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A Comparative Study of Biomethane Liquefaction Processes

Joseph Al Khoury*, Maroun Nemer, Chakib Bouallou

MINES ParisTech, PSL Research University, Centre for Energy Efficiency of Systems (CES), Paris, France.

Joseph.al_khoury@mines-paristech.fr

Made from organic waste, biomethane is a source of renewable energy with reduced emission of greenhouse gases, that could replace fossil fuels in transportation, heating, and electricity production. Liquefaction of biomethane is necessary to reduce its volume and facilitate its transport from the production site to the site of use. The liquefaction processes suffer from low efficiency operating with less than a third of the Carnot coefficient of performance. This paper study and compare the performance of different potential refrigeration processes, to select the best candidate for the liquefaction of biomethane. All possible liquefaction processes were examined and two potential processes have been selected and modelled. The non-integrated cascade operating with pure refrigerants and the integrated cascade operating with mixed refrigerants were thermodynamically investigated and optimised. The results show that the non-integrated pure refrigerant cascade has a COP of 0.411, approximately twice as high as the integrated mixed refrigerant cascade which had a COP of 0.191. Consequently, it was selected as the best candidate for micro-scale biomethane liquefaction. This study highlights a new refrigeration cycle for the liquefaction of biomethane.

1. Introduction

To fight climate change, the world is trying to reduce the usage of fossil fuels and to rely more on renewable energy. Made from organic waste such as animal, agricultural and industrial waste, biomethane is a source of renewable energy that reduces emissions and the greenhouse effect. It can replace fuels for heating, propulsion, or electricity production. The carbon content of biomethane is approximately 10 times lower than that of natural gas (NG). Using biomethane instead of diesel or gasoline decreases greenhouse gas (GHG) emissions by 95 % and the NO_x emissions drastically, and eliminates the fine particles emissions. What makes biomethane carbon neutral is that it releases the same amount of carbon dioxide that the organic matter used to produce it, has absorbed as it grows, so it doesn't break the carbon balance. The use of biomethane presents additional advantages like the reduction of dependence on imports, lower water, soil, and air pollution, development of the local economy, environmental sustainability, a perfect example of circular economy, and maximum flexibility since it can be used in many places.

The liquefaction of the biomethane is essential to facilitate its transportation from the site of production to the site of use when the grid is not available near the biomethane factory. The liquefaction reduces the biomethane volume 600 times which leads to a reduced number of shipments and thus reduced transportation costs. The liquefaction is helping the development of this renewable energy sector because it allowed the construction of sites of production in places far from the grid. To be liquified, the biomethane is cooled to extremely low temperatures below -120 °C, and this cooling is achieved by a refrigeration cycle.

There are many refrigeration cycles for liquefaction and they are classified into three large categories: pure refrigerants cycles, mixed refrigerants cycles, and gas expansion cycles. Nowadays, liquefaction processes suffer from low-efficiency operating with less than a third of the Carnot coefficient of performance (COP).

Most of the previous research involves modelling a specific liquefaction process and optimising its operating parameters using a numerical optimisation algorithm (Yoon et al., 2012). Some studies have compared the performances of the different natural gas liquefaction processes (Vatani et al., 2014). However, there is a lack of research on biomethane liquefaction and no clear comparison between the performance of its liquefaction processes. Moreover, the non-integrated pure refrigerant cascade cycle is not previously investigated for biomethane liquefaction.

Therefore, this paper investigates the liquefaction processes of the biomethane to find the highest efficiency refrigeration cycle. The first step is selecting the potential refrigeration cycles from all possible liquefaction processes. The second step is a modelization and thermodynamic optimisation (Refrigerants composition, temperatures, pressures, and mass flow rates) of the selected candidates, using Excel, Refprop, and the Generalized Reduced Gradient (GRG) solver.

2. Identifying the potential liquefaction cycles

The liquefaction processes could be divided into three main categories. First, the Pure refrigerants cycles, which include, the Non-integrated pure refrigerant cascade cycle (NIPRC) with or without progressive cooling (Kamalinejad et al., 2015). The NIPRC can consist of several Multi-stage vapor compression. Second, the mixed refrigerants cycles, which include the single mixed refrigerant (SMR) (Kohler et al., 2014), the dual mixed refrigerant (DMR) (Vikse et al., 2018), the propane pre-cooled mixed refrigerant (C3/MR) (Sanavandi and Ziabasharhagh, 2016), the integrated mixed refrigerant cascade cycle (IMRC) (Yousfi et al., 2018), and the Multiple Mixed fluid cascade (MMFC) (Vatani et al., 2014). Third are the gas expansion cycles, which include the Single or Double N₂ expander (Kohler et al., 2014), and the Reverse Brayton close-loop (Cryostar).

Classifying the liquefaction processes from the lowest efficient to the highest efficient process gives the following order: The Single N₂ expander, Double N₂ expander, SMR, C3/MR, DMR, MMFC (Vatani et al., 2014). This is the same classification from the lowest to the highest complexity and fixed process cost.

The N₂ expander and the SMR dominate small-scale liquefaction because of their low price. The DMR and the C3/MR are also widely used. The gas expansion cycles are very simple with few components and available at a moderate price. The mixed refrigerant (MR) fluids at a specific composition are capable to imitate the very steep Composite Curve of the NG and thus reduce the Exergy destruction.

Using a gas expansion cycle for biomethane liquefaction results in a very low process COP due to high Exergy destruction in the heat exchanger which provides the cooling and the liquefaction. From one side the refrigerant gas stays in a gas state and from the other side, the biomethane passes from vapor to two phases then to liquid which leads to the big spacing between the temperatures Composites Curves of the biomethane and the operating refrigerant gas (Venkatarathnam, 2008). Moreover, using gas to accomplish the liquefaction duty requires a high expansion and consequently a high compression ratio to be able to reach a very low refrigerant temperature, because the gas temperature increase very fast since it does not exhibit a phase change.

The NG composite curve is much steeper than that of biomethane, due to 3 main reasons, which make us reconsider the investigation of the liquefaction processes for the biomethane. These reasons are as follows: First, the NG is present in pockets underground at a certain depth and high pressure, so the NG when extracted from pipes has a high pressure (90 bar). This pressure is higher than the critical pressure (46 bar), which means that the NG is liquified at supercritical pressure without passing inside the two-phase zone. This is not the case with the biomethane available at around 8 bar. Second, the presence of other substances in the NG composition (Ethane, Propane, Azote, CO₂, ...) so it does not exhibit phase change at a constant temperature, meanwhile the biomethane is around 99 % methane. Third, the liquefied NG is transported at 1 bar in ships, so it requires to be subcooled at a very low temperature to avoid its vaporization after expansion from high pressure to this low pressure. All these factors give the NG a steep Composite Curve in the heat exchanger, unlike the biomethane which has an almost constant temperature in a two-phase zone and is barely subcooled.

One or many mixed refrigerants in series are capable to approach the NG Composite Curve but not the biomethane curve. So the SMR, the DMR, the C3/MR, and the MMFC will result in high Exergy destruction in the heat exchangers and thus a low process efficiency.

The cycles that may have high COPs are the ones that will have close temperatures in their heat exchangers. The IMRC is a good candidate because the mixed refrigerant composition in this type of cycle changes, and the methane constitute a very high percentage of the mixed refrigerant that is used to liquefy the biomethane. The methane is used to liquefy the biomethane at the lowest stage in the NIPRC cycle and consequently, it will be selected for the study as a competitor of the IMRC. The two-cycle architectures are described in detail later.

3. Modelization and Optimisation

The thermodynamic modelling of the refrigeration cycles was done in an excel sheet linked to refprop and optimised with GRG non-linear solver. The biomethane is available at 8 bar and ambient temperature (25 °C) after the biogas purification, and it's stored at its saturated liquid state for transportation. Then, it is injected at 8 bar in the grid. Referring to the methane phase diagram, the biomethane could be liquefied in a range of temperature between -90 °C and -170 °C. At 8 bar the biomethane should be cooled to -129 °C (saturation temperature). The biomethane mass flow rate considered for the study is 100 Nm³/h which corresponds to the micro-scale application. The water temperature is considered 15 °C, the minimum cycle pressure is 1.2 bar, the

minimum heat exchanger Pinch is 3 degrees, compressor isentropic efficiency is 70 %, and 2 degrees of subcooling before valves. The COP Carnot is equal to 1.4 and calculated with Eq(1) or Eq(2). Where T_C is the average temperature of the fluid that is cooled (168 K), and the T_H is the average temperature of the environment where the heat is rejected, in this case, it's water at 288 K. Both temperatures could be obtained using Eq(3).

$$COP_{carnot} = \frac{T_C}{T_H - T_C} \quad (1)$$

$$COP_{carnot} = \frac{Q}{W_{min}} \quad (2)$$

$$T_{H/C} = \frac{h_{in} - h_{out}}{S_{in} - S_{out}} \quad (3)$$

Q is the total heat to be removed from the fluid (refrigeration capacity). W_{min} is the minimum work required to cool the fluid, in other meaning to bring the fluid from one state to another. The W_{min} is equal to the Exergy difference between the inlet and the outlet of the fluid. The minimum work required for a specific refrigeration duty depends only on the fluid (to be cooled) inlet and outlet states and the temperature at which the heat is rejected, calculated with Eq(4). Where m (kg/s) is the fluid mass flow rate. h_{in} (Kj/kg) and S_{in} (kJ/kg.K) are the enthalpy and entropy of the feed biomethane. h_{out} and S_{out} are the enthalpy and entropy of the outlet biomethane.

$$W_{min} = m. (h_{in} - h_{out} - T_H. (S_{in} - S_{out})) \quad (4)$$

The Carnot COP decreases when the biomethane exit temperature decreases, and increases when the biomethane inlet pressure increases. Thus, the COP Carnot varies in an opposite way to the variation of the minimum required work for the refrigeration. The Refrigeration Capacity Q equals 15.24 kW calculated with Eq(5), where h_{in} and h_{out} are the biomethane inlet and outlet enthalpies.

$$Q = m. (h_{in} - h_{out}) \quad (5)$$

The refrigeration cycle COP is calculated with Eq(6), where W_{comp} is the sum of all compressors' work.

$$COP = \frac{Q}{W_{comp}} \quad (6)$$

Exergy destruction occurs when there is entropy generation in an irreversible process. The entropy is generated because of two main reasons. First, the friction (case of compressors, valves, turbines). Second, the heat transfer across a finite temperature difference (Heat exchangers). Table 1 shows the calculations of the Exergy destruction ΔEx for each component. Where W_c is the compressor work (positive) and W_T is the turbine work (positive). ex_{in} and ex_{out} are the specific Exergy flow (kJ/kg) at the inlets and the outlets of the component respectively calculated with Eq(7). The Exergy rate Ex (kW) is calculated with Eq(8). The index 0 refers to the dead state or the reference state.

$$ex = h - h_0 - T_0. (S - S_0) \quad (7)$$

$$Ex = m. ex \quad (8)$$

Table 1: Exergy destruction of mechanical components

Component	Exergy destruction
Compressor	$\Delta Ex = m(ex_{in} - ex_{out}) + W_C$
Turbine	$\Delta Ex = m(ex_{in} - ex_{out}) - W_T$
Valve	$\Delta Ex = m(ex_{in} - ex_{out})$
Mixer and Separator	$\Delta Ex = \sum_{i=1} m_{i,in} ex_{i,in} - \sum_{i=1} m_{i,out} ex_{i,out}$
Heat Exchanger	$\Delta Ex = \sum_{i=1} m_i (ex_{i,in} - ex_{i,out})$

The process Exergy efficiency η_{eff} is calculated with Eq(9).

$$\eta_{eff} = \frac{\text{useful Exergy}}{\text{total spent Exergy}} = 1 - \frac{\text{total Exergy loss}}{\text{total spent Exergy}} = \frac{W_{min}}{W_{comp}} = \frac{COP}{COP_{carnot}} \quad (9)$$

3.1 Integrated Mixed Refrigerant Cascade cycle

The IMRC cycle is a three-stage refrigeration cycle (Figure 1) operating with a mixed refrigerant which is a combination of 4 pure refrigerants methane, ethylene, propylene, and isobutane. For the same pressure, the saturation temperatures of these fluids are as follows: $T_{methane} < T_{ethylene} < T_{propylene} < T_{isobutane}$. The MR is compressed in the compressor Comp, then it is cooled in the condenser Cond using cold water. Through the heat exchangers HEX1, HEX2, and HEX3, the MR is cooled by the low-pressure MR going back to the

compressor. After each HEX, the liquid and the vapor of the MR are separated using a separator SEP. The liquid is expanded in an expansion valve V to the low pressure and goes back in a recuperator to cool the high-pressure MR that continues its way through the recuperators until it reaches a desired low temperature at the end of the cycle, capable of liquefying the biomethane. After each separator, the MR composition varies. It gets richer in the light pure refrigerants that have low saturation temperature. This means that the methane remains to the end with a small proportion of ethylene, and passes in the HEX4 (liquefier) and HEX5 (desuperheater). At point 12 the MR is completely liquid. This method allows refrigeration with one mixed refrigerant at several temperature levels. The flow going back to the compressor cools the flow going forward in the 3 recuperators.

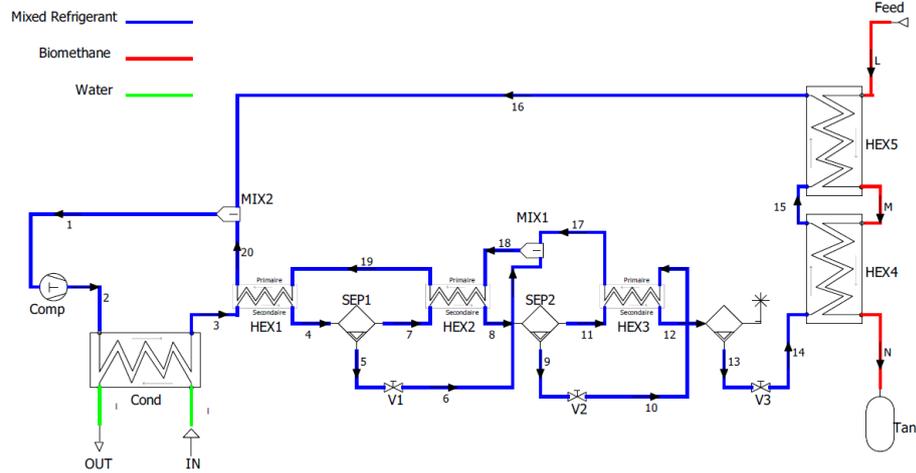


Figure 1: Integrated Mixed Refrigerant Cascade Cycle Schema.

The COP of the cycle after optimisation is 0.191 and its Exergy efficiency is 0.136. The optimisation was done in function of the following parameters: Refrigerants molar composition (36 % Methane, 33 % Ethylene, 19.6 % Propylene, 11.4 % Isobutane), the MR low and high pressures (2.3 and 27.1 bar), the MR mass flow rate (0.26 kg/s), and the temperatures T4, T8, and T12 (-5.45 °C, -60 °C, and -98 °C) while respecting the Minimum Pinch (3 °C). The compressor exit temperature is 162 °C. The values in parentheses are those optimised. Figure 2 shows the Exergy destruction of every component in the cycle.

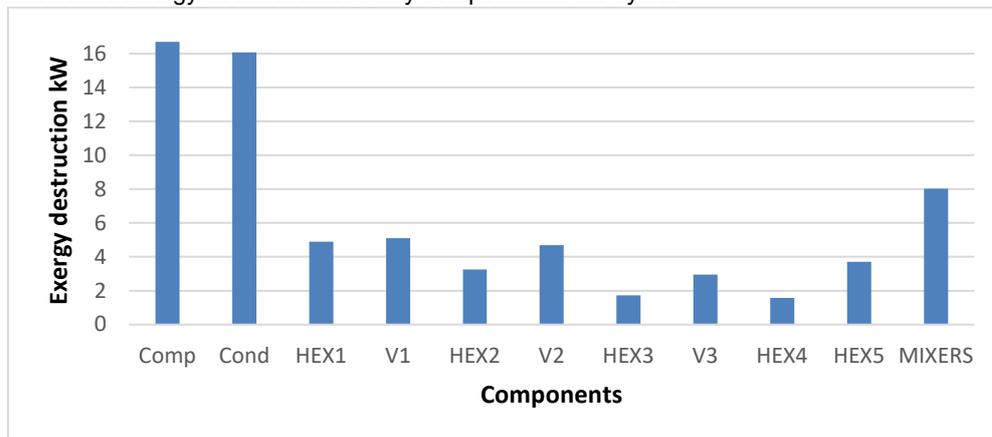


Figure 2: The IMRC components Exergy destruction.

The cycle consists of one compression stage which requires a high compression ratio and thus resulting in a high compressor exit temperature. The compressor exit temperature could be reduced by changing the mixed refrigerant composition, the pressures, and the temperatures, but the reduction of 20 degrees lead to 10 points COP reduction. The highest Exergy destructions occur in the compressor and the condenser. The Exergy destruction in the condenser can't be reduced because the heat must be rejected outside the cycle. However, making the compression in two stages by adding an intercooler will reduce the compressor's Exergy destruction. Replacing the expansion valve with expander permits recuperate the mechanical power and reduces the energy consumption of the electric motor driving the compressor. However, these improvements complicate the cycle

and make it more expensive. The Exergy destruction of V1 is higher than V2, which is in its turn higher than V3 because the 3 valves do the same expansion ratio but the high-pressure MR mass flow rate decrease from 1 to 3. The compressor's Exergy destruction is affected directly by the compressor's isentropic efficiency.

3.2 Non-Integrated Pure Refrigerant Cascade cycle

The non-integrated pure refrigerant cascade cycle presented in Figure 3 is a three-stage vapor compression refrigeration cycle in a cascade configuration working respectively from top to bottom with propylene, ethylene, and methane. Each stage operates with one pure refrigerant. The lowest cycle allows refrigeration at a relatively low temperature without excessively low evaporator pressures. The highest cycle permits condensation at the ambient temperature without excessively high condenser pressures. The choice of the refrigerants is mainly based on their saturation temperatures that can condense the fluid of the lower stage while having a positive pressure. The 3 chosen refrigerants are compatible together, they lead to close compression ratios of the three stages which are good for the compressors' technical constraints and to lower the Exergy destruction. Hydrocarbons are eco-friendly, have zero Ozone Depletion Potential (ODP), a negligible Global Warming Potential (GWP), and are not toxic. However, they have high flammability and must be handled with care. The compression ratio and the compressor's exit temperatures are not very high because the refrigeration is split into three stages. Adding an aftercooler IC after each compressor increases the performance of the cycle because it reduces the refrigerant's mass flow rate in the upper stage and so does its compressor work.

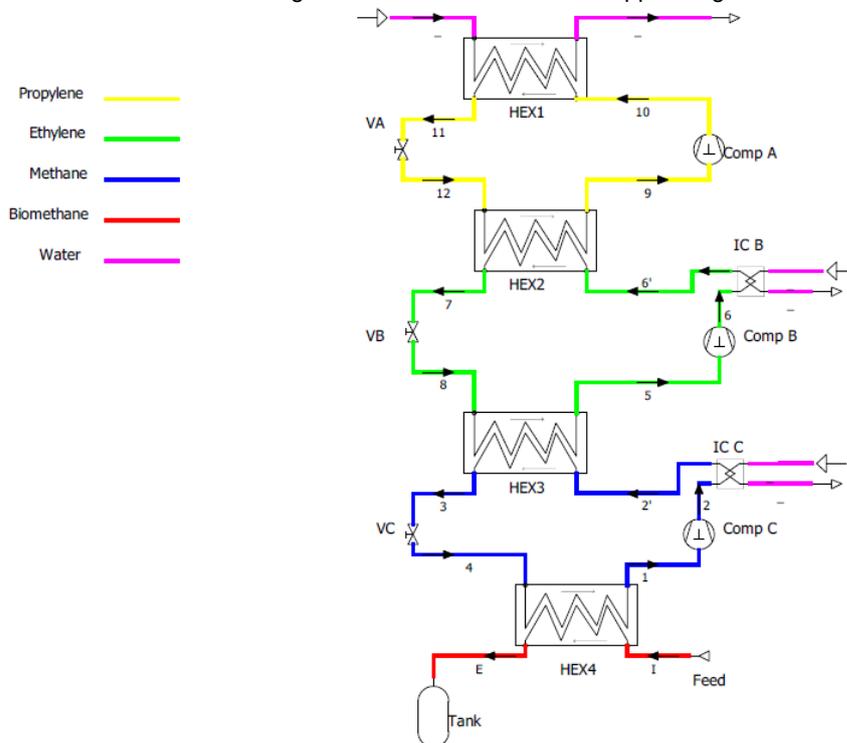


Figure 3: Non-Integrated Pure Refrigerant Cascade Cycle schema.

The COP of the cycle after optimisation is 0.411 and its Exergy efficiency is 0.294. The optimisation was done in function of the following parameters: The saturation temperatures of the evaporators of the three stages T12, T8, and T4 (-43.6 °C, -97 °C, -134 °C), and the mass flow rates of the propylene, ethylene, and methane (0.065 kg/s, 0.049 kg/s, 0.033 kg/s). The values in parentheses are those optimised. The constraints are the minimum Pinching in the heat exchanger (3 °C), the minimum temperature at the compressor inlet (-50 °C), the maximum temperature at the compressor exit (135 °C), and the minimum pressure (1.2 bar). The A, B, and C compressors' inlet temperatures are (0.7 °C, -48 °C, -43 °C), their exit temperatures are (117 °C, 132 °C, 117 °C) and their compression ratios are (8.41, 10.23, 5.57). Figure 4 shows the Exergy destruction of every component in the cycle.

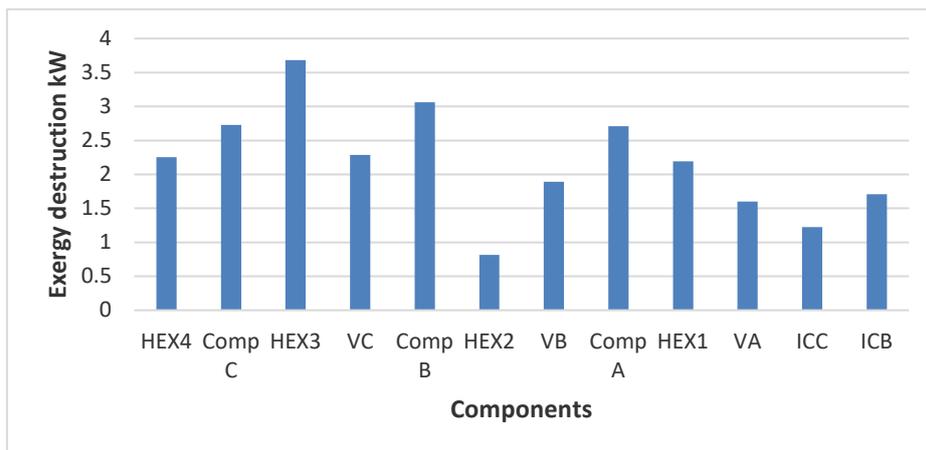


Figure 4: The NIPRC components Exergy destruction.

4. Conclusion

To find the best biomethane liquefaction process, all possible refrigeration cycles have been examined. Two potential candidates were selected based on Exergy and composites curves analyses. The selected cycles were modelled and their efficiencies were optimised while respecting specific technical constraints. Exergy analysis was performed on each cycle. The best combinations of the pressures and temperatures levels, the mass flow rates, and the refrigerant composition that results in the highest process efficiency were found.

The non-integrated pure refrigerant cascade cycle had a COP of 0.411 twice as high as the integrated mixed refrigerant cascade cycle which had a COP of 0.191. Consequently, it was selected as the best candidate for biomethane liquefaction at the micro-scale.

Nomenclature

T – temperature, °C

H – enthalpy, kJ/kg

S – entropy, kJ/kg.K

m – mass flow rate, kg/s

In – inlet

Out – outlet

COP – coefficient of performance

NIPRC – non-integrated pure refrigerant cascade

IMRC – integrated mixed refrigerant cascade

MR – mixed refrigerant

NG – natural gas

GRG – generalized reduced gradient

HEX – heat exchanger

Comp – compressor

V – valve

SEP – separator

MIX – mixer

IC – aftercooler

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