A Novel LNG and Oxygen Stoichiometric Combustion Cycle without CO₂ Emission

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ABSTRACT

Liquefied natural gas (LNG) supplies relatively clean energy due to its low contribution to environmental pollution. LNG has high valuable cryogenic exergy (at ~110 K). So it is better to convert its cryogenic exergy into power instead of uselessly cooling the seawater used for its re-vaporization in many LNG receiving terminals. In addition, due to the increasing concern about global climate change, the development of zero CO_2 emission system is of great interest.

In this paper a novel cycle is proposed which combines LNG fuel and pure O_2 . The cycle employs H_2O as the main working medium. Oxygen and fuel methane are introduced at stoichiometric ratio, and thus the turbine exhaust is merely a mixture of carbon dioxide and water steam. The LNG coldness is used to cool exit stream and capture CO_2 . Internal combustion and recuperation are adopted to increase the average heat absorption temperature. The proposed cycles are simulated using the commercial ASPEN PLUS code. Parametric studies are carried out to evaluate the influence of key parameters, including the top temperature, pressure ratio, on the cycle performance and component sizes.

KEY WORDS:

Novel cycle, Liquefied natural gas (LNG), CO₂ emission, Oxygen

NOMENCLATURE

Р	Pressure	bar				
Q	Heat duty	kJ				
R	The mass rate ratio of recirulating feed water t					
	reaction product water					
S	Entropy	kJ/kgK				
Т	Temperature	⁰ C				
η_2	Exergy efficiency					

1. INTRODUCTION

Natural gas is regarded as a rather clean energy resource due to its relatively lower contribution to environmental pollution; the volume traded and consumed yearly worldwide increases steadily, of which the percentage of LNG (Liquefied natural gas) increases even more dramatically. During the process of LNG preparation, lots of power is consumed for compression and refrigeration and a considerable portion is preserved as cryogenic exergy in LNG, which has a final temperature of about 110K. At the same time, its volume drops to 1/600 and is therefore convenient for long distance transportation.

LNG is loaded into insulated tankers and transported to receiving terminals. According to practical requirement, it is first pumped to certain pressure, and then heated and vaporized to approximately ambient temperature for pipeline transmission to the consumers. Currently there are two kinds of delivery pressure available in the receiving terminals: supercritical pressure for long distance pipeline supply and subcritical pressure for nearby users. It is better to use the LNG cryogenic exergy before it is supplied to the consumers; otherwise the LNG is commonly heated by seawater, besides exergy waste, there would be sea pollution due to seawater temperature decrease.

In fact people usually employ the LNG coldness for some purposes, such as liquefying and separating air, cooling the goods etc, but not to convert cryogenic exergy to power. The possible power cycle for cryogenic power generation mainly includes: natural gas direct expansion cycle, closed-loop Ranking cycle, Brayton cycle and the combination of two or more of them. Besides, the use of LNG cold exergy to improve the performance of thermal cycle is also of great interest. For example, LNG vaporization can be integrated with gas turbine inlet air cooling or steam turbine condenser system (Zhang et al, 2002). Closed-loop Ranking cycle usually uses refrigeration coolant as working medium, sea water as heat source and LNG as cool sink (Cheng et al, 1999). For higher heat source temperature, Brayton cycle commonly is adopted, which usually use nitrogen or helium as working fluid(Chiesa, 1997). Some commercial plants have been established in Japan from last 80's, represented by the combination of closed-loop Rankine cycle (with pure or mixture organic working fluid) and direct expansion cycle (Karashima et al, 1982).

Due to the increasing concern about greenhouse effect on climatic change, the research and practice of CO_2 emission mitigation have drawn more and more attention in recent years. Riemer (1995) summarized the technologies available and indicated that the amount of energy consumed for CO_2 capture could commonly lead to the reduction of power generation efficiency up to 10 percentage points. CO_2 zero-emission cycles are proposed by some authors, such as



Fig.1 Flow chart of the cycle

F—separator IC—intercooler LC/HC—low/high pressure compressors H—heat exchanger P—pump R—recuperator T—turbine

Mathieu et al (1999), Deng et al (2002), Kosugi et al (2003). MATIANT cycle comprises a supercritical CO_2 Rankine-like cycle combined with a regenerative Brayton cycle with reheat. Deng proposed a gas turbine cycle with nitrogen as its main working fluid. Kosugi analyzes economics of solar thermal hybrid H₂O turbine power generation system.

In this paper, we propose a new turbine cycle with combustion of LNG and oxygen. Internal combustion and recuperation are adopted to increase the average heat absorption temperature. O_2 and fuel CH_4 are introduced at stochiometric ratio, and H_2O is preheated and injected in combustion chamber to decrease combustion temperature. Therefore the turbine exhaust is merely a mixture of CO_2 and H_2O . Without consuming additional power, the water and CO_2 generated from combustion can be easily separated with seawater and LNG evaporation process. We capture liquid CO_2 and recover pure water. This cycle has an attractive

performance of both high power generation efficiency and low environment impact.

2. DESCRIPTION OF CYCLE CONFIGURATION

There are two different nature gas delivery pressures: supercritical pressure (70bar) for long distance pipeline networks and subcritical one (30bar) for nearly combined cycle power stations and local distribution. We choose the subcritical one. It is assumed that LNG is pure methane in this paper.

The evaluation criteria are very important for thermodynamic analyses (Deng et al, 2002). In the paper we mainly use the second law efficiency. Since this cycle employs both fuel heat value and LNG evaporation process as its input resources, the second law efficiency is a more suitable criterion for performance evaluation, it can be defined as the ratio between obtained and consumed exergy.

Exergy efficiency: $\eta_2 = W/(m_2e_2+m_1e_1)$

Where m_1 and m_2 are the LNG mass flow rate and fuel mass flow rate respectively; e_1 and e_2 are the inlet exergy of the LNG and fuel combustion respectively, W is the overall net power output from cycle.



Fig.2 T-S diagram of the cycle

The proposed cycle flow sheet and the corresponding T-S diagram are shown in Fig.1 and 2. The pure oxygen O_2 from air separation unit first flows through low-pressure compressor LC1, intercooler IC1 and high-pressure compressor HC1 in turn to be compressed. After being further heated in recuperator R2, it enters the combustor. According to stoichiometric proportion, low temperature LNG (~110K) is preheated through intercooler IC1 and recuperator R1 to enter combustor, where oxygen and fuel (CH₄) are burnt. Some quantitative condensing-water is pumped (pump P2) to certain pressure and preheated in recuperator R3. And then entering the combustor, it absorbs heat to decrease combustion temperature to currently technically allowable degree. The combustion products are mere CO₂ and H₂O with the highest cycle temperature and pressure; the mixture expands in turbine (T) to produce electricity until its pressure drops to certain pressure. The turbine exhaust enters the recuperator R1, R2 and R3 in turn; and at heat exchanger H1 most part of water releases heat and condenses, then the mixture enters the separator F1 where water is separated. Remaining CO_2 and a little bit steam flow through heat exchanger H2 to be further cooled and the much left of water can be condensed and discharged at the separator F2. CO₂ capture part is followed. The triple point pressure and temperature of CO_2 are 5.178 bar and -56.6° C respectively, these figures would be damage to the power plant if the condensing pressure were too low to introduce solidification of CO2 medium. Therefore, it is better to select the condensing pressure higher than the triple point pressure, for example 5.5 bar, which corresponds to a saturated higher temperature. Since the turbine exhaust pressure is selected to a value lower than 5.5 bar, the working medium CO₂ must be compressed before entering CO₂ condenser H3. In order to reduce the compression work to a possibly low value, an intercooler IC2 is adopted. The compressed CO₂ from high-pressure compressor HC2 outlet exchanges heat with low temperature LNG to be liquefied and captured.

The LNG subcritical evaporation process is chosen since it is possible to obtain a better heat transfer temperature matching with the cycle exothermal process. LNG off-loaded from its storage tank is first pumped to the subcritical pressure, and then enters heat exchanger H2, intercooler IC2 and heat exchanger H3 respectively, where liquefied natural gas is heated to ambient temperature at the outlet and then sends out via pipeline to user's end.

In the paper, ambient temperature seawater ($\sim 15^{\circ}$ C) is used to cool the mixture stream to make water steam to condense.

3. PERFORMANCE OF THE CYCLE

A typical case is first simulated by commercial ASPEN PLUS code. The most relevant data assumptions for the calculation in this paper are summarized in Table 1. Table 2 summarized the parameters, including temperature, pressure and flow rate, of each stream for the cycle.

0.8kg CH₄ and 3.2kg O₂ is combined to form 1.8kg H₂O and 2.2kg CO₂ in the reactor. At the same time, the released energy is used to superheat the preheated 1.8R kg recirculating condensate feed water in which *R* is the factor to control the maximum working medium outlet temperature (in the case, R=4.24). The reaction product and heated steam are mixed directly to form (1+R)1.8+2.2=11.63kg superheated mixture and to expand in the turbine. Since the pressure of the cycle is lower and the cycle maximum temperature is comparatively high, the turbine exit temperature will still high ($\sim 413^{\circ}$ C). The thermal energy of this part (process S6-9) can be used to preheat the condensate feed water and reactant of CH₄ and O₂. The turbine exit back pressure is 0.1bar lower than the normal gas turbine atmospheric one owing to the condensation of H₂O. So the specific power output is much larger than that of gas turbine. Although the pressure of feed water is lower than the conventional steam cycle, which perhaps has unfavorable influences on the cycle efficiency, however less power is needed to compress O_2 . So the cycle efficiency is still higher for high turbine inlet temperature. The main point is that the cycle is an internal combustion one and can obtain a high cycle maximum temperature to raise the efficiency. If the temperature is permitted to have a high enough value in the future, the cycle efficiency will reach a very high value with rather small amount of or even without recirculating the condensate feed water.

The mass flow rate of LNG regasificated is 7kg/s, of which about 11.4% should be sent to the combustor as fuel of the cycle. Meanwhile, the effective amount of water is 1.8kg/s (condensing water minus recirculating feed water). And CO₂ recovered is 2.2kg/s. Totally 20.907MW power can be produced with the thermal efficiency of 47.6% and exergy efficiency (including LNG cold exergy input) of 43.3% basically without CO_2 emission. The capacity of the plant should be 255 MW or so for a LNG receiving terminals of 95 kg/s import capacity, which corresponding to 3000,000 ton yearly (the imported amount of Chinese first LNG receiving terminal). In the paper, we think that O₂ from air separation system is at the gas state of ambient pressure and 1kg O₂ consumes 720kJ work. Before entering combustor, it first be compressed to the required pressure. So the consumption work of 1kg O₂ is equal to 720kJ plus compressor work. At last, the efficiency will lose about 3%.

Table.1 Main assumptions for	r the calculation *	
Turbine	Inlet temperature (⁰ C)	1250
	Isentropic efficiency (%)	88
Compressor	Pressure ratio	16
	Isotropic efficiency (%)	88
Pump	Efficiency (%)	77
Combustor	Efficiency (%)	99
	Pressure loss (%)	3
Recuperator	Minimum temperature difference (⁰ C)	20
	Pressure loss (%)	3
Heat exchanger	Minimum temperature difference (⁰ C)	>=7.5
	Pressure loss (%)	3
LNG vaporization system	LNG Efficiency (%)	77
	Pressure loss (%)	3

* According to Cai (1998), the heat transfer temperature differences are selected to be the evaluation criteria of all heat exchangers including recuperator, but not some other criteria such as recuperator effectiveness, since the latter can not reflect the correct level of the recuperator.

Table.2 The stream parameters of cycle

No.	Temp	Pres	MFR	No.	Temp	Pres	MFR
	(⁰ C)	(bar)	(kg/s)		(⁰ C)	(bar)	(kg/s)
S1	-162.0	1	0.8	S17	5.0	0.687	2.3
S2	-1611.23	17	0.8	S18	5.0	1.0	0.1
S3	-30.92	17	0.8	S19	5.0	0.687	2.2
S4	200.0	16.5	0.8	S20	200.85	5.5	2.2
S5	1250	16	11.63	S21	-52.18	5.5	2.2
S6	413.43	0.1	11.63	A1	15.0	1.0	3.2
S7	392.27	0.097	11.63	A2	173.77	4.12	3.2
S8	379.07	0.094	11.63	A3	-30.0	4.12	3.2
S9	55.4	0.091	11.63	A4	106.6	17	3.2
S10	35.0	0.089	11.63	A5	200.0	16.5	3.2
S11	35.0	1.0	7.87	B1	35.0	1.0	7.63
S12	35.0	0.089	3.76	B2	35.26	17	7.63
S13	5.0	0.086	3.76	B3	203.02	16.5	7.63
S14	5.0	1.0	1.46	W1	15.0	1.0	228.32
S15	5.0	0.086	2.3	W2	35.0	1.0	228.32
S16	206.25	0.708	2.3				

In the paper, the main losses are heat exchange losses in the reactor. In the case, the inlet temperature of the recirculating condensate feed water (stream B3) is 203^{0} C, but the temperature of stoichiometric absolute combustion is about 3000^{0} C in the combustion chamber. There is a much larger temperature difference of 2700^{0} C. In order to decrease the loss, feed water can be recuperated to higher temperature steam in a certain place of turbine. It means separating the turbine into two parts and install a regenerator between these two turbines. Such study will be carried out later.

The cryogenic exergy of LNG regasificated is used to cool and liquefy CO_2 in heat exchanger H2, intercooler IC2 and heat exchanger H3. Adoption of intercooler can effectively reduce the compression work. Fig.3 shows T-Q relation of LNG evaporation process. From T-Q diagram, we see that the temperature matching of hot stream CO_2 and

cool stream LNG is not good, especially in heat exchanger H2. The heat exchanged in H2 is about 64%, 11% in the intercooler IC2 and the left 25% all in the heat exchanger H3. But if the temperature of stream S10 is cooled to lower temperature, the heat load of heat exchanger H2 will rapidly decrease; heat transfer loss also decreases. If solid CO₂ can be easily removed from condensation set, the liquefaction part of CO₂ can be omitted.

We have investigated the effect of cycle maximum pressure, cycle maximum temperature and parameter R (ratio of recirculating condensate feed water mass flow rate to reaction product water steam mass flow rate) on the characteristics. The range of temperature is $1100 \sim 1400^{\circ}$ C; the range of pressure is $9 \sim 25$ bar. The most relevant data assumptions for the calculation in this part are same with Table 1.



Fig.3 T-Q diagram of LNG vaporizing processes



Fig.4 Exergy efficiency for different cycle maximum pressure and temperature

The cycle maximum pressure and temperature are important parameter of cycle analysis. The exergy efficiency variations with pressure and temperature are shown in Fig.4. In the paper, the pressure expansion ratio in the cycle is much higher than the pressure compression ratio, which condition is entirely different from the gas turbine pressure ratio in common use. It is shown in the figure that the cycle efficiency sharply increases with maximum temperature going up. For the highest permitted cycle maximum temperature in recent advanced gas turbine –about 1400°C, the exergy efficiency can be higher than 47% without CO₂ emission, equivalent to more than 51% thermal efficiency without CO₂ emission. When the stoichiometric reaction of LNG and oxygen is permitted, the efficiency will reach maximum value. The pressure has a smaller effect on efficiency, and in the recently common used pressure range,

there does not exit an optimum pressure for each temperature. Because of the utilization of turbine exhaust heat to preheat the recirculating condensate feed water, the pressure effect on efficiency become less evident, and curves are flatter.



Fig.5 The mass flow ratio of the cycle

The mass flow ratio of recirculating condensate feed water to product steam is an important key factor for controlling the cycle temperature as shown in Fig. 5. From the figure, both the pressure and temperature have effect on R, but the effect of temperature is more evident. The R decreases with increase of temperature and pressure. Therefore, the lower R is, the better the cycle efficiency will be.

4. THE MODIFICATION OF THE CYCLE

In the cycle, the maximum loss is in the combustion chamber. The reason is from two ways. One is that temperature of the feed water is lower. The other is that injected water in the combustion chamber first vaporizes and then the temperature increases. So the temperature of feed water should be modified. The modified cycle is shown in Figure 6. There are two modifications. Firstly, before the fuel and oxygen enter combustion chamber, they were not preheated by turbine exhaust. Oxygen intercooling compression was omitted and oxygen was directly compressed to increase the temperature. Secondly, before entering, feed water was preheated two times. In the recuperator R2, feed water absorbs the latent heat of turbine exhaust. And in the recuperator R1, feed water absorbs sensible heat of turbine exhaust.

After modification, the temperature of oxygen goes up to 388° C from 200°C. Steam percentage of feed water enhances from 0 to 0.141. The final temperature of exhaust gas decreases from 55.4°C to 43.3°C. Fuel percentage of vaporized LNG increases from 11.4% to 22.3%. Figure 7 shows the exergy efficiency of modified cycle. From Fig. 7, the exergy efficiency heightens 5 percent point to 52.1% (equivalent to 54.7% thermal efficiency). In short, the modification schedule is valid.



Fig.6 Flow chart of the modified cycle

F-separator LC/HC-low/high pressure compressors

H-heat exchanger P-pump R-recuperator T-turbine



Fig.7 Exergy efficiency of modified cycle

5. CONCLUSIONS

A novel cycle is proposed in this paper with stoichiometric combustion of oxygen and LNG. Thermal analyses are made with different cycle parameters, such as maximum cycle temperature and pressure.

Adoption of internal combustion, turbine inlet temperature can be selected at a higher level. The employment of recuperation cycle can improve the temperature of recirculating condensate feed water to decrease heat exchange loss. Lower back pressure makes mixture expand to lower temperature than common gas turbine. In the simulation range of temperature and pressure, there are attractive thermal performances with the thermal and exergy efficiency of 48.9%--54.7% and 46.5%--52.1%. If the cycle maximum temperature is permitted to a high enough value in the future, the cycle efficiency will reach a maximum point without recirculating water.

The cycle works in harmony with environment; water and carbon dioxide generated from combustion can be recovered and captured. At the same time, LNG can be evaporated to ambient condition to send to users.

It should be pointed out that utilization of O_2 from air separation system, in the proposed cycle, imposes a penalty to the cycle performance by about 3 percentage points. However, if air separation system and the power cycle can be integrally constructed with LNG receiving terminal, the above problem can be possibly resolved.

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