

Can process intensification of liquefaction technology for LNG and LH₂ accelerate adoption for transportation use?

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Abstract: One of the reasons gaseous fuels, methane, and hydrogen, are renewable and sustainable replacements for traditional liquid hydrocarbon-based transportation fuels is their small carbon footprint. Global awareness of the immediate need to address impacts of emissions from transportation energy use has emphasized urgency of changes from business as usual. However, the transition from existing fuels to new fuels is complex because fuel usage is huge, and so many variables influence the rate of adoption. When one reads excellent energy outlooks of major energy companies, data driven reports of international and national energy agencies, along with thoughtful studies of the water, energy, food nexus, the systemic complexities are daunting. Marchetti's insightful numerical modeling of the rate of transition among different energy sources over the past two centuries with credible validation from recorded usage data shows the time scale for appreciable changes among energy systems is several decades. A further important observation of Marchetti's work is that transitions among energy sources were and are driven by substitution of superior technology rather than by depletion of prevalent sources. These observations incentivize developments of more efficient, less expensive, robust, scalable methods of production, liquefaction, storage, transport, delivery, and dispensing of hydrogen and natural gas to accelerate adoption by transportation customers. This paper presents a few examples of process intensification in advanced liquefiers for LNG and LH₂ at the same location could reduce capital costs, energy costs, and footprints of different sized liquefiers. These combinations could help address gaps in existing technology for several essential needs such as liquefiers for heavy-duty vehicle refueling stations or marine vessel bunkering systems, or refrigerators for storage tank boil-off management systems. Modular, containerized liquefiers plants with several tonne/day capacity could be scaled by interconnecting multiple units to make small industrial plants that match localized fuel demands from distributed mobile users.

1. Introduction

A paper in 2000 by Stankiewicz and Moulijn succinctly defined process intensification (PI) as any chemical engineering development that yields a substantially smaller, cleaner, and more energy efficient technology.¹ Several years later in 2009 van Gerven and Stankiewicz² refined their vision of the fundamentals of PI and gave examples of implementation at all scales in spatial (structure), thermodynamic (energy), functional (synergy) and temporal (time) domains. Over the last two decades, the discipline of process intensification has continued to evolve rapidly as illustrated by the following clips taken from recent reviews.^{3 4}

- PI refers to technologies that replace large, energy-intensive equipment or processes with ones that are smaller, less-costly, more efficient, or that combine multiple functions.
- PI is any chemical engineering development that leads to a significant improvement in scale, manufacturing, processing, efficiencies, safety, quality, capital and operating costs.
- Over the last 25 years, PI has expanded to encompass chemical engineering, physics, mathematics, chemistry, thermodynamics, transport phenomena, electrodynamics.

Many examples of PI are available in the references above. In this short paper we present three conceptual designs with the PI devices below relevant to efficient liquefiers for NG and H₂:



- Micro-channel recuperative heat exchangers manufactured with multiple separated parallel micro-flow paths where multiple unit operations alternatively occur.^{5,6} In liquefiers where the working fluid is separated from the process fluid, compact microchannel heat exchangers with PI are important components. Convective heat transfer conductances in these devices can be enhanced by micro-channels to be as large as $\sim 20,000 \text{ W/m}^2 \text{ K}$. Some high-performance reactor designs can only be made using additive manufacturing techniques.
- Micro-channel distillation columns⁷ are another impressive example of PI. By using alternative parallel paths for the liquid and gas phases of a mixture, the rate of mass diffusion is increased which reduces effective length of the packing necessary to accomplish an equilibrium single liquid-vapor phase separation. This reduction in the length of horizontal equivalent of a theoretical plate (HETP) reduces the length of a multi-plate column by 10x or more. These are also made using additive manufacturing techniques.
- Active magnetic regenerators. Regenerators are periodic heat exchangers that are passive thermal components. They are usually made using diamagnetic solids configured into compact porous devices with large specific area, large thermal mass, low longitudinal thermal conductance, good structural integrity, and low pressure drop. These components are used to effectively cool or heat a reciprocating fluid by 10's to 100's of Kelvin during thermodynamic cycles in regenerative gas-cycle refrigerators such as Stirling-cycle or pulse-tube cryocoolers. By making the regenerator with ferromagnetic solids that exhibit a magnetocaloric effect near their respective Curie temperatures when put into or removed from a region of high magnetic field strength, PI occurs because the passive regenerator is converted into an active magnetic regenerative refrigerator (AMRR)⁸ when flows of the heat transfer fluid are coupled with changes in the applied magnetic flux density. Instead of solely performing regeneration of the reciprocating fluid, the regenerator provides colder fluid to absorb a cold thermal load, regenerates the fluid between the cold temperature and hot temperatures, and provides hotter fluid to reject heat into a hot heat sink. AMRRs based on the 4-step AMR cycle replace relatively inefficient gas compression in conventional gas-cycle devices with magnetization/demagnetization of ferromagnetic refrigerants as they are moved in and out of a high-field superconducting magnet. The reaction of attractive magnetic forces in these two steps of the AMR cycle provides excellent work recovery. High thermodynamic efficiency in an AMRR is achieved by minimizing irreversible entropy creation in the regenerator design rather than in gas compression/expansion.

2. Learn from Experience

Circa 1990, road, rail, marine, and aircraft end users consumed 25-30% of total annual U.S. energy use. Significant fractions (e.g., 10-25%) of the other energy use energy sectors were supplied by NG, but about 99.7% of the transportation sector energy came from diesel and gasoline and only 0.3% came from NG. At that time health and air quality were key emissions issues which incentive passage of the Clean Air Act Amendment. This law limited noxious emissions from vehicles with specific limits on nitrous oxides (NO_x) and particulate matter (PM) of 2.5-micron diameter. Because NG was plentiful and less expensive per MMBtu than oil, and conventional compression of pipeline gas into CNG and liquefaction into LNG technologies were well established, there was an opportunity to begin transition from diesel (14-15 carbons) or gasoline (7-8 carbons) to NG (1 carbon) fuel to address the health and environmental issues. With pipeline NG prices, CNG/LNG was produced for \$0.50-\$1.50/energy-equivalent gallon less than diesel or gasoline and it seemed this would catalyze the change. The DOE and many others projected NG would supply $\sim 20\%$ of transportation sector fuels by 2020. Today, however, NG supplies only about 4% of transportation sector fuels which includes NG used to pump NG through the national pipeline network. Given there are many analogies between NG and H_2 , and aggressive projections about use of H_2 in the transportation sector have been made, it seems very insightful to understand what happened with NG? The list of reasons was compiled from personal experience for ten years (1993-2003) with a start-up company that designed, built, installed, and operated small-scale conventional LNG systems to monetize shut-in stranded gas wells and flared

landfill gas for clients who sold LNG to heavy duty fleet users. An independent report to DOE also identified similar issues.⁹

- Lower equivalent fuel prices needed to be compelling and sustainable for end users. State and federal tax incentives were short-lived and sometimes excessive.
- Lack of competitively priced CNG/LNG vehicles compared to gasoline/diesel vehicles. Surcharges for new vehicles or for conversion kits for existing vehicles were expensive.
- Technology competition, i.e., hybrid gas-electric vehicles.
- Lack of extensive publicly accessible refueling infrastructure.
- Surcharges for LNG transport charges from large central liquefiers directly passed onto end users which reduced savings.
- Few consequences for not adopting lower emission CNG/LNG vehicles with ~25% lower CO₂/mile driven.
- Lack of education about the use of gaseous fuels.
- Safety assurances and avoidable insurance coverages for end users

This list sounds familiar when identifying the challenging barriers impeding rapid adoption of H₂ and NG fuels so important in multiple approaches to address climate change issues.

Some lessons from these observations include:

- The transportation energy supply chain is unique when compared to other sectors. Its distributed nature requires efficient, small-scale, expensive liquefier technology to create distributed refueling infrastructure near end users.
- Among the most important items on the list above is the need to reduce the price of LH₂ and LNG to ~50% of energy equivalent diesel/gasoline!
- Focus early adoption on larger niche end user applications such as heavy-duty trucks, railways, or marine vessel where LH₂ creates attractive economic returns and has distinct advantages over competing vehicle and fuel choices.

3. Hydrogen and Natural Gas liquefaction factors

The higher heating value gravimetric energy density of normal H₂ is 1141.8 MJ/kg and of NG (methane) is 55.5 MJ/kg, both of which are attractive properties. However, the volumetric energy densities of these gaseous fuels at ambient (295 K) and 0.1013 MPa are 0.012 MJ/L and 0.037 MJ/L. This latter property requires LH₂ and LNG for cost-effective storage, transport, and delivery with densification by ~800 times for H₂ and ~600 times for NG at 0.1013 MPa.

To liquefy NG from 295 K at 0.1013 MPa requires about 1 MJ/kg and to liquefy H₂ from 295 K at 0.1013 MPa requires about 14 MJ/kg. LH₂ is by far the toughest gas to liquefy under these starting conditions. Starting T and P conditions matter as illustrated in Table 1 below.

Table 1. Effect of starting temperature and pressure on ideal specific energy for LH₂

GH ₂ Inlet Temperature (K)	Pressure (MPa)	Means to Pre-cool & Heat Sink	Ideal Specific Energy for LH ₂ (MJ/kg) [kWh/kg]	Pressure (MPa)	Ideal Specific Energy for LH ₂ (MJ/kg) [kWh/kg]
300	0.1013	Air/water	14 [3.92]	2.1	7 [1.95]
290	0.1013	Air/water	13.6 [3.79]		
260	0.1013	Propane @ 0.31 MPa	11.8 [3.28]		
140	0.1013	LCNG	4.96 [1.38]		
120	0.1013	LNG @ 0.19 MPa	3.93 [1.09]		
100	0.1013	LAir @ 0.66 MPa	2.92 [0.81]		
80	0.1013	LN ₂ @ 0.14 MPa	1.99 [0.70]		

This table was compiled for equilibrium H_2 using version 10 of REFPROP¹⁰. These data show the expected impact of lower starting temperature. The means to provide the lower starting temperatures must be included when comparing the performance and capital costs of different liquefiers. The 7x reduction in specific energy for LH_2 by using LN_2 pre-cooling is impressive. This fact has been used in most common conventional 30 tonne/day LH_2 liquefiers which use the LN_2 pre-cooled Claude cycle.¹¹

Note also that increasing the starting pressure reduces the specific energy. If the H_2 feedstock can be produced and purified at higher pressure without a separate compressor module, this approach is beneficial for a liquefier. If a hydrogen compressor is required, the extra capital expense and work input must be added to the liquefier cost and work input to compare net benefits of using higher pressure GH_2 .

4. Process Intensification examples to reduce cost of LH_2 and LNG

With a target of \$1-2/kg for liquefaction of LH_2 in mind and synergies between NG and H_2 , three conceptual examples of how PI could increase liquefier efficiency without increasing capital cost are presented below.

4.1. Magnetic liquefiers and microchannel distillation columns combined to make an LN_2 -precooled liquefier for LH_2 .

Figure 1 is an active magnetic regenerative liquefier that combines the efficient and low-cost production of LN_2 that is used to pre-cool GH_2 to 80 K before it is liquefied at 20 K in a single-stage active magnetic regenerative liquefier (AMRL) using LN_2 as the heat sink. This design also produces LO_2 which can be used to reduce the cost of making GH_2 from autothermal reformation of methane or from partial oxidation of organic biowaste streams. The upper two stages have 3-layer regenerators with ferromagnetic refrigerants that span from 295 K to 172 K in the first (upper) stage and from 172 K to 100 K in the second (lower) stage. The magnetic stages each use a partial tokamak superconducting magnet that uses high-performance NbTi wire to produce magnetic flux density in the absence of the refrigerants of 5.5, 6.0 and 6.5 T over $\sim 120^\circ$ arc of the mean circumference of the wheel-shaped regenerator. Saturated liquid propane is used as the heat transfer fluid in the upper two stages and pressurized helium gas is used in the third AMRL stage. The input air is compressed to 0.69 MPa (100 psia) before it is dried and cleaned to remove any residual oil before it is liquefied and sent into the dual microchannel distillation columns where they are separated into 99.9% pure LO_2 and LN_2 . The cooling for the second column condenser is provided by the AMRL and the return gas is used to help pre-cool the incoming air. The overall efficiency of the upper 2 stages designs is $\sim 60\%$ of ideal. The LN_2 is expanded to ~ 80 K for the single stage LH_2 AMRL. This design should have a composite efficiency of ~ 0.5 on a small-scale unit such as 1-3 tonne/day. This example shows how multiple instances of PI improve liquefier efficiency by almost 2x.

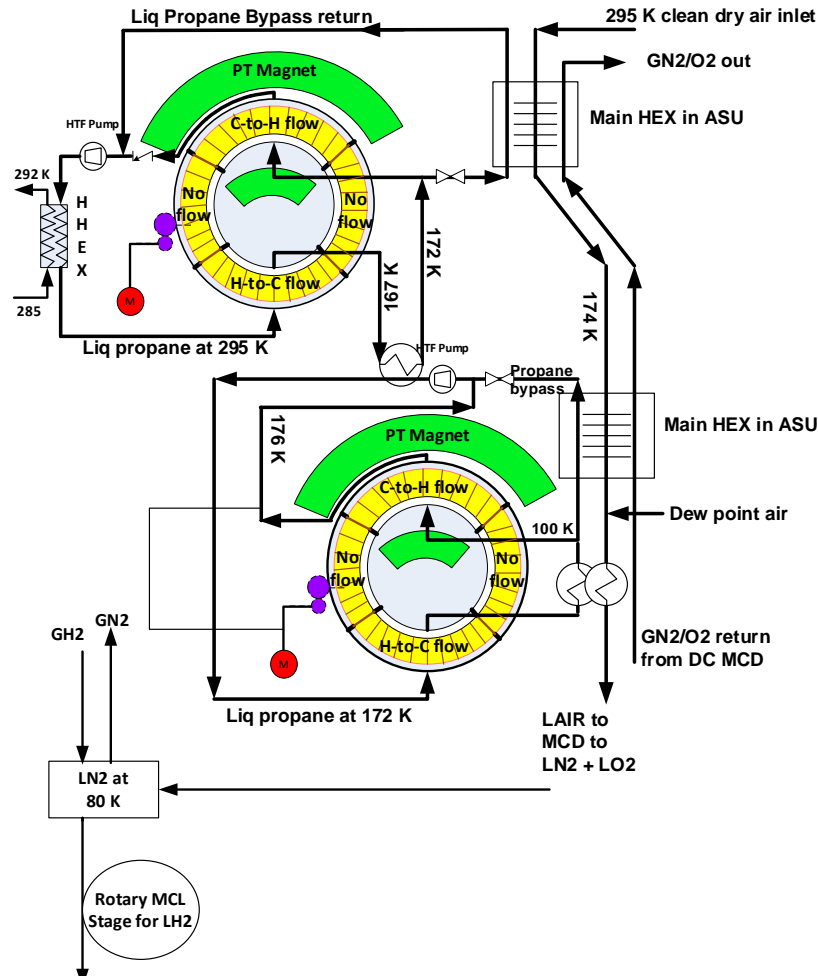


Figure 1. Process intensification by combining a small-scale cryogenic air separation unit and an 80 K to 20 K AMRL using LN_2 as a precooling and heat sink medium.

4.2 Liquefaction of a NG mixture with 10% GH_2 to produce, NG, LNG, and LH_2

One of the methods being investigated for inexpensive and wide-spread distribution of GH_2 is to inject GH_2 into the existing NG pipeline network. If a cost effective, small-scale, efficient, and safe method to separate the H_2 from NG, it could help create the distributed refueling infrastructure necessary for faster adoption of H_2 fuel into the transportation sector and remote, distributed low carbon power generation. The second example of process intensification is the separation of H_2 from NG by liquefying the dried, cleaned lower pressure (~ 0.25 MPa) mixture from the pipeline network in a separate process stream of a two-stage rotary wheel AMRL designed to cool to as low as ~ 102 K where the NG is expected to liquefy. The solubility of H_2 in LNG at this temperature is very low based on a NASA study of solubilities of several gases in liquid methane.¹² Therefore, a conventional liquid-gas phase separator can be used to separate the GH_2 from LNG. The LNG can be used as the heat sink of a single stage AMRL to liquefy the purified pre-cooled GH_2 . This dual liquefier design should be scalable to match locations on the existing NG network and provide purified NG, LNG, and LH_2 . Figure 2 schematically illustrates the process block flow diagram of this process intensified system.

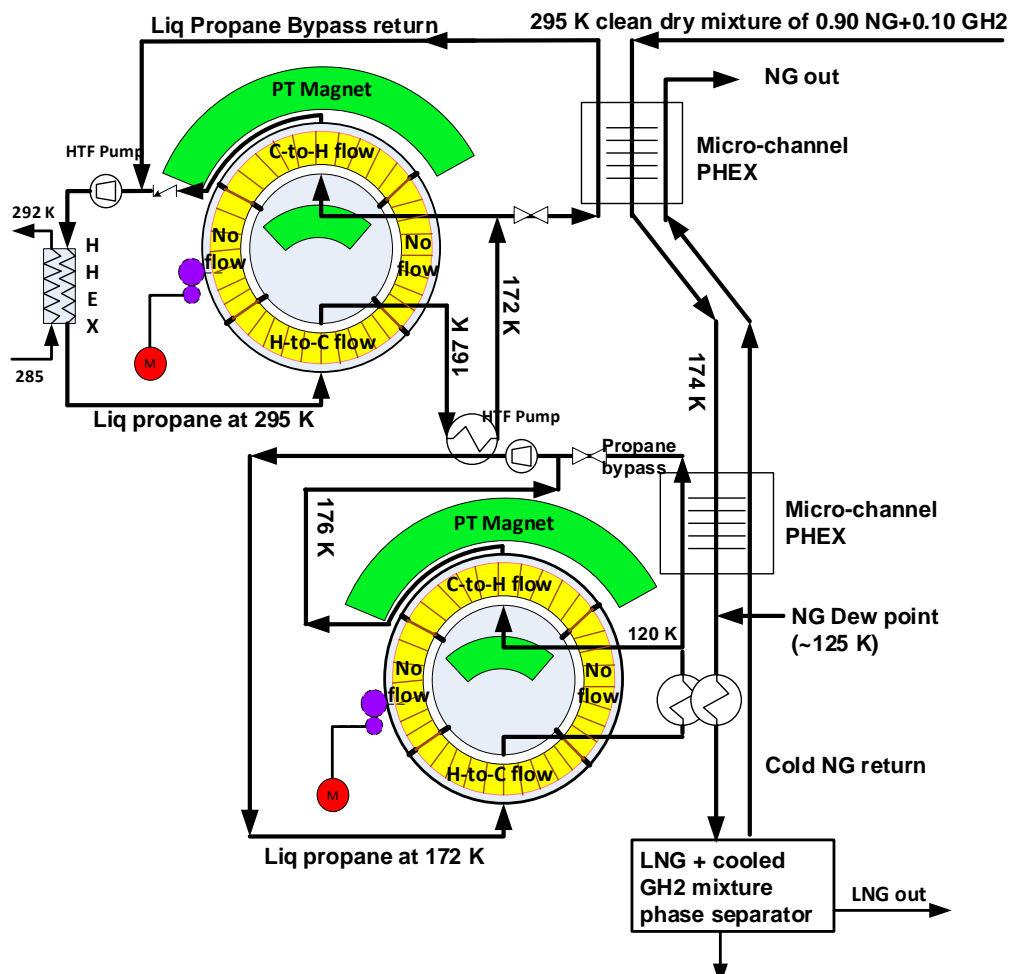


Figure 2. Combined liquefier to separate a mixture of pipeline NG and H₂ that efficiently and cost-effectively makes NG, LNG, and LH₂

4.3 Use of GH₂ as the Heat Transfer Fluid and Process Gas in a 3-stage magneto-caloric liquefier.

The third example of PI is the use of gaseous H₂ simultaneously as the process gas and the heat transfer gas within three stages of rotary magnetic regenerative wheel type AMRL.¹³ This example uses a unique feature of magnetocaloric liquefiers caused by temperature and magnetic flux density dependence of the heat capacity of ferromagnetic refrigerants below for their respective Curie temperatures. For about a temperature span equal to 20% of the Curie temperature, the heat capacity in high magnetic field is about 10% smaller than the heat capacity in low to zero magnetic field. This difference in thermal mass (temperature span times heat capacity) means more heat transfer fluid flow is needed to cool demagnetized portion of the wheel from hot-to-cold during a flow step of the AMR cycle. It also means that less heat transfer fluid is needed to warm the magnetized refrigerants in the high field section of the wheel from cold-to-hot in the second flow step of the AMR cycle. More maximum efficiency the excess cold heat transfer fluid is returned to the hot temperature before rejoining the heat transfer fluid circuit. It is sometimes called bypass flow.

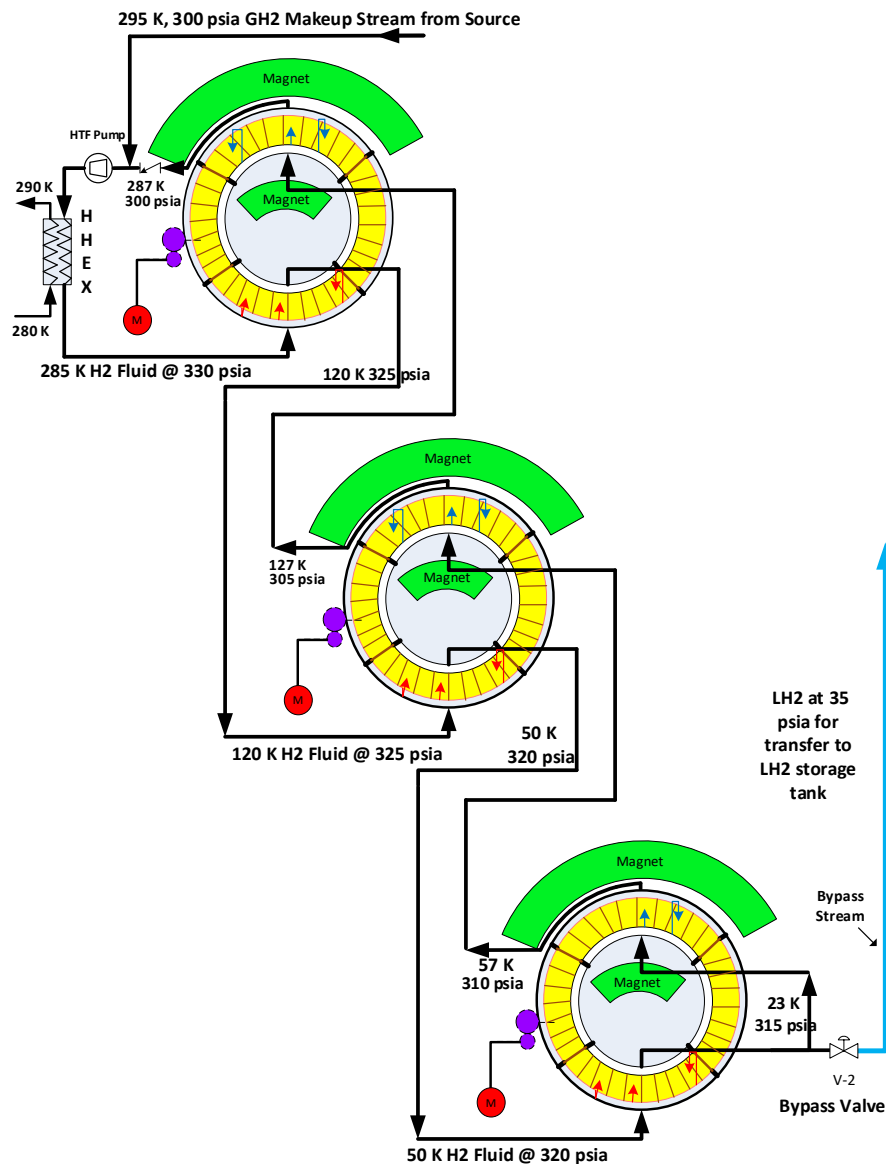


Figure 3. Three stage rotary AMRL for LH₂ that combines hydrogen gas as process stream and heat transfer fluid.

In Figure 3, the first stage has 4 layers of ferromagnetic refrigerants, the second stage has 3 layers of ferromagnetic refrigerants, and the third stage has two layers of refrigerants. The rotary wheels act as high performance active magnetic regenerators and highly effective process heat exchangers at the same time. Each refrigerant has an optimum loading of ortho to para catalyst to continuously maintain equilibrium hydrogen concentrations and remove the exothermic heat load at the highest temperature. The changing hydrogen properties are used to design each layer of the regenerator for the highest efficiency by minimizing irreversible entropy generation. The continuously flowing hydrogen enters the demagnetized flow section of the first rotary stage at 285 K and leaves at 120 K and continues through the demagnetized flow section of the second rotary stage where it leaves at 50 K and continues through the demagnetized flow section of the third rotary stage where it leaves subcooled fluid at ~23 K where about 10% of the flow is split off as bypass flow and expanded through a J-T valve to produce LH₂ at ~20.7 K. The remaining portion of heat transfer fluid flows back through the magnetized sections of all three stages to ~288 K where make up GH₂ is continuously added just before the single circulation pump. This integrated device¹³ promises to be an efficient, compact, relatively inexpensive, and simpler LH₂ liquefier than other AMRL designs.

5. Conclusion

The answer to the question posed in the title is yes! Among the numerous challenging barriers to be overcome to accelerate the adoption of LH₂ and LNG as fuels in the transportation sector, dispensed LH₂ and LNG at lower equivalent fuel prices than gasoline/diesel is perhaps the most important. Process intensification can improve LNG and LH₂ liquefaction technology in numerous ways to reduce capital cost and increase efficiency as illustrated by the examples in this paper. Further work on the three concepts presented in this paper includes detailed process flow analysis of each design for a pilot-scale liquefier using minimization of irreversible entropy techniques for liquefiers with FOM of 0.5-0.6 as has been previously done by the authors.

6. References

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