Proceedings of the ASME 2011 5th International Conference on Energy Sustainability
ES2011
August 7-10, 2011, Washington, DC, USA

ES2011-54702

EXERGY RECUPERATION OF MID AND LOW QUALITY HEAT BY CHEMICAL REACTIONS

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ABSTRACT

Conventional thermal power generation, as typified by gas turbines, has steadily increased power generation efficiency by elevating temperature of heat, but there is a limit to the maximum availability of electric energy. Exergy rate is a unified index indicating the quality of energy in deferent forms. We have no way in thermal conversion to extract all of the availability, while almost hydrocarbon fuels have exergy rate around 95%. 25% of exergy is inevitably lost through the combustion process from chemical to heat at maximum temperature of 2000°C. Hydrogen's low exergy rate provides "exergy recuperation" in which degrading 12% from 95% to 83% can take low quality heat up to availability of 83% as a kind of chemical heat pump. Chemically Recuperated Gas Turbine (CRGT) is a specific example, and dimethyl ether (DME) is one of the most suitable fuels because steam reforming occurs around 300°C. Electrochemical partial oxidation (EPOx) is another way to convert mid-quality heat into electric energy as much as difference between change in Gibbs free energy and change in enthalpy. This paper reports concept and industrially-feasible applications of this unconventional and non-cascadic use of heat.

INTRODUCTION

Energy conversion technologies between different forms, especially among three forms of chemical, thermal and electrical energy, are very important in the use of fossil fuel and the suitable technology should be selected taking advantage of each energy form. Chemical energy, which is an energy form suitable for massive storage and high-density transport medium, has to be converted into electric energy and thermal energy in some way to get our desirable amenity. Nowadays, electrified life style pushes up demand of power rather than heat, so power generation efficiency become more important. Table 1 summarizes storage features of three energy forms in terms of capacity, time span and potential of convertibility to other form. Conventional thermal power generation, which converts fuel (chemical energy) into work (electric energy) via heat (thermal energy) with irreversible combustion process, has steadily increased power generation efficiency by elevating temperature of heat, but there is a limit to the maximum availability of electric energy due to limitation of thermal barrier technology. Exergy rate ε defined as the ratio of exergy to enthalpy is a unified index indicating the quality of the energy in deferent forms. Kinetic energy or electric power have exergy rate of 100%. In the case of heat, the exergy rate of heat depends on the temperature and equation (1) gives exergy rate ε ignoring temperature dependence of specific heat capacity as first approximation.

$$\varepsilon = 1 - \frac{T_0 \ln \frac{T}{T_0}}{T - T_0} \tag{1}$$

In the case of chemicals, the exergy rate is approximately equivalent to $\Delta G/\Delta H$ that is the ratio of Gibbs free energy change to enthalpy change of specified reaction. For example, the exergy rates of combustion and steam reforming of methane are calculated as following equations (2) and (3), respectively:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(l) \tag{2}$$

$$\varepsilon = \Delta G°/\Delta H° = -817.9\text{kJ/mol} / -890.3\text{kJ/mol} = 91.9\%$$

$$CH_4 + 2H_2O(l) \rightarrow CO_2 + 4H_2 \tag{3}$$

$$\varepsilon = \Delta G°/\Delta H° = 130.8\text{kJ/mol} / 253.0\text{kJ/mol} = 51.7\%$$

According to this definition, complete combustions of almost hydrocarbon fuels are approximately 95% that is high rate compared favorably with 100% of electric energy, but we have no way in thermal engines to extract all of the availability even in fuel cells. Heat at 2000°C, which is thought to be the upper limit of thermal resistance commercially available in industry, has exergy rate of 70%. This means that 25% of exergy is inevitably lost through the conversion process from chemical to heat energy. Hydrogen is a unique fuel in terms of exergy rate of 83% that is lower than that of other fuels. This value is also well-known as theoretical conversion efficiency of proton conducting fuel cells, and this lower quality provides two implications: One is decreasing the exergy loss due to combustion by 13%. The other is exergy recuperation by hydrogen-producing chemical reactions in which degrading 12% from 95% to 83% can take low-quality waste heat up to availability of 83% as a kind of chemical heat pump. Hydrogen production by methane steam reforming requires only exergy rate of 51.7% that is equivalent to the heat at 800°C. Energy conversion direction of chemical recuperation is conceptually shown in table 1, which goes just opposite direction of the conventional thermal power generation.

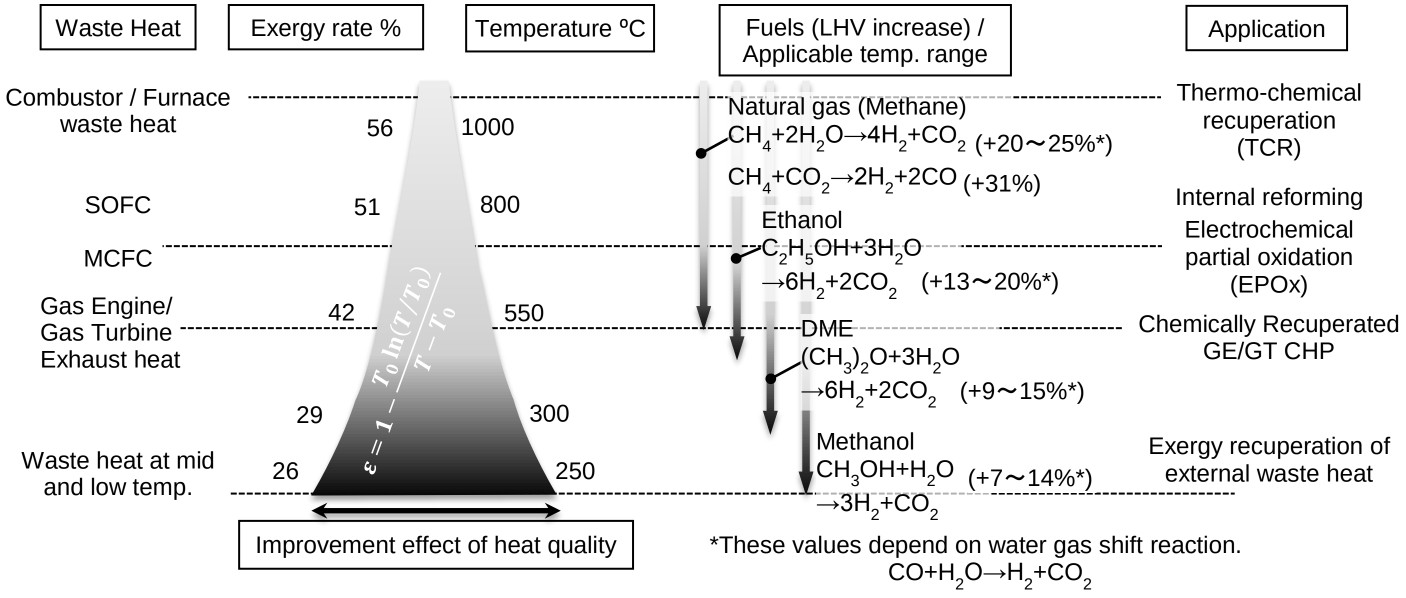
Figure 1 shows available fuels and applications of the chemical recuperation sorted by temperature ranges of unused or waste heats. Industrial combustor or furnace used in steel, ceramics, glass and cement industry emits a vast amount of high-temperature waste heat to keep product quality by controlling the temperature distribution uniformly. Methane reforming by steam or CO_2 occurs sufficiently at temperatures over 1000°C and recovers waste heat as increase in heating value and sensible heat of hydrogen-rich reformed gas. Percentage of LHV (Lower Heating Value) increase is shown in figure 1 beside each reaction as an index of chemical reaction effect, which is equivalent to the reduction in fuel consumption or CO_2 emission. This new technology called TCR (thermo-chemical recuperation) is now under development to reduce fuel consumption and corresponding CO_2 emission [1]. Fuel cells operated at high temperature generate power with high conversion efficiency, but inevitably generate heat due to internal resistance as well. Internal reforming of fuel is a reasonable system taking the internally generated heat into chemical enthalpy of hydrogen and almost all fuels are available at temperatures around 800°C.

Table 1. Storage features of three energy forms

	Chemical	Thermal	Electric
Convertibility to other	Via oxidation reaction	Limited due to irreversibility	Theoretically-lossless
Storage Time span	Long term Lossless	Short term Degrading with time	Middle term Degrading with time
Capacity	Massive High-density	High-density	Low-density
Media	Hydrocarbons H_2	Molten salt Water	Rechargeable battery
Exergy rate potential	HCs:90-95% H_2:83%	Temperature-dependent 2000°C:70%	100%
Energy conversion direction	Conventional thermal power generation → Fuel cells → ← **Chemical recuperation**		

Chemically recuperated gas turbine (CRGT) can increase power generation efficiency by recovering the exhaust heat with endothermic reaction of steam reforming. Reciprocating gas engine is also available for the power source. Natural gas is a commonly-used fuel for GTs and methane contained mainly in natural gas can be partially reformed even at temperatures around 550°C that is exhaust temperature of most GTs [2, 3].

Dimethyl ether (DME) is one of the most suitable fuels for chemical recuperation because on top of nonhazardous fuel for environment and human, the steam reforming reaction of DME can occurs even at low temperatures around 300°C in terms of thermodynamic equilibrium [4]. LHV increase from the original fuel expresses not quality but quantity, and generation of H_2 and CO from methane reaches up to 25.7% increase.



*These values depend on water gas shift reaction.
$CO+H_2O \rightarrow H_2+CO_2$

Figure 1. Temperature ranges of waste heats and available fuels / Applications of chemical recuperation

Vaporized ethanol also reaches around 24% increase of which 5% is physical contribution by latent heat of ethanol, while the value is relatively large. The waste heat of 300°C has exergy rate of 29%, which means that only 29% of all enthalpy can be extracted from this heat of finite quantity. However, the heat chemically recuperated into hydrogen has been given again an 83% possibility to convert the 100% exergy. Horizontal width of the mountain-shaped object in figure 1 indicates improvement effect of heat quality that depends on temperature of heat. High-temperature heat has originally high quality and even for same quantity of heat, the lower the temperature of heat is, the bigger the jump of heat quality is expected. In addition, adoption of suitable fuel for the exergy rate of the heat is important. In one example, both methane and DME are applicable for the heat of 800°C, but methane is more suitable than DME because DME requires only the heat of 300°C and 800°C is too high. This unconventional and non-cascadic use of heat is an important concept for energy conversion from the viewpoint of efficient use of energy.

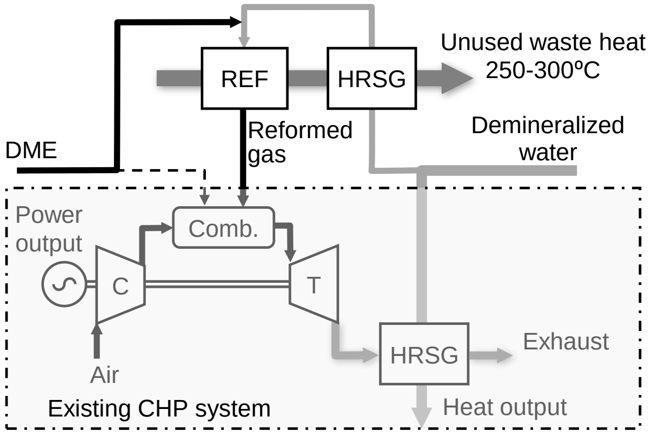


Figure 2. Schematic of chemical recuperation system for waste heat around 300ºC using DME

PRACTICE OF CHEMICAL RECUPERATION

If there are a combined heat and power (CHP) system and a source of unused waste heat in a same plant, chemical recuperation can be realized by addition of a catalytic reformer and can converts from the heat to the electric energy via chemical energy. Figure 2 shows the flow diagram of chemical recuperation system realized by means of a combination the existing CHP system and unused waste heat. In this case, assuming that the temperature of intended waste heat is at around 300°C, the reformed gas recovers and transports the external waste heat as the enthalpy change of DME steam reforming reaction and the exergy of the waste heat is recuperated as the exergy of electric power. Moreover, the heat energy incorporated once into the increase of heating value of reformed gas can keep lossless for a long time even though the reformed gas cool down to the ambient temperature. Phase change heat storage materials never have this notable feature of chemical storage.

The CRGT fueled by Dimethyl Ether (DME) was demonstrated using commercially available Micro GT (MGT) in 2007 with support of the Ministry of Economy, Trade and Industry of Japan [5]. The overview of demonstration test apparatus is shown in figure 3. The CRGT consisted of heat recovery steam generator and reformer which were directly attached to the outlet of turbine and recover its own exhaust

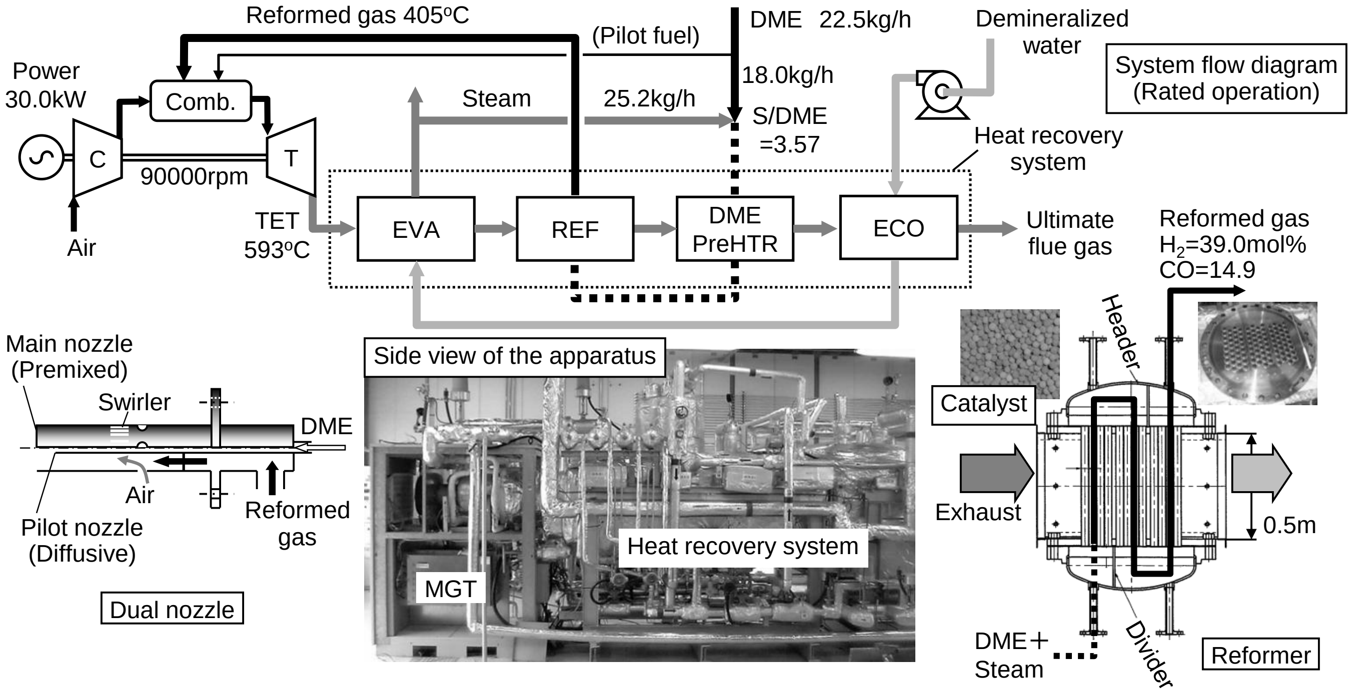


Figure 3. Overview of demonstration test apparatus for DME-fueled CRGT

heat recursively. DME and steam were mixed in the molar ratio of S/DME=3.5 and passed into the reformer through the preheater. The reformed gas heated up to 405°C and contained 39.0mol% hydrogen and 14.9mol% CO of which LHV increased by 7.9% compared to LHV of DME. Figure 4 shows summary of the test results. Power generation efficiency increased with increasing steam mass flow corresponding to reformed gas ratio in the mixed fuel gas. In terms of burning characteristics, the combustion efficiency increased and NO_x emission reduced with increasing reformed gas ratio because flame speed increased with increasing hydrogen and steam reduced the production of thermal NO_x attributed to the flame temperature. The demonstration test successfully accomplished both 10% reduction of fuel consumption compared with steam injected GT (STIG) cycle and NO_x emission level of less than 10ppm.

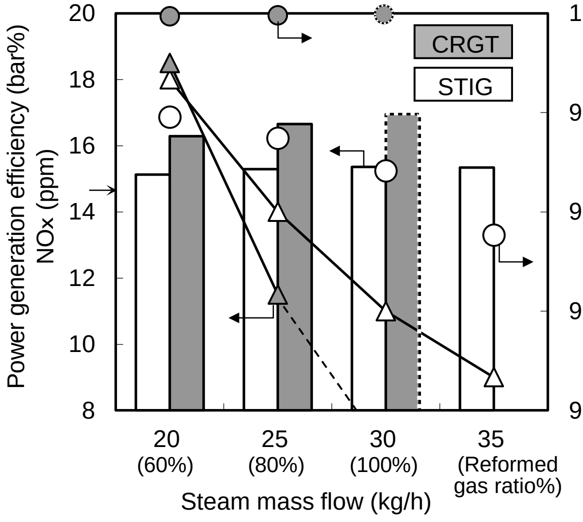


Figure 4. Results of power generation efficiency and NO_x emission in demonstration test

Both CRGT systems in figure 2 and 3 need two specific equipments; the fuel nozzle and reformer. The fuel nozzle equipped on the combustor is designed in accordance with the fuel properties such as heating value, density and Wobbe index. Operation of CRGT needs to switch the fuel from DME to the reformed gas without flame-out. There is a much difference in the fuel properties between almost original fuel and reformed gas due to not only the temperature and steam addition but also increase in number of moles by reaction. In the above-mentioned case, the volume-specific heating value and Wobbe index of the reformed gas were about a seventh and a quarter of those of DME, respectively. The demonstration test used the modified fuel nozzle shown in figure 3 to fit to the original mounting surface. The nozzle had concentric double pipe, one of which was designed to burn DME directly with diffusive combustion, and the other was premixed combustion of low-calorific reformed gas. The reformer, which is the key component of the chemical recuperation system, typically consisted of the tube bundle attached to the header and the duct designed to fit to other heat exchangers. As shown in figure 3, each tube is filled with a catalyst and the tube bundle arrangement is determined by numerical calculation including reaction rate data. The demonstration test used the catalyst of Pt-0.5wt% supported on γ-alumina which generated mainly H_2 and CO with sufficient reaction rate at around temperatures of 450°C. H_2/CO selectivity is one of the most important characteristics for chemical recuperation in terms of LHV increase. The reformer shown in figure 2 also requires the catalyst that meets high H_2/CO selectivity and low-temperature activity as well as basic requirement of long life or reasonable price. DME steam reforming proceeds in two steps via methanol [6]. The hydrolysis reaction from DME to methanol is caused by solid acid such as alumina and zeolite [7].

$$C_2H_6O + H_2O \rightarrow 2CH_3OH \quad \Delta H=23.6\text{kJ/mol} \tag{4}$$

H-ZSM5 is more effective than γ-alumina for this reaction in our laboratory test. H_2 and CO are generated by methanol decomposition on the surface of metal catalyst, preferably avoiding water gas shift because of exothermic reaction.

$$CH_3OH \rightarrow CO + 2H_2 \quad \Delta H=90.7\text{kJ/mol} \tag{5}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H=-41\text{kJ/mol} \tag{6}$$

Figure 5 shows the steam reforming performance of several kind of catalyst intended for DME chemical recuperation at 300°C. All catalyst is prepared in our laboratory by physically-mixing metal catalyst and H-ZSM5 except La/Pd catalyst supported on H-ZSM5 directly by solution impregnation process. The catalyst mixed La/Pd/CeO and H-ZSM5 showed high H_2/CO selectivity and increase in metal catalyst ratio increased the hydrogen production rate. Ni based catalyst is more economical than precious metal catalysts. The catalyst mixed Ni/Al_2O_3 and H-ZSM5 also showed high H_2/CO selectivity, but hydrogen production rate was poor. The SiO_2-supported Ni catalyst improved hydrogen production rate, but methane was generated as a byproduct which accompanied undesirable large exothermic reaction.

The CHP system combined with external waste heat shown

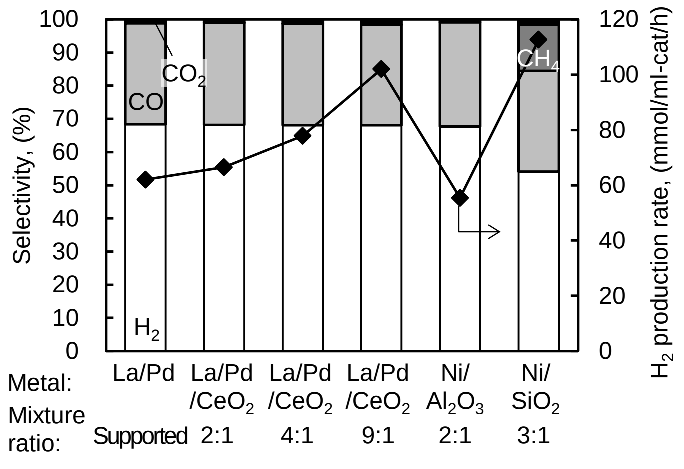


Figure 5. Steam reforming performance of Pd and Ni-based catalysts mixed with H-ZSM5 (Mixture ratio=Metal : H-ZSM5)

in figure 2 can be operated in the same way as it was but with fuel consumption reduction. STIG-CHP system can flexibly change the output of both heat and power according to demand. The CRGT-CHP system in one package that modifies STIG-based system can improve operation flexibility by expanding the range of heat to power ratio. Figure 6 shows the operation diagram of virtual CRGT-CHP system modified a STIG-CHP system of which power output is 4MW with 30% power generation efficiency based on LHV by simple cycle mode. The maximum steam output and maximum power output of original STIG-CHP system are assumed 9t/h and 7MW, respectively, and the latter operation mode reaches 41% power generation efficiency by maximum steam injection. The maximum power output is expected to reach 45% power generation efficiency by adopting chemical recuperation that gives 4 points increase in power generation efficiency assuming 10% relative increase same as the demonstration test. Power output being equal to STIG, CRGT can increase heat output by reducing steam consumption. The shaded region in figure 6 indicates the expanded operation area with increase in power generation efficiency. The heat demand is followed by changing steam to carbon molar ratio (S/C) and mixture ratio of reformed gas and original fuel because follow-up control of heat demand affects the steam flow rate for reforming use. When a demand point of heat and power is below the minimum S/C line, operation mode shifts from CRGT to STIG by direct combustion of the original fuel and steam injection using the superheated steam through the reformer to avoid catalyst coking. As just described, the CRGT-CHP system can adapt all output area surrounded by the limitation line of heat and power and S/C maximum line. This operation flexibility is expected to promote widespread of CHP system for the plant that has hesitated to make a decision of adopting GT-CHP due to mismatch of heat to power ratio or unavailability of power demand peak in summer season. CRGT can apply even to simple cycle or air-recuperation cycle GT models to which STIG has not applied yet due to limitation of surge margin because the power generation efficiency of CRGT is expected to increase by less steam flow rate than STIG.

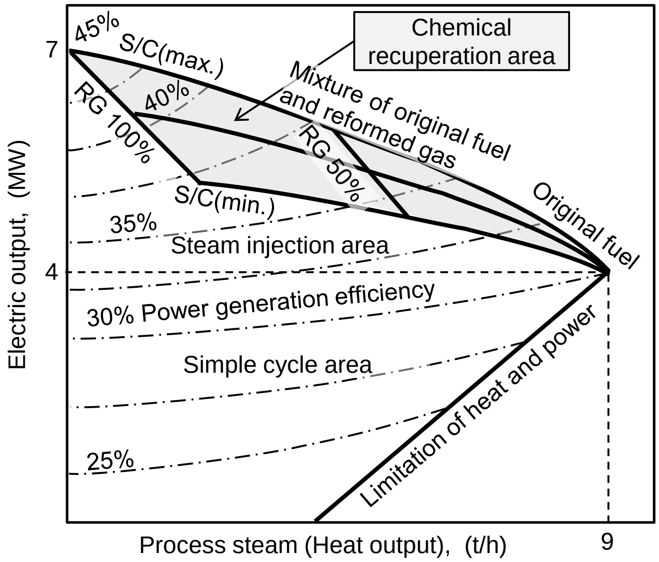


Figure 6. Operation diagram of CRGT-CHP system

EXERGY RECUPERATION BY EPOX

Electrochemical partial oxidation (EPOx) of methane can convert exhaust heat into work as much as difference between change in Gibbs free energy Δ*G* and change in enthalpy Δ*H*. Partial oxidation of methane is expressed as equation (7) and produces syngas that mainly consists of H_2 and CO.

$$CH_4 + 1/2O_2 \rightarrow 2H_2 + CO \tag{7}$$

Table 2 shows values of Δ*H*, Δ*G* and the ratio between them in partial oxidation of typical hydrocarbon fuels under the constant conditions of 1atm and 593°C. Δ*H* is negative value that means exothermic reaction and absolute value of Δ*H* is less than that of Δ*G* because the product gas still has large heating value. Δ*G* is equivalent to the available work extracted by an ideal reactor and difference between. Δ*G* and Δ*H* is can be compensated by low-quality heat, ideally even by heat at ambient temperature. Each Δ*G*/Δ*H* of these reactions exceeds 1.0 and methane has peculiar value more than seven times.

Table 2. Δ*H*, Δ*G* in partial oxidation at 593°C

Fuel	Δ*H* kJ/mol	Δ*G* kJ/mol	Δ*G*/Δ*H*
Methane (CH_4)	-23.46	-184.9	7.883
Ethylene (C_2H_4)	-262.4	-474.1	1.807
Ethane (C_2H_6)	-119.6	-441.9	3.695
Propane (C_3H_6)	-206.5	-688.7	3.335

Electrochemical partial oxidation using solid oxide fuel cell (SOFC) can extract Δ*G* as DC power directly with minimum loss. Figure 7 shows the power generation system combined MGT and SOFC as an application of EPOx of methane. SOFC uses Gadolinium Doped Ceria (GDC) as the electrolyte, which has high oxide ion conductivity below 600°C, NiO as the anode electrode and complex oxide material of La/Sr/Co/Fe (LSCF) as the cathode electrode, respectively. The cylindrical-shaped SOFC is operated around turbine exhaust temperature recovering heat and accompanying production of H_2 and CO. This system is an example of application to CHP and moreover, EPOx can apply to the chemical production process using both syngas and electric power.

The reaction in the SOFC is not only EPOx but also oxidation of the products.

$$CO + 1/2O_2 \rightarrow CO_2 \tag{8}$$

$$H_2 + 1/2O_2 \rightarrow H_2O \tag{9}$$

In addition, complete oxidation of methane expressed as equation (10) can occurs, and sequentially, the generated steam causes methane steam reforming and reverse water gas shift reactions expressed as equation (11) and (12), respectively.

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \tag{10}$$

$$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2 \tag{11}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{12}$$

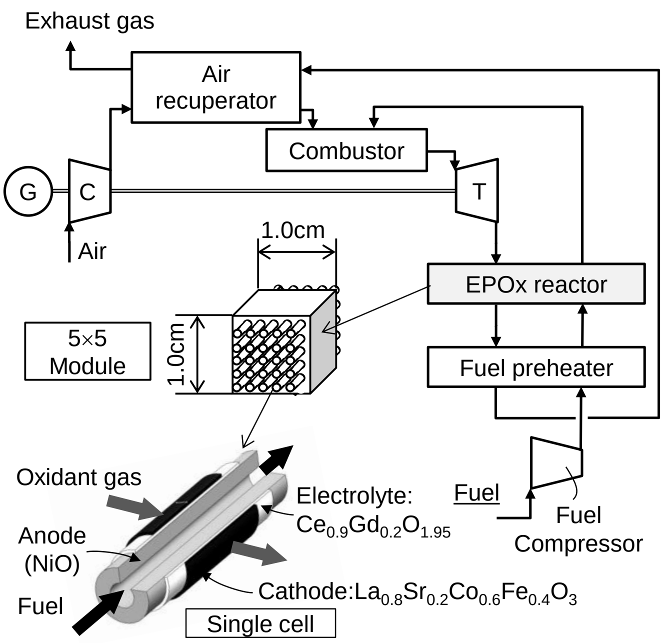
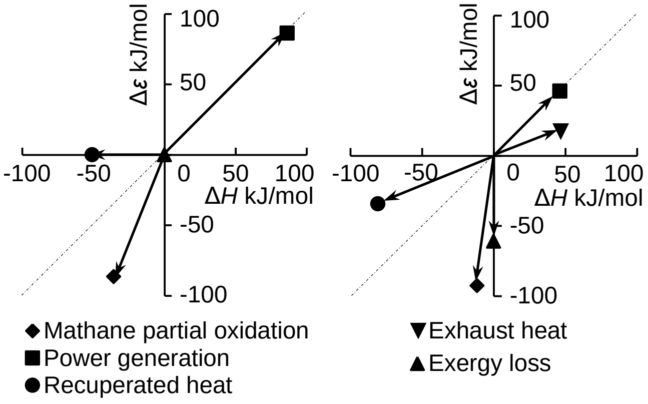


Figure 7. Schematic of exergy recuperation system combined EPOx and MGT

The energy balance including enthalpy change of reactions, power output and recuperated heat is estimated to compare between in the case of EPOx only and in the case of reactions from equation (8) to (12) under the following assumptions. Firstly, EPOx is operated at the constant and uniform temperature of 550°C and O_2/CH_4 is assumed 0.25, which means that fuel utilization by EPOx is 50%. SOFC efficiency defined as the energy ratio of output to input is assumed 50%, which means the energy conversion efficiency from three inputs; chemical ΔH of EPOx, recuperated heat from MGT exhaust and irreversibly generated heat due to internal resistance of SOFC, into electric energy. Figure 8 shows the result of energy balance by "thermodynamics compass" that simultaneously expresses quality and quantity of energy in one scatter plot [8, 9]. X and Y axes show change in exergy $\Delta\varepsilon$ and ΔH, respectively, and the 45-degree line of $\Delta\varepsilon=\Delta H$ expresses electric energy equivalent to exergy rate of 1.0. Negative and positive ΔH means energy donor and acceptor, respectively, and for example, an external heat source or an exothermic reaction behaves as donor and a power generation process or an endothermic reaction behaves as acceptor. Negative and positive $\Delta\varepsilon$ expresses independent process and dependent process, respectively, which have same meaning of ΔG. By comparison, figure 8(a) shows ideal and lossless EPOx that takes heat of zero exergy at 298K into the process and outputs electric energy of which ΔH is just equivalent to sum of recuperated heat and ΔH of EPOx, which satisfies thermodynamics first law of $\sum \Delta H = 0$. SOFC efficiency is 100% in this case of theoretical EPOx at 298K, but there is no electrolyte material operable at this temperature. Meanwhile, as shown in figure 8(b), EPOx outputs electric energy (46.2kJ/mol) of which ΔH is just equivalent to exhaust heat of SOFC (46.2kJ/mol) derived from SOFC efficiency of 50%, while the exhaust heat at 550°C has exergy rate of 42%. The exhaust heat of SOFC is recursively taken into EPOx as a part of recuperated heat with ΔH of EPOx (−11.7kJ/mol) and the remaining value (–34.5kJ/mol) is equal to net external recuperated heat from MGT exhaust. Sum of exergy, which means exergy loss and $\sum \Delta\varepsilon \leqq 0$ satisfies thermodynamics second law, is equal to zero in the case of theoretical EPOx at 298K, but in the case of practical EPOx at 823K with the assumption mentioned above, EPOx generates exergy loss of 60.8kJ/mol. However, in the case of other oxidation reactions from equation (7) to (9), the net external recuperated heat is 17.2kJ/mol, and also in the case of combination reactions from complete oxidation of equation (10) to (12), the net external recuperated heat is 15.9kJ/mol. These positive value means that the overall process cannot take and upgrade external heat to electric energy. Therefore, only EPOx can realize exergy recuperation of heat, and for which it is important to develop material or configuration of triple phase boundary of anode to cause selectively partial oxidation of methane instead of H_2 or CO.



(a) Theoretical EPOx at 298K (b) EPOx at 823K

Figure 8. Thermodynamic compass of EPOx

CONCLUSIONS

If all waste heat is used as desired amenity of heat, it is not necessary to adopt the complex system such as chemical recuperation for heat use and total thermal efficiency is just equivalent to energy utilization efficiency. Actually, the energy utilization efficiency never improves without compensating heat demand variation by new technology beyond time and space. Quality of heat inevitablly degrades in conventional heat exchangers that use waste heat as only heat transfering in one way by temperature difference. However, Chemically-recuperated heat can be available as high quality chemical energy, not just as low-quality heat anymore. Chemical recuperation system can bring about drastic improvement in energy conversion efficiency and effective utilization and is sure to contribute to sutainable use of energy resource.

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