital cost liquefaction technology, this business case assessment is focused on micro-, small-, and mid-scale liquid natural gas (LNG) domestic U.S. markets that are impacted by better liquefaction technology. The primary objective of this report is to whether there is a business case for magnetocaloric liquefier technology. PNNL wants to know if there is a good business case for active magnetic regenerative liquefaction (AMRL) technology, and if so, what are the potential niche areas, who are potential companies active in these areas, and when they may collaborate with and eventually license AMRL technology for cryogenic applications such as LNG.

Emerald Energy NW (EENW) was retained to assess whether an attractive business case exists for a successful company in the domestic U.S. LNG energy industry.

From the complementary domestic LNG marketing study recently completed by EENW prior to this business-case study, It is clear that adoption of LNG fuels depends primarily on: i) price differential between LNG and diesel/gasoline on equivalent energy basis; ii) much more distributed supply and end-use infrastructure; iii) increasing rate of adoption by niche-market customers; and iv) mandates related to lower-carbon fuels that reduce noxious and/or climate-related emissions. Among these drivers, the growth of LNG use is primarily caused by its energy-equivalent price advantage over diesel with simultaneous reduction of problematic emissions. Good examples are in the transportation sector by high-horsepower terrestrial vehicles, and by marine fleets that want to economically comply with various fuel emission-related state, federal, and international regulations.

Key supply business attractors are: i) surplus of cheap natural gas, ii) new customers, iii) marketing innovations to reduce new fuel adoption risks for customers, and iv) new, improved micro-scale purification and liquefaction technologies. Today's micro- and small-scale U.S. merchant supply is primarily from conventional LNG plants of ~100,000+ gpd size (i.e., small scale) with limited coupling to existing PNG peak-shaving plants at utilities with surplus, but restricted, liquefier capacity. The perception of most U.S. LNG energy businesses is that conventional liquefaction technology is mature, proven, and widely available in a range of capacities that allow for simplicity, modularization and acceptable efficiency. Small-scale liquefaction capacity for localized U.S. merchant LNG markets has increased slowly from 2010 to 2019 resulting in total daily production capacity that meet existing LNG demands. The continued localized micro- and small-scale LNG plant growth fits well with a better appreciation of the negative price impact on the price advantages that LNG has over diesel and gasoline of truck delivery costs for round trip deliveries longer than ~300 miles. Distributed, smaller LNG liquefiers closer to end users gives a larger price advantage to LNG which in turn, encourages investment in additional wide-spread infrastructure. Both are critical to growth of micro- and small-scale LNG markets.

The existing need for LNG liquefiers is satisfied by gas-cycle technologies that execute several steps to execute a liquefier cycle. These steps include gas compression with rejection of heat of compression into a heat sink, cooling high pressure gas in heat exchangers, expansion of gas to obtain cooling for thermal loads, and warming low pressure gas in heat exchangers to complete the cycle. Conventional LNG liquefiers such as turbo-Brayton or mixed refrigerant cycle devices have maximum efficiencies characterized by a figure of merit (FOM) defined as the ratio of ideal work input to real work input of ~0.35 at best.

Turbo-Brayton or mixed refrigerant cycle devices are used to produce most of the merchant LNG used today for **marine and high-horsepower engine fuel** markets. Conventional gas-cycle refrigerators are also used for **re-liquefaction of boil-off gas from ocean transport of LNG**. These two applications were selected to determine whether an attractive business case exists for MCL plants.

If highly efficient active magnetic regenerative liquefiers can decrease delivered LNG fuel prices by an additional 20-30% to provide fuel customers $1-2/energy-equivalent gallon price advantage over existing diesel fuel prices, heavy duty truck fleet owners and high-horsepower equipment users will make economic driven choices to switch to LNG with its excellent environmental benefits as the extra incentive. Based on examination of the reasons why adoption of LNG fuel for these applications has been far slower than DOE and others projected ~8-10 years ago, one of the primary issues is that the end-users in this LNG conversion had to accept too much risk with insufficient economic or other benefits to act. Creating a stable, large fuel price advantage that small-scale modular MCL technology can provide for LNG close to end users. This eliminates excessive transport cost adders onto fuel price and helps overcome the margin of indifference to change and to provide near-term ROIs of at least 15% on strategic investments in conversion equipment and/or trucks from diesel fuel to LNG. A related example in the transportation sector is the fact that low-sulfur emission requirements for ocean going vessels agreed to by all members of the International Maritime Organization have gone into effect over the last decade and caused rapidly increasing use of LNG as fuel. Bunkering (refueling) this fuel along the expansive coasts of the U.S. is a rapidly growing segment in the transportation sector. Supplying LNG for localized bunkering operations is a distributed growth market for highly efficient and inexpensive liquefiers that needs to be aggressively pursued to potential find a partner to help PNNL commercialize LNG MCL plants. The transportation fuel market has the potential to grow enormously because the U.S. spends ~$675 billion/year on transportation fuel, mostly on diesel fuel and gasoline. If market entry for LNG can be successfully accomplished, this is a huge growth market for small-scale MCL plants.

There are approximately 500 ocean-going LNG vessels operating today. All of them have to effectively manage the intrinsic boil off from heat leak into the cryogenic liquid during the 10-30-day voyages to global NG import customers in the EU and Asia. The higher efficiency of active magnetic regenerative refrigerators (AMRR) that re-condenses the boil off with less input power (produced by a small fraction of the boil-off gas) which increases the net amount of the LNG delivered to customers. Further, the robust operational features of an AMRR system with its structurally strong features, ~1 Hz operation, solid-state refrigerants, and stationary superconducting magnet systems contribute to an AMRR capable of managing boil-off gas in LNG vessels under harsh ocean-transport environment, i.e. in rough seas and from continuous wave action. As the array of LNG-fueled vessels increases from small to large (e.g., harbor ferries and tugboats up to massive 200,000 m^3 of LNG carriers and 6,000 passenger cruise ships), the need for an array of bunkering vessel will increase. The modular features of efficient and low-cost MCL designs should be attractive to companies who are developing such vessels as the primary business model.

<u>Task 3. Industry Engagement</u>.

The goal of this task was to identify business partners to collaborate in the commercialization of this work. PNNL's business plan is to license the technology to motivated partners and then serve as consultants as the technology is moved to commercialization. This task helped identify of one or more industrial partners interested in collaboration to accelerate commercialization of the MCL technology.

We have had several good discussions with Air Liquide, Shell, Air Products, Southern Cal Gas and others as part of this effort. Shell visited PNNL in August to see our lab-scale system and to discuss possibilities for future collaboration. We've continued to have numerous telephone conversations, mostly to explore if they are interested in cost-sharing for PNNL proposals to the DOE. We know Shell is interested in both terrestrial and marine applications but appear reluctant to enter into meaningful cost-sharing arrangements at this time. Southern Cal Gas is also expressed significant interest in MCL technology for LNG applications the decision-making executives want small-scale commercial systems, rather than an engineering-scale or pilot-scale MCL systems. We are working with several others on a confidential basis. Details of the engagements are business sensitive and available upon request from the DOE.

VI References

Barclay J A, K. Brooks, J. Cui, J. Holladay, K. Meinhardt, E. Polikarpov, E Thomsen. 2019. "Propane Liquefaction with an Active Magnetic Regenerative Liquefier." *Cryogenics*. 100 (2019) 69-76. doi.org/10.1016/j.cryogenics.2019.01.009

Holladay J, Meinhardt K D, Polikarpov E., Thomsen E., Teyber R., Barclay J., Cui J., Jensen B., Anderson I. 2017, "Magnetocaloric Hydrogen Liquefaction". DOE Hydrogen and Fuel Cell Program FY2017 Annual Progress Report. Available at: https://www.hydrogen.energy.gov/annual_progress17.html

Holladay J D, Teyber R., Meinhardt K D, Polikarpov E, Thomsen E C, Archipley, C., Cui J., Barclay J A, 2018a, "Investigation of Bypass Fluid Flow in an Active Magnetic Regenerative Liquefier" Cryogenics (2018a), doi.org/10.1016/j.cryogenics.2018.05.010.

Holladay J, Meinhardt K D, Polikarpov E., Thomsen E., Barclay J., Archipley C., Cui J., Wolf S., Anderson I. 2018b, "Magnetocaloric Hydrogen Liquefaction". DOE Hydrogen and Fuel Cell Program FY2018 Annual Progress Report. Available at: https://www.hydrogen.energy.gov/annual_progress18.html

Meinhardt K D, Polikarpov E, Thomsen EC, Teyber RP, Holladay JD, Cui J, Barclay J A; 2019. "Design and experimental analysis of a superconducting Active Magnetic Regenerative Refrigerator" *Applied Thermal Engineering* (submitted)

Teyber RP, Meinhardt K D, Thomsen EC, Polikarpov E, Holladay JD, Cui J, Barclay J A; 2017. "Passive force balancing of a Superconducting Active Magnetic Regenerator" Journal *of Magnetism and Magnetic Materials* 451:79-86. 10.1016/j.jmmm.2017.11.002.

Teyber R, J Holladay, K Meinhardt, E Polikarpov, E Thomsen, J Cui, A Rowe, J Barclay, 2019. "Performance investigation of a high-field active magnetic regenerator," Applied Energy, 236(C), 426-436.

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