Production of LNG with an Active Magnetic Regenerative Liquefier

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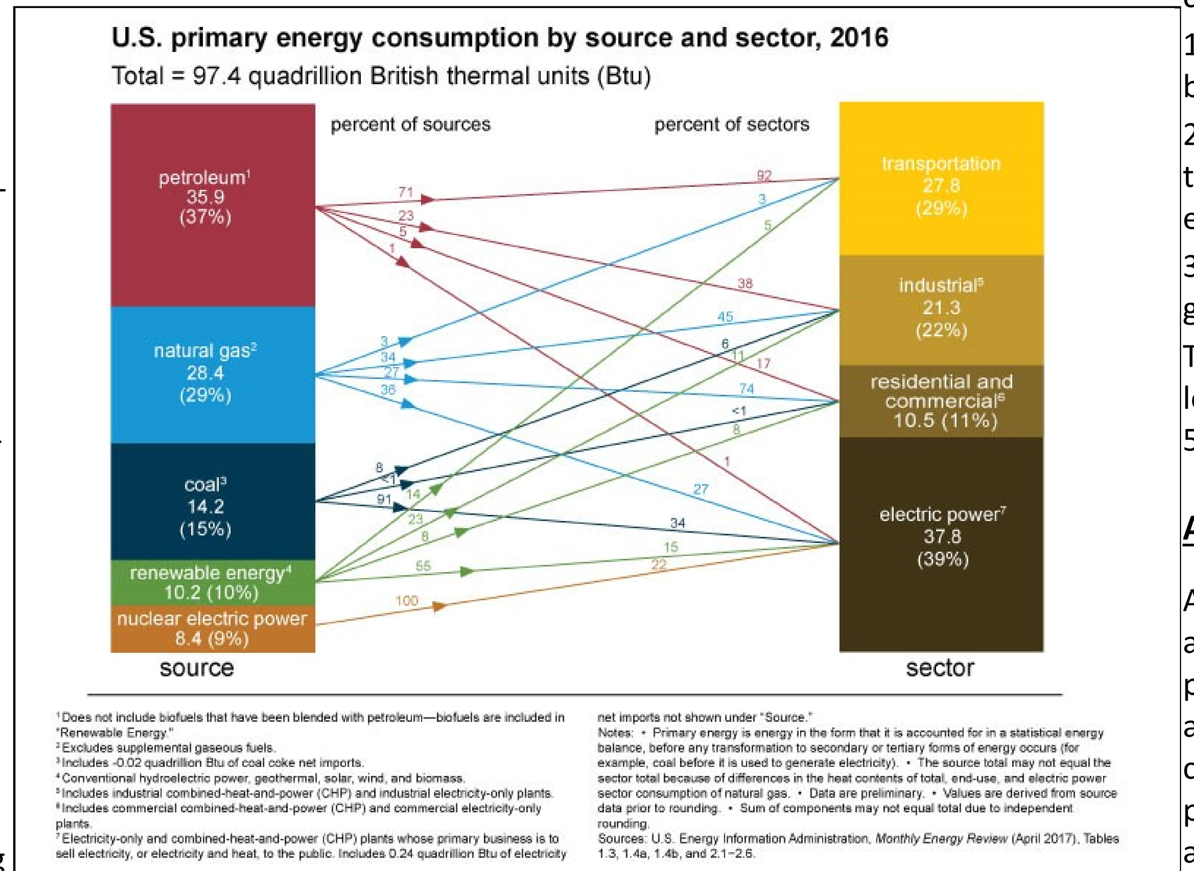
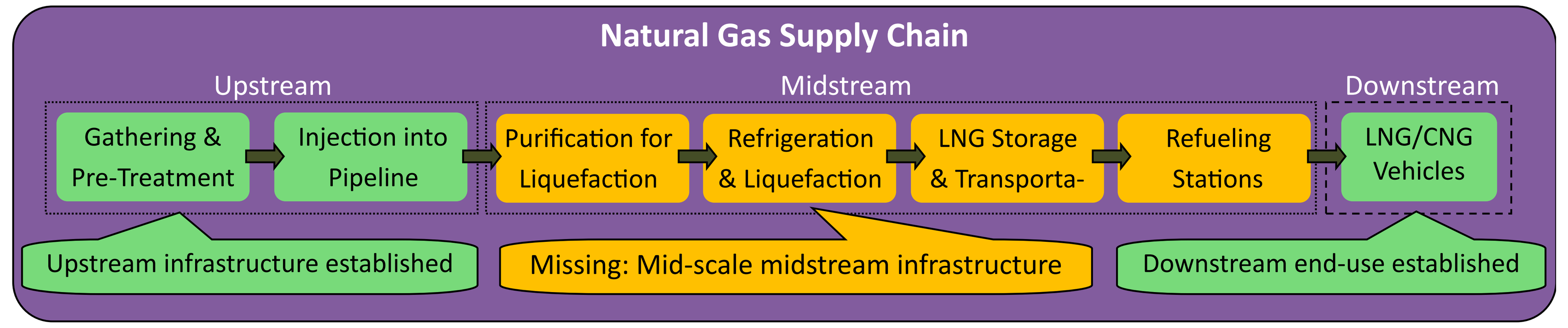
Introduction

In its various forms, energy is tightly linked to essentially all aspects of our life including food, water, environment, climate, quality of life, jobs, security, waste, and especially economics. The US energy source to end use diagram below summarizes the complexity of this essential element of our life.

Natural gas is a mixture coming from many sources such as gas wells, associated gas with oil, coal mine gas, anaerobic digestion of complex organic materials in digesters and landfills. Since 2006 improved horizontal drilling and shale-fracturing techniques have enabled the economic development of numerous large, deep U.S. shale deposits. Injection of plentiful shale gas into the extensive U.S. pipeline network has caused the price of pipeline natural gas (PNG) to be low and stable. The resultant stable domestic price of bulk PNG is ~$4/MMBtu or less. The additional processing of this PNG feedstock to make, store, distribute, and use liquid natural gas (LNG) increases its value to ~$10-$12/MMBtu.



For many end users, the most reliable and cost-effective means to use inexpensive NG involves local production, storage, transport, and delivery as LNG. Given the low feedstock costs, the operating costs are a key component of the price of LNG. A major technical barrier for LNG is the lack of highly efficient methods of liquefaction that are simultaneously less expensive than existing technology. At smaller liquefier sizes such as those needed for distributed-scale plants, this technology gap must be met to enhance adoption of LNG into the US$675 billion/year transportation fuels market. Active magnetic regenerative refrigeration (AMRR) technology offers promise in this industry.



Conventional Liquefaction Techniques

The Figure of Merit (FOM) for liquefaction of natural gas is defined by the ideal work rate per mass flow divided by the actual work rate per mass flow. It depends upon gas composition, initial temperature and pressure of the gas and final condition of the cryogenic liquid. Natural gas is primarily methane so it provides a easy reference case. The ideal work of liquefaction of methane is 1050 kJ/kg starting from 300 K and 1 atmosphere. Three natural liquefaction techniques dominate the commercial large scale plants are:

1. Cascade type based on Hampson-Linde stages, each with different but usually pure gaseous refrigerants
2. Several types of Mixed Refrigerant Cycle designs with similar cocktails of refrigerant mixtures, e.g., iso-pentane, butane, propane, ethane, methane, argon, and nitrogen.
3. Turbo-Brayton types with a single pure refrigerant such as nitrogen gas.

The FOMs range from 0.25 to 0.35 for large-scale turn-key plants and lower values as the capacity decreases to small-scale plants below 50,000 gpd of LNG.

Active Magnetic Regenerative Liquefier (AMRL)

A regenerative magnetic refrigerator uses working materials such as magnetic solids whose magnetic order or magnetic entropy depends on temperature and applied magnetic field. With such a magnetic refrigerant, cooling is accomplished by a 4 step mechanical cycle as follows: **1)** The magnetic refrigerant is adiabatically placed in a magnetic field. The conservation of total entropy in this adiabatic process requires that the refrigerant increase in temperature to compensate for the increased order in the magnetic moments or decrease in magnetic entropy of the magnetic refrigerant due to the external magnetic field. This temperature change is sometimes called the adiabatic temperature change. **2)** A working fluid such as helium or liquid propane is pumped through the magnetic refrigerant to transfer heat created by the adiabatic temperature change in the solid to a heat sink. **3)** The magnetic refrigerant is then removed adiabatically from the magnetic field, producing a corresponding temperature decrease. **4)** The working fluid is passed through the magnetic refrigerant again to transfer the cold from the bed to a thermal load such as a process stream. (The change in temperature of a magnetic material that occurs as a result of an adiabatic change in externally applied magnetic field is called the magnetocaloric effect.) The magnitude of this temperature change is typically about 2 K per Tesla or a total of about 10-15 K for 5-6 T. Unlike traditional techniques for liquefaction, the work performed by the AMR cycles is distributed between inducing a magnetic field, pumping a working fluid through the magnetocaloric material, and any irreversible losses in these processes. Subsequently, FOMs associated with the AMR cycles are over double that of traditional techniques: 50—80%.

Design Basis

- A mid-sized stage-type device that cools a methane process stream at 300 psia and 280 K to produce 1000 gallons of LNG per day.
- Formulation of magnetocaloric porous bed materials for maximized adiabatic temperature changes and field/temperature-dependent effects to heat capacity for specific and narrow operating temperature ranges.
- 20 K spans per stage resulting in 8 stages to cool to 120 K
- Substantial reduction in irreversible entropy through the use of bypass to decrease approach temperatures in process stream heat exchangers.

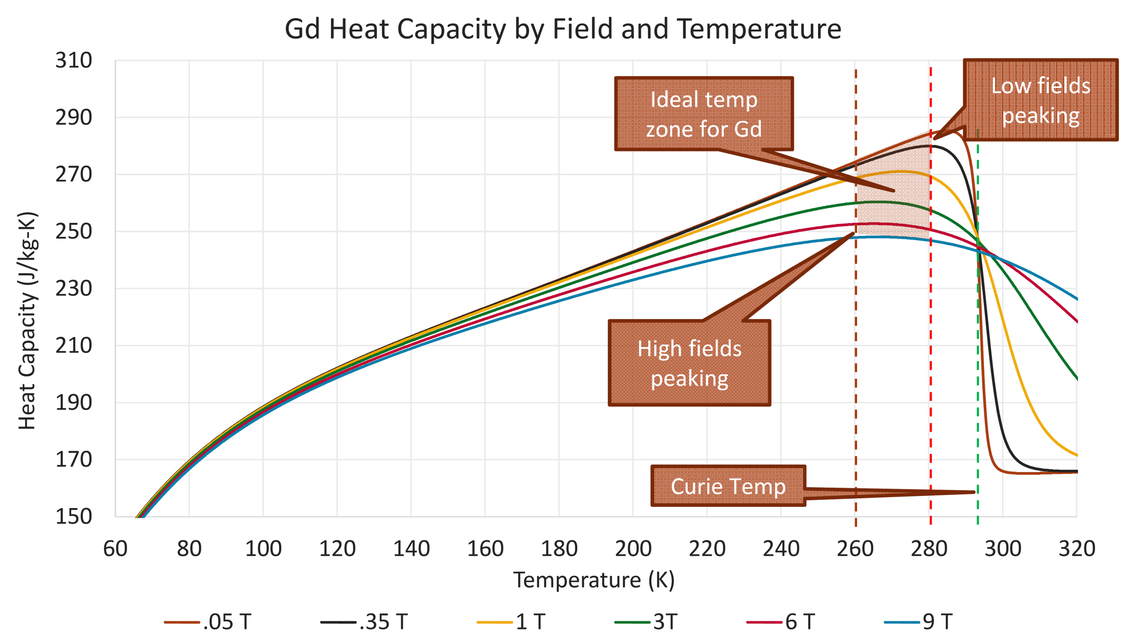


Figure 1: Graph of total heat capacity for Gadolinium showing the magnetocaloric effect driven by field and temperature ranges

	Bed Material	Curie Temp (K)	Temperature Range* T_h and T_c (K)	Adiabatic dT_h Up* (K)	Adiabatic dT_c Down* (K)
Stage 1	Gd	293.00	280 - 260	10.25	6.95
Stage 2	GdY	274.00	260 - 240	10.15	5.83
Stage 3	GdTb	250.00	240 - 220	9.71	6.37
Stage 4	GdEr	232.00	220 - 200	9.43	6.15
Stage 5	GdDyI	214.00	200 - 180	9.12	5.91
Stage 6	GdDyII	193.00	180 - 160	8.91	5.65
Stage 7	GdHoI	173.00	160 - 140	8.86	5.50
Stage 8	GdHoII	153.00	140 - 120	8.56	5.19

*Temperature ranges and adiabatic dTs for 6 T field change

Figure 2: Table of magnetocaloric alloys, properties, and temperature ranges of operation per stage (patent pending)

Results

$$massrate_{CH4} = 0.018 \frac{kg}{s}$$

$$W_{dotLNGideal} := massrate_{CH4} \cdot \left[T_{H1} \cdot \left(s_{CH4280} - s_{CH41207liq} \right) + \left(h_{CH4Liq} - h_{CH41} \right) \right]$$

$$W_{dotLNGideal} = 8.674 \times 10^3 \, W \qquad W_{spLNGideal} = 484.228 \cdot \frac{kJ}{kg}$$

Higher PNG pressure and pre-cooling to 280 K reduce specific liquefaction energy for LNG by about 50 %

Stage No. and Temperature Span (K)	NG Process Stream Thermal Load (W)	Total Reject Heat Load per Stage (W)	Work Rate for Each Stage (W)
1: 280 to 260	838	27100	2249
2: 260 to 240	844	24010	2144
3: 240 to 220	862	21020	2031
4: 220 to 200	902	18130	1908
5: 200 to 180	993	15310	1771
6: 180 to 160	7442	12550	1609
7: 160 to 140	1435	3496	503
8: 140 to 120	1299	1566	255

Figure 3: Table of Temperature ranges, CH4 process stream loads, total heat reject loads, and work rates for each stage

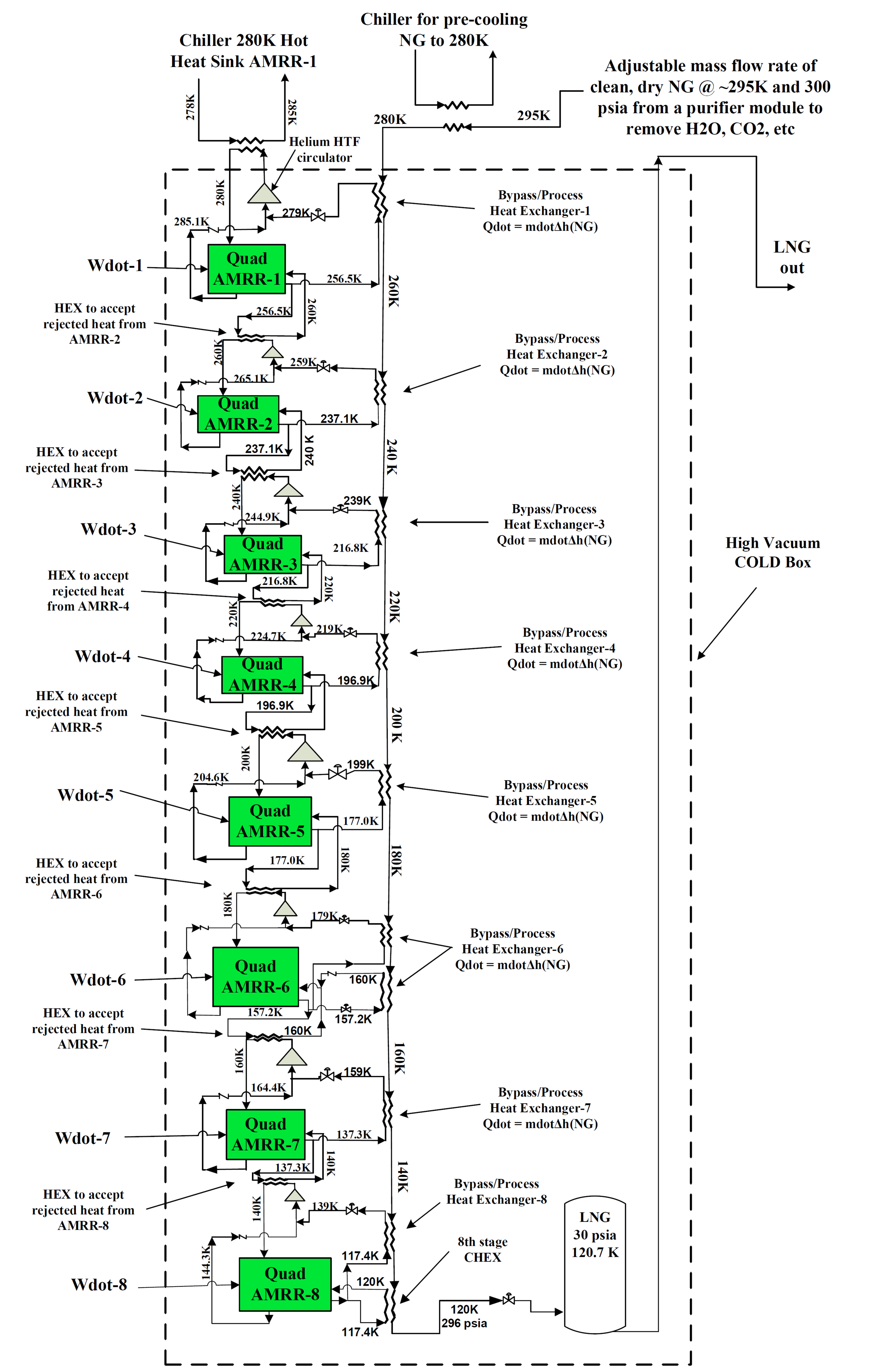


Figure 4: Basic process flow diagram of 8 stages producing 1000 gallons of LNG per day (patent pending)

The FOM for the 8-stage AMRL for 1000 gpd of LNG is given by the calculated work rate for all 8 stages assuming an internal stage efficiency based on detailed analysis of irreversible entropy mechanisms and also from numerical simulation model calculations for AMRR designs with validated properties, etc.

$$\eta_{stage} := 0.85 \qquad Q_{dotparasitic} := 2 \cdot W$$

$$W_{dotTOTALnobp} := W_{dotCH48} + W_{dotCH47} + W_{dotCH46} + W_{dotCH45} + \ldots$$

$$W_{dotTOTALnobp} = 1.247 \times 10^4 \, W$$

$$FOM := \frac{W_{dotLNGideal}}{W_{dotTOTALnobp}}$$

$FOM = 0.696$ *small parasitic but no HTF pump power

COST ESTIMATE

At 1 Hz and 6 T change in applied magnetic induction, our calculations based on experimental results indicated that the cooling power per kg of magnetic refrigerant is between 0.5 and 1.0 kW/kg. The cost of the rare earth metals, fabricating spheres, and assembly of high performance monolithic regenerators, we project a cost of $500/kg at the scale needed for this device. This gives a total cost of the magnetic regenerators for the 8-stage LNG AMRL of ~$250,000. Based on previous work, the s/c magnets and the associated cryocooler packages are about equal in cost to the magnetic regenerators. These two subsystems contribute ~65% of the cost so a complete AMRL will cost ~$750,000. The balance of plant for a turn-key plant for LNG liquefiers is ~1.6 times the liquefier cost of a total of $1.2 MM. This gives a specific cost of $1200/gpd for this very small-scale LNG plant. At this early stage of detailed development this result is comparably less than conventional gas-cycle liquefiers in this size range.

Conclusions

Bypass flow and 8 stages of refrigeration substantially eliminate a large source of irreversible entropy that reduces FOM. The calculations of heat transfer fluid pumping power confirm that to maintain a high FOM the pressure drop in the magnetic regenerators must be reduced by higher pressure (500 psia) helium transfer gas. High pressure (800 psia) methane can be used simultaneously as the process gas and heat transfer gas. This is very promising. Finally, we are investigating use of liquid propane as a liquid heat transfer fluid for a LNG AMRL. The specific costs estimates are encouraging and should scale well if frequency can be increased to 2 Hz or higher but this is very coupled to density of heat transfer fluid. An AMRL for LNG should scale well as the capacity increases.

Acknowledgments

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