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Organic Rankine Cycle with Pure and Mixed Working Fluids for LNG Cold Energy Recovery

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Liquefied Natural Gas (LNG) contains a large amount of cold exergy, which is normally wasted during the regasification process. Organic Rankine Cycles (ORCs), which have been widely employed for low-temperature waste heat utilization above ambient temperature, can also exploit LNG cold energy efficiently. Due to the low regasification temperature of LNG, the ORC for LNG cold energy recovery is quite different from the conventional ORCs recovering low-temperature waste heat. In this study, we investigate the working fluids for such an ORC recovering LNG cold energy. Both pure and mixed working fluids are studied and compared. According to open literature, mixed working fluids perform better than pure working fluids because the mixed working fluid can achieve a better match with the heat source. Therefore, the main motivation for mixed working fluids is to obtain gliding temperature for a better match with sensible heat sources. However, a few studies show that pure working fluid outperform mixed working fluids when the evaporating condition is close to the critical point. In addition, if the evaporation pressure is greater than the critical pressure, pure working fluids can also match well with a sensible heat source. Therefore, it is too general to claim that mixed working fluids will perform better than pure working fluids. For cases where the mixed working fluids perform better than pure working fluids, the optimal composition of the working fluid has to be determined. In this study, the performance of ORCs with pure and mixed working fluids are investigated for different types of ORCs. The optimal working fluid and composition for an ORC recovering LNG cold energy can be determined based on a simulation-based framework. The results show that mixed working fluids do not show significant improvement in net power output of the integrated system.

1. Introduction

Liquefied Natural Gas (LNG) plays an increasingly important role in the world energy market. LNG occupies 10 % of the total natural gas share and 70 % of the LNG is consumed in the Asia-Pacific area, where pipeline transportation of natural gas is impossible or uneconomic (Sung and Kim, 2017. LNG has to be vaporized before distributed to the end users. LNG contains a significant amount of cold exergy, which is normally discarded without proper utilization during the regasification process (La Rocca, 2010. Traditional vaporization technologies include Open Rack Vaporization (ORV) (Chen and Chen, 2010), Submerged Combustion Vaporization (SCV) (Tagliafico et al., 2013), Ambient air-based Heating Vaporization (AHV) (Zihang et al., 2012) and Intermediate Fluid Vaporization (IFV) (Pu et al., 2014. The ORV technology, which uses seawater to vaporize the LNG, requires that the LNG terminal is close to the sea, and the temperature change of seawater can exert disadvantageous influence on the marine system. The SCV technology, which combusts natural gas to vaporize LNG, is applied if there are no other thermal sources and therefore the combustion of LNG itself must be adopted. The AHV technology has no restriction on the terminal location, but the heat transfer coefficient is much lower. Therefore, a larger heat transfer area is required. IFV technology uses an intermediate fluid (e.g. propane) to transfer heat from seawater to LNG. For an 8 GSm3/year vaporization facility, the seawater flowrate can be as large as 3000 m3/h in the ORV technology, where the pumping work is considerable, and almost 2 % of the main LNG stream is burned in the SCV unit (Le et al., 2018. Therefore, a significant amount of pump work must be consumed in the ORV technology and a certain portion of LNG is lost in the SCV technology. These technologies not only waste the cold energy of the LNG but also consume extra energy. For traditional technologies, the cold energy of LNG is totally wasted. In addition, environmental impacts on the marine

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ecosystem are not negligible or extra energy is consumed to vaporize LNG. Therefore, LNG cold energy recovery has at least three merits: (1) recovery of cold energy to increase energy efficiency, (2) energy savings related to pump work (seawater) or compressor work (air) and avoiding consuming extra LNG for regasification, and (3) alleviate the environmental impact caused by the regasification processes.

Power generation with LNG cold energy recovery is considered as a promising option to overcome the limitations for traditional regasification technologies. Direct expansion and Organic Rankine Cycle (ORC) are both effective ways to utilize LNG cold energy, which not only generate power but also reduce the environmental impacts of the regasification process and avoid combusting natural gas to vaporize LNG. Direct expansion of natural gas aims at recovering the pressure-based exergy of LNG, while ORC focuses on utilizing the temperature-based exergy of LNG. If direct expansion and ORC are combined in the regasification system, the LNG recovery efficiency can be substantially improved.

Working fluids are crucial factors for the performance of an ORC system. Due to the cryogenic temperatures of the system, the working fluids of an ORC system recovering LNG cold energy are different from those for conventional ORCs operating above ambient temperature. All published studies have investigated working fluid performance under given system configurations or LNG regasification pressures. Yu et al., 2019) investigated pure working fluids under various natural gas applications. However, the pinch limitation in the evaporator with sensible heat sources results in poor thermal matching between the heat source and working fluid due to the isothermal phase change of pure working fluids (Yu and Feng, 2014. To alleviate the pinch limitation, mixed working fluids can achieve "gliding match" because of the non-isothermal phase change of mixed working fluids. Therefore, use of mixed working fluids is a promising way to improve system performance.

Mixed working fluids can be classified into binary zeotropic mixed working fluids (Abed et al., 2013) and multicomponent zeotropic mixed fluids (Yu et al., 2018. Mixed working fluids can not only improve the thermal efficiency of the ORC system but also reduce the turbine size (Prasad et al., 2015. Therefore, mixed working fluids show advantages from both thermodynamic and economic perspectives. However, all the above literature focus on mixed working fluids for ORCs operated above ambient temperature. Mixed working fluids for cryogenic ORC systems recovering LNG cold energy have not been investigated in the open literature. This study investigates mixed working fluids for ORC systems recovering LNG cold energy, which is operated at cryogenic temperature levels.

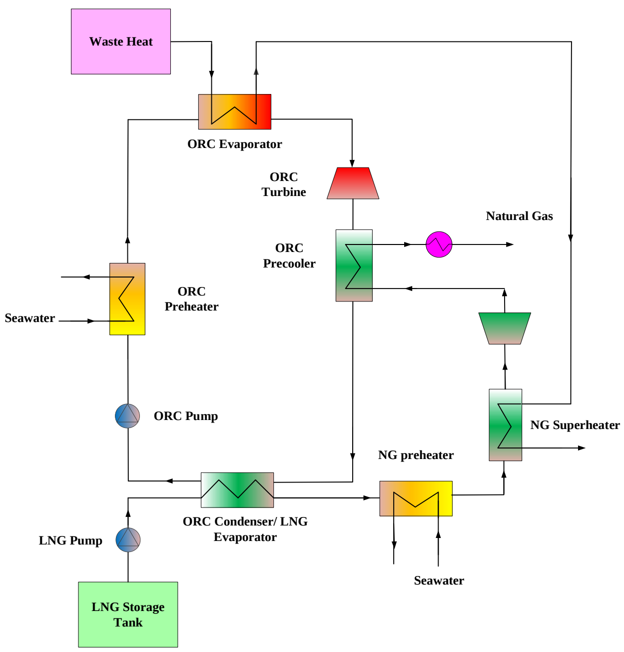

Figure 1: Flowsheet of the integrated system (Yu et al. 2019)

2. Process description

LNG contains both temperature-based exergy and pressure-based exergy, and an ORC can exploit temperature-based exergy efficiently. However, the pressure-based exergy cannot be recovered properly if only an ORC is adopted in the system. Direct expansion of natural gas can recover the pressure-based exergy of

LNG. To recover both the temperature-based and pressure-based cold exergy efficiently, ORC and direct expansion of natural gas should be considered simultaneously in an integrated system. The complete process flowsheet is sketched in Figure 1, where LNG cold energy and waste heat are utilized simultaneously. There are three streams in the integrated systems; one cold stream (LNG), one hot stream (waste heat) and the organic working fluid, which can be both a hot and a cold stream. LNG is evaporated by the organic working fluid, seawater, and waste heat in sequence before being fed to the natural gas turbine. After direct expansion, the natural gas cools down the organic working fluid in the ORC to improve the efficiency of the ORC and then natural gas is heated to its target temperature. The waste heat is utilized to heat the organic working fluid and natural gas successively. The waste heat can be any available heat source from industry or renewable heat sources such as biomass and solar energy near the LNG terminal. In this study, the waste heat source is assumed to be flue gas from a natural gas based power plant. The organic working fluid is cooled by natural gas first and then condensed by LNG in the ORC condenser, which is also called LNG evaporator. After pumping, the organic working fluid is heated by seawater and waste heat consecutively. In this integrated system, both the waste heat and LNG cold energy are utilized in a reasonable sequence. After regasification, natural gas is transported to the end users for the further application.

3. Simulation and optimization

The combined ORC and direct expansion cycle shown in Figure 1 are developed and simulated in Aspen HYSYS. Peng-Robinson equation of state is chosen as the thermodynamic property method. The adiabatic efficiency of the pumps is assumed to be 75 %. The polytropic efficiency of the turbine is assumed to be 80 %. The pressure drop in heat exchangers is neglected. The temperatures of the working fluid and natural gas after being heated by seawater are assumed to be 10 °C. Yu et al., 2019) have investigated pure working fluids for ORC systems recovering LNG cold energy. To make a fair comparison with previous studies, the waste heat is the same as the waste heat in the reference (Yu et al. 2019. The waste heat source is assumed to be pure CO_2 at 150 °C and 2 bars. The mass flow rate is 9509 kg/h based on data from a natural gas power plant (Lee et al. 2015. The composition of LNG is the same as in previous studies (Lee et al. 2015) as shown in Table 1. A total of 21 organic working fluids and CO_2 were investigated by Yu et al., 2019. However, they found that only 15 organic working fluids can attain condensation temperature lower than 0 °C. Therefore, 15 working fluids are investigated in this study, as shown in Table 2. The goal of this study is to compare the performance of pure working fluids and mixed working fluids. The optimal composition of the mixed working fluids will be determined.

Table 1: LNG composition

Component	Mole fraction
Nitrogen	0.0007
Methane	0.8877
Ethane	0.0754
Propane	0.0259
Butane	0.0056
Iso-butane	0.0045
Pentane	0.0001
Iso-pentane	0.0001
Total	1.0000

To get the optimal composition of the mixed working fluids and the optimal operating conditions of the system, optimization must be performed along with simulation. In this study, a simulation-based evolutionary optimization framework is adopted. Particle Swarm Optimization (PSO) algorithm implemented in Matlab and a process simulation model in Aspen HYSYS are connected by a COM object through the actxserver command. The variables in the simulation have to be decided before sent to Matlab for optimization. Based on the assumptions and a degree of freedom analysis, there are 7 independent variables in the integrated system. The following 7 variables are chosen as the independent variables in this study: (1) ORC evaporation pressure, (2) ORC condensation pressure, (3) LNG evaporation pressure, (4) Heat load of LNG evaporator, (5) Heat load of ORC evaporator, (6) Heat load of natural gas superheater, and (7) Molar flowrate of the organic working fluid.

For the mixed working fluids, composition of the working fluid has to be determined, which results in more variables. Unfortunately, composition data cannot be transferred from Matlab to Aspen HYSYS as variables for optimization purposes. As a way to overcome this problem, the mixed working fluids can be simulated by a mixer where pure working fluids are mixed. The balance block in Aspen HYSYS can then be used to transfer the mixed working fluid to the ORC system. In this way, the molar flow rate of each component becomes the independent variables and composition variables are avoided. In the PSO algorithm, the population size is set to 50 and the maximum number of iterations is limited to 100 in order to get results in practical times. Larger population size and more iterations can improve the solution to some extent. The code and PSO algorithm are implemented and run in Matlab 2014b environment on a PC with 4 cores 2.8 GHz Intel i7 CUP and 32 GB of RAM.

Table 2: Working fluids investigated in this study

Working fluid	Chemical formula	T_c (°C)	P_c (bar)	T_s (°C) [a] at 1 bar	P_s (bar) [b] at T_0
R1150	C_2H_4	9.2	50.5	-104.20	-
R116	C_2F_6	19.9	30.4	-78.37	23.97
R23	CHF_3	25.9	48.2	-81.88	32.82
R170	C_2H_6	32.2	48.8	-88.94	30.37
R125	C_2HF_5	66.0	36.2	-48.39	9.07
R143a	$C_2H_3F_3$	72.7	37.6	-47.42	8.39
R32	CH_2F_2	78.1	57.8	-51.66	11.13
R290	C_3H_8	96.8	42.5	-42.49	6.36
R1270	C_3H_6	91.1	45.5	-48.24	7.78
R134a	$C_2H_2F_4$	101.0	40.6	-26.36	4.13
R227ea	C_3HF_7	101.7	29.1	-16.73	2.79
R3110	C_4F_{10}	113.2	23.2	-2.65	1.61
R152a	$C_2H_4F_2$	113.3	45.2	-24.20	3.72
R236fa	$C_3H_2F_6$-D1	124.9	32.2	-1.15	1.56
R600a	C_4H_{10}-2	134.7	36.4	-11.96	2.19
R600	C_4H_{10}-1	151.9	37.9	-0.77	1.48

[a] saturation temperature at 1 bar

[b] saturation pressure at ambient temperature (15 °C)

4. Results and discussion

According to the operating pressure of the ORC system, ORCs have been classified into subcritical ORC and supercritical ORC (Braimakis et al., 2015. However, if the condensation process passes through the two-phase region, it should be called trans-critical ORC instead of supercritical ORC even if the heating pressure is supercritical. On the other hand, thermophysical properties become unstable near the critical point, where the operation is difficult to control, and equipment design is challenging. However, the latent heat can be very small and the thermal match between the heat source and the working fluid can be improved if the working fluid evaporates in the near-critical region. Therefore, near-critical region operation needs special attention. In this study, ORCs are classified into three subtypes, namely sub-critical ORC, near-critical ORC and trans-critical ORC. Quantitatively, subcritical ORC refers to the one operated below 90 % of the critical pressure of the organic working fluid. Near-critical ORC means that the evaporating pressure of the ORC lies within 90 %-100 % of the critical pressure. In the near-critical region, the properties of the working fluid are very sensitive to temperature and pressure. Therefore, special attention has to be paid to the ORC operating in the near-critical region. For trans-critical ORC, the maximum pressure is set to 130 % of the working fluid critical pressure (Braimakis et al., 2015.

For different types of ORCs, Figure 2 illustrates the net power output of pure and mixed working fluids for different types of ORC. For pure working fluids, R170 and R290 perform better than other working fluids. However, due to the very low critical temperature of R170, it becomes pure vapor phase at subcritical pressure after being heated to 10 °C by seawater and the degree of superheat can reach as high as 130 °C. Since the critical temperature of R600 (151.9 °C) is higher than the waste heat inlet temperature, trans-critical ORC is not attainable for R600. Therefore, only sub-critical and near-critical results are shown in Figure 2 for R600. R290 (Propane) performs well for sub-, near- and trans-critical ORCs. R290 has been reported as the promising working fluid for an ORC recovering LNG cold energy by Le et al., 2015. In this study, R290 and R1270 are chosen as the components of the mixed working fluids. Since the composition of the mixed working fluids are variables and the critical properties of mixed working fluids strongly depend on the composition, it is difficult to distinguish the sub-critical and near-critical ORCs. The upper bound for the evaporation pressure is set to 45 bar for sub- and near-critical ORC and the upper bound for the evaporation pressure is set to 60 bar for trans-critical ORC with mixed working fluids. The model can determine the optimal operation mode, namely sub-critical or near-critical ORC automatically. The results show that the final optimal results are within the sub-critical region and the near-critical results is not available for mixed working fluids. The optimal molar compositions of the mixed working fluid for sub-critical and trans-critical ORC are 0.56:0.44 (R290:R1270) and 0.51:0.49 (R290:R1270) respectively. Based on the results shown in Figure 2, the mixed working fluids perform a little better than the pure working fluids (R290, R170 and R32. However, the improvement is quite limited. The reason can be explained as follows. Since both waste heat and LNG are considered in the integrated system, the improvement in thermal match has marginal effect on the system power output. Not only waste heat recovery efficiency but also the efficiency in LNG cold energy recovery exert great influence on the net power output of the integrated system. In addition, the working fluids with lower critical temperature can also match well with the waste heat source but at the cost of a large degree of superheating. The optimal working fluids tend to be the ones with lower critical temperatures, which results in lower condensation temperature. The lower the condensation temperature, the higher the LNG cold energy recovery. However, lower critical temperature limits the thermal efficiency of the ORC and the waste heat utilization efficiency. Therefore, there is a trade-off between waste heat recovery and LNG cold energy recovery. Critical temperature can reflect the ability of the working fluid to recover waste heat and LNG cold energy. The working fluids with higher critical temperature show better ability to recover waste heat and the working fluids with lower critical temperature show higher ability to recover LNG cold energy. As for the trans-critical ORCs, our results do not show any indication that mixed working fluids have advantages over the pure working fluids from the power output point of view. Thus, it seems as if mixed working fluids are not very promising for improving the performance of the system.

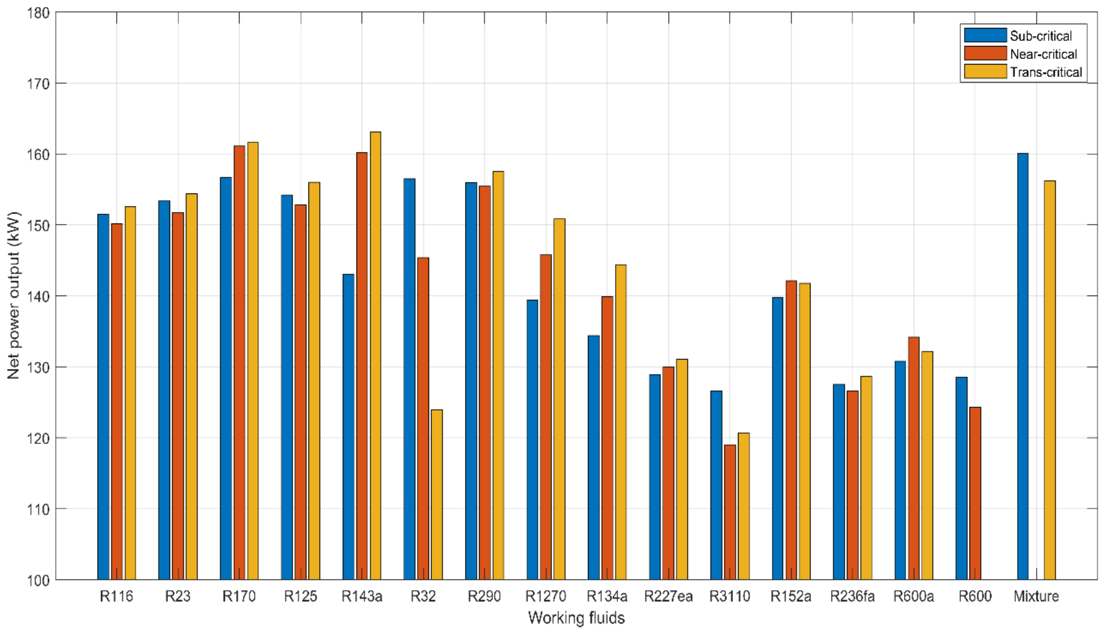

Figure 2: Power output of pure and mixed working fluids

Last but not least, the waste heat inlet temperature is assumed to be 150 °C in this case study. For the working fluids investigated in this study, those whose critical temperature is close to the waste heat inlet temperature cannot attain a very low condensation temperature. Working fluids whose critical temperature is much lower than the waste heat inlet temperature have to be superheated to a large extent for the sub-critical and near-critical ORC. However, if the waste heat inlet temperature decreases, the mixed working fluids can probably perform much better than pure working fluids, which should be investigated in the future work.

5. Conclusion

Pure working fluids and mixed working fluids for different types of ORC are investigated in this study. ORCs are classified into sub-critical, near-critical and trans-critical (or super-critical) ORCs with pure and mixed working fluids. For sub-critical ORCs, mixed working fluids perform a little better than pure working fluids. For near-critical and trans-critical ORCs, mixed working fluids do not show any improvement in net power output from the system. Since both waste heat and LNG cold energy are utilized in this system, the advantage of mixed working fluids to improve the thermal match between the heat source and the working fluid is marginal. The trade-off between waste heat recovery and LNG cold energy recovery cannot be improved by mixed working fluids. However, the waste heat inlet temperature exerts great influence on choice of working fluids significantly. If the waste heat inlet temperature decreases, the advantages of mixed working fluids will be enhanced according to the results of this study. The relationship between waste heat inlet temperature and mixed working fluids will be investigated in the future work.

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