# MULTI-OBJECTIVE OPTIMIZATION OF MIXED MEMBRANE REACTORS FOR AUTOTHERMAL REFORMING OF METHANE

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**Abstract—** Autothermal reforming (ATR) of methane is an important process for hydrogen production, which supplies the heat for endothermic steam reforming by the internal combustion of methane. Axial distributed feeding of oxygen using membrane reactor (MR) can reduce the peak temperature and improve the reactor performance. Mixed membrane reactor (MMR) provides an extra degree of freedom by allowing part of the reactor wall to be non-permeable. The optimal solutions of the design and operation conditions for the MR and MMR for ATR of methane are determined via the genetic algorithm for ternary (production rate/selectivity/conversion) objective functions. Compared to MR, the optimal solutions of MMR provide significantly better performance, the hydrogen production rate can be increased by 100%.

**Index Terms**—Methane Reforming, Membrane Reactor, Mixed Membrane Reactor, Multiobjective Optimization

## I. INTRODUCTION

The generation processes of hydrogen, as a key energy carrier, continuously attracts considerable attention. Autothermal reforming (ATR) of methane is a hydrogen generation processes of significance because of the availability of natural gas and the advantage of supplying heat for steam reforming by internal combustion. The overall chemical reactions taking place in the ATR include total oxidation (Eq. (1)), steam reforming (Eqs. (2), (4)), and water gas shift (Eq. (3)).

$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad \Delta H_1 = -802.30\ kJ/mol$ (1)

$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_2 = 206.10\ kJ/mol$ (2)

$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_3 = -41.15\ kJ/mol$ (3)

$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H_4 = 165.00\ kJ/mol$ (4)

Membrane reactor (MR) [1] is a process intensification application. By penetrating reaction species through a membrane, either adding into or extracting from the reactor, the performance of the reactor can be enhanced. The oxygen stream enters the system from the shell side and permeates into the tube side to react with methane. The shell-side oxygen also acts as a heat transfer fluid. Simulation study of MR for ATR of methane has been reported [2] and the comparison with conventional reactors indicates that MR is a promising alternative and the reactions can be carried out at milder conditions. Mixed membrane reactor (MMR) [3] provides an extra freedom by making part of the reactor wall to be a non-permeable wall, which allows the adjustment of the location for oxygen permeation. The MR and MMR for ATR of methane are illustrated in Fig. 1

Multi-objective optimization provides Pareto optimal solutions for multiple performance criteria. In this study, multi-objective optimization analysis for MR and MMR for ATR of methane have been conducted and the optimal solutions of both types of reactors are compared.

## II. MODELING

The model is one-dimensional, i.e. the radial variations are neglected. The model is pseudo-homogeneous in that the catalyst particles are not simulated. The temperature of the catalyst particles are assumed to be the same as the fluid. The internal mass transport limitations of the catalyst particles are accounted for by constant effectiveness factors [4]. Ergun equation is employed to calculate the pressure drop of the packed bed.

The tube-side mass balance and energy balance equations take into account the reactions, the permeation flux (for oxygen) and the heat transfer between shell and tube.

$$\frac{dF_j}{dz} = A_t\rho_B \sum_{i=1}^{4} \nu_{i,j} r_i \eta_i + J_j \pi d_T \quad j = CH_4, H_2, H_2O, CO_2, CO, O_2 \quad (1)$$

$$\frac{dT}{dz} = \frac{A_t}{\sum_{i=1}^{6} F_j Cp_j}\left[\rho_B \sum_{i=1}^{4} r_i(-\Delta H_{r_i})\eta_i - \frac{4}{d_T}(J_{O_2} Cp_{O_2} + U)(T - T_S)\right] \quad (2)$$

The shell-side mass balance and energy balance equations takes into account the permeation flux of oxygen and the heat transfer between shell and tube.

$$\frac{dF_S}{dz} = -J_{O_2}\pi\, d_T\, n_T \quad (3)$$

$$\frac{dT_S}{dz} = \frac{\pi U d_T n_T (T - T_S)}{F_S C_{ps}} \quad (4)$$

The permeation of oxygen is calculated considering the Knudsen diffusion and Poiseuille flow inside the membrane pores.

$$J_{O_2} = -\frac{1}{RT_m}\Delta P_{mem}\left[\left(\frac{D_{k,O_2}}{\delta}\right) + \left(\frac{BP_m}{\delta\mu_{O_2}}\right)\right] \quad (5)$$

The reaction kinetics in [4] is used. The reactor dimensions and membrane characteristics follow [2]. The model has been verified with the industrial reactor information provided in [4] and simulation results from [2].

For the MMR, to avoid the convergence problem, the permeation flux of oxygen across the membrane is not defined as a step function, but employs a logistic function as:

$$f(x) = r_A\left(1 - \frac{1}{(1+e^{-k(x-x_0)})}\right) \quad (6)$$

The parameters $r_A$, k and $x_o$ can be adjusted. The profiles with different k values are shown in Fig. 2.

## III. OPTIMIZATION PROBLEM

The optimization problems for MR and MMR are both defined for maximizing three objective function, i.e. the production rate of hydrogen ($F_{H2,out}$), the non-combustion selectivity of methane ($S_{non\text{-}comb}$) and the conversion of methane ($X_{CH4}$). The decision variables with their lower/upper bounds for MR and MMR are listed in Table 1, including feeding rates of tube-side methane and steam as well as the shell-side oxygen, the tube-side inlet pressure and temperature, the transmembrane pressure drop, the reactor length and the catalyst packing density. For the MMR, the number of the permeable/non-permeable segments is also a decision variable for the optimization. The profile shown in Fig. 2 depicts one segment (n=1).

The optimization search employs the multi-objective genetic algorithm provided in Matlab, which is based on the NSGA-II (Non-Dominated Sorting Genetic Algorithm) developed by Srinivas and Deb [5].

## IV. RESULTS AND DISCUSSION

For the MMR optimization problem, a binary optimization for $F_{H2,out}$ and $S_{non\text{-}comb}$ are carried out first to determine the best logistic function parameter k and the segment number n. The effects of segment number are shown in Fig. 3. The use of k=8 and n=1 gives higher values in all three objective functions.

To show the effect of employing MMR, the temperature, mole fraction of oxygen in the tube-side and the transmembrane oxygen flux profiles of three optimal solutions are presented in Fig. 4. MMR-TO-1, MMR-TO-2 and MMR-TO-10 gives highest conversion, selectivity and hydrogen production rate, respectively. Each case holds very different profiles as well as peak values.

The Pareto optimal solutions for MR and MMR are summarized in Fig. 5 and Fig. 6, respectively.

For MR and MMR, similar trends can be found in their optimal solutions. Both $F_{H2,out}$ and $S_{non\text{-}comb}$ show trade-off relationship with $X_{CH4}$; higher catalyst packing density gives higher $H_2$/CO in product and requires higher shell-side inlet flow rate and inlet steam-methane ratio, but the tube-side inlet temperature is lower in MR and higher in MMR. For all catalyst packing density, the reactor length increases with $F_{H2,out}$.

The optimal solutions for MR and MMR are summarized in Table 2. The selectivity and conversion of MMR are much higher than MR. The hydrogen production rates of MMR are also significantly higher than MR for up to two times.

## CONCLUSION

For autothermal reforming of methane to produce hydrogen, this study has developed simulation models for both membrane reactor and mixed membrane reactor and has carried out the multi-objective optimization analysis for both types of reactors. The optimal solutions are obtained. It can be concluded that mixed membrane reactor can significantly outperform membrane reactor.

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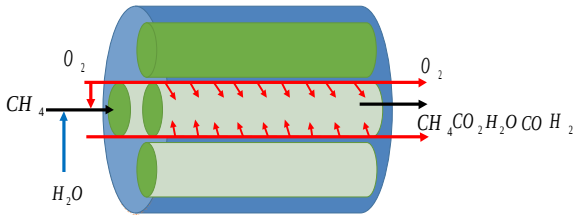
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**Table 1. Decision variables of optimization problems**

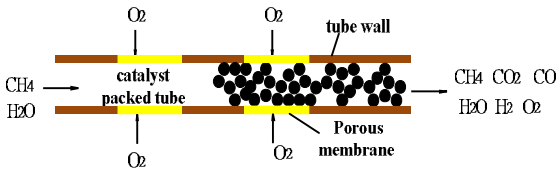
| MR | MMR |
|---|---|
| $1 \leqq F_{t,CH4,in} \leqq 3$ kmol/hr | $1 \leqq F_{t,CH4,in} \leqq 5$ kmol/hr |
| $1 \leqq F_{t,H2O,in} / F_{t,CH4,in} \leqq 3$ | $1 \leqq F_{t,H2O,in} / F_{t,CH4,in} \leqq 5$ |
| $1 \leqq F_{s,in} \leqq 4$ kmol/hr | $1 \leqq F_{s,in} \leqq 4$ kmol/hr |
| $0.5 \leqq \Delta P_{mem} \leqq 1$ bar | $0.5 \leqq \Delta P_{mem} \leqq 2$ bar |
| $500 \leqq T_{t,in} \leqq 700$ °C | $500 \leqq T_{t,in} \leqq 700$ °C |
| $24 \leqq P_{t,in} \leqq 30$ bar | $24 \leqq P_{t,in} \leqq 30$ bar |
| $1 \leqq L \leqq 4$ m | $1 \leqq L \leqq 4$ m |
| $1200 \leqq \rho_\beta \leqq 1800$ $kg_{cat}/m^3$ | $1200 \leqq \rho_\beta \leqq 1800$ $kg_{cat}/m^3$ |

**Table 2. Optimal performance of MR and MMR**

| Performance | MR | MMR |
|---|---|---|
| Catalyst packing density ($kg/m^3$ bed) | ***1200*** | ***1200*** |
| $F_{H2,out}$ (kmol/hr) | **1.548-6.454** | **2.079-11.537** |
| $S_{non-comb}$ | **0.659-0.783** | **0.611-0.814** |
| $X_{CH4}$ | **0.310-1.000** | **0.303-1.000** |
| $F_{H2,out}$ / $F_{CO,out}$ | 3.043-8.342 | 3.151-11.540 |
| L (m) | 0.624-2.821 | 1.013-2.856 |
| Catalyst packing density ($kg/m^3$ bed) | ***1413*** | ***1413*** |
| $F_{H2,out}$ (kmol/hr) | **2.143-6.496** | **2.089-11.613** |
| $S_{non-comb}$ | **0.674-0.783** | **0.614-0.813** |
| $X_{CH4}$ | **0.371-1.000** | **0.370-1.000** |
| $F_{H2,out}$ / $F_{CO,out}$ | 3.156-7.658 | 3.647-13.825 |
| L (m) | 0.940-2.906 | 0.971-2.937 |
| Catalyst packing density ($kg/m^3$ bed) | ***1600*** | ***1600*** |
| $F_{H2,out}$ (kmol/hr) | **1.438-6.563** | **1.980-11.282** |
| $S_{non-comb}$ | **0.674-0.801** | **0.610-0.850** |
| $X_{CH4}$ | **0.241-1.000** | **0.168-1.000** |
| $F_{H2,out}$ / $F_{CO,out}$ | 3.164-9.783 | 3.219-14.566 |
| L (m) | 0.566-2.870 | 0.555-2.972 |
| Catalyst packing density ($kg/m^3$ bed) | ***1800*** | ***1800*** |
| $F_{H2,out}$ (kmol/hr) | **1.865-6.594** | **1.632-11.719** |
| $S_{non-comb}$ | **0.665-0.798** | **0.601-0.859** |
| $X_{CH4}$ | **0.246-1.000** | **0.318-1.000** |
| $F_{H2,out}$ / $F_{CO,out}$ | 3.203-9.270 | 3.409-18.109 |
| L (m) | 0.665-2.927 | 0.501-2.909 |




(a) MR




(b) MMR

**Fig. 1 Schematic illustrations of MR and MMR**

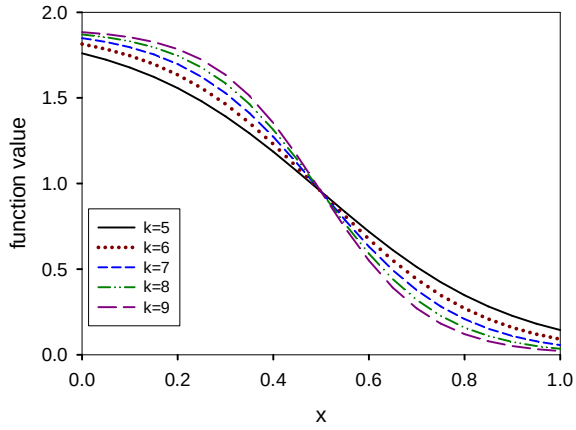
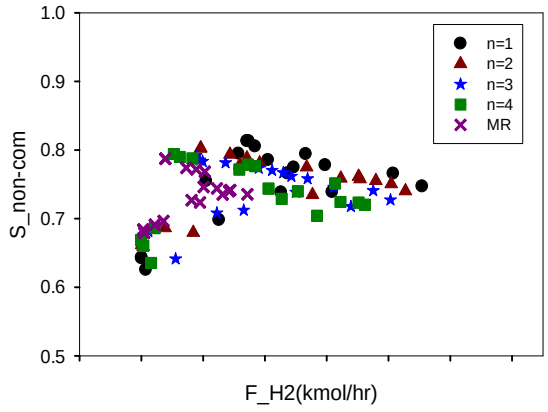
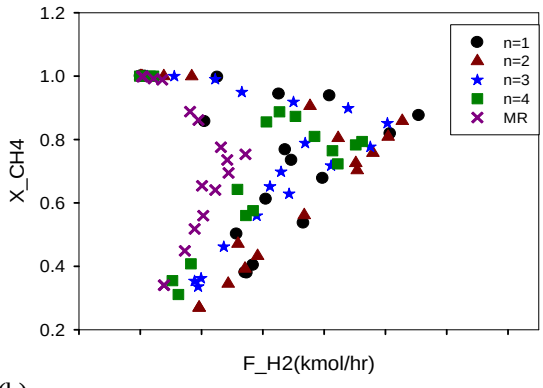



**Fig. 2 Effects of logistic funtion parameters**

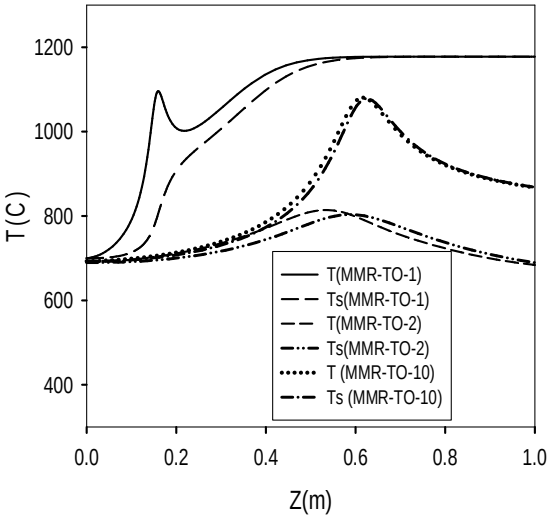



(a)

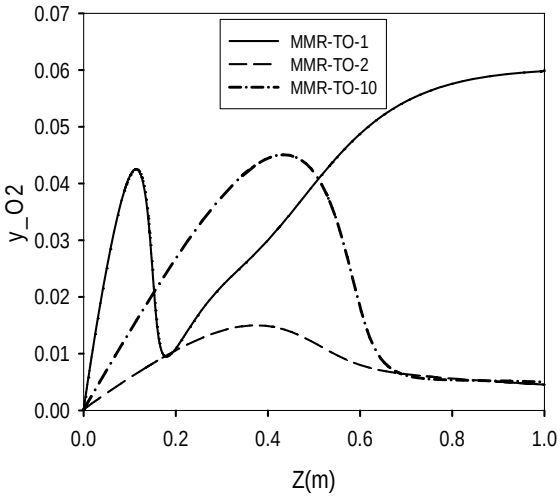



(b)

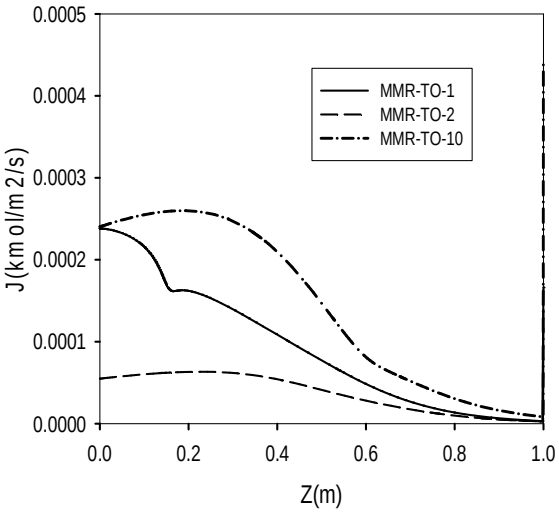
**Fig. 3 Effect of segment number of MMR**




**(a) temperature**




**(b) $O_2$ concentration**




**(c) permeation flux of $O_2$**

**Fig. 4 Internal profiles of three optimal solutions of MMR (L=1m, k=8, n=1)**

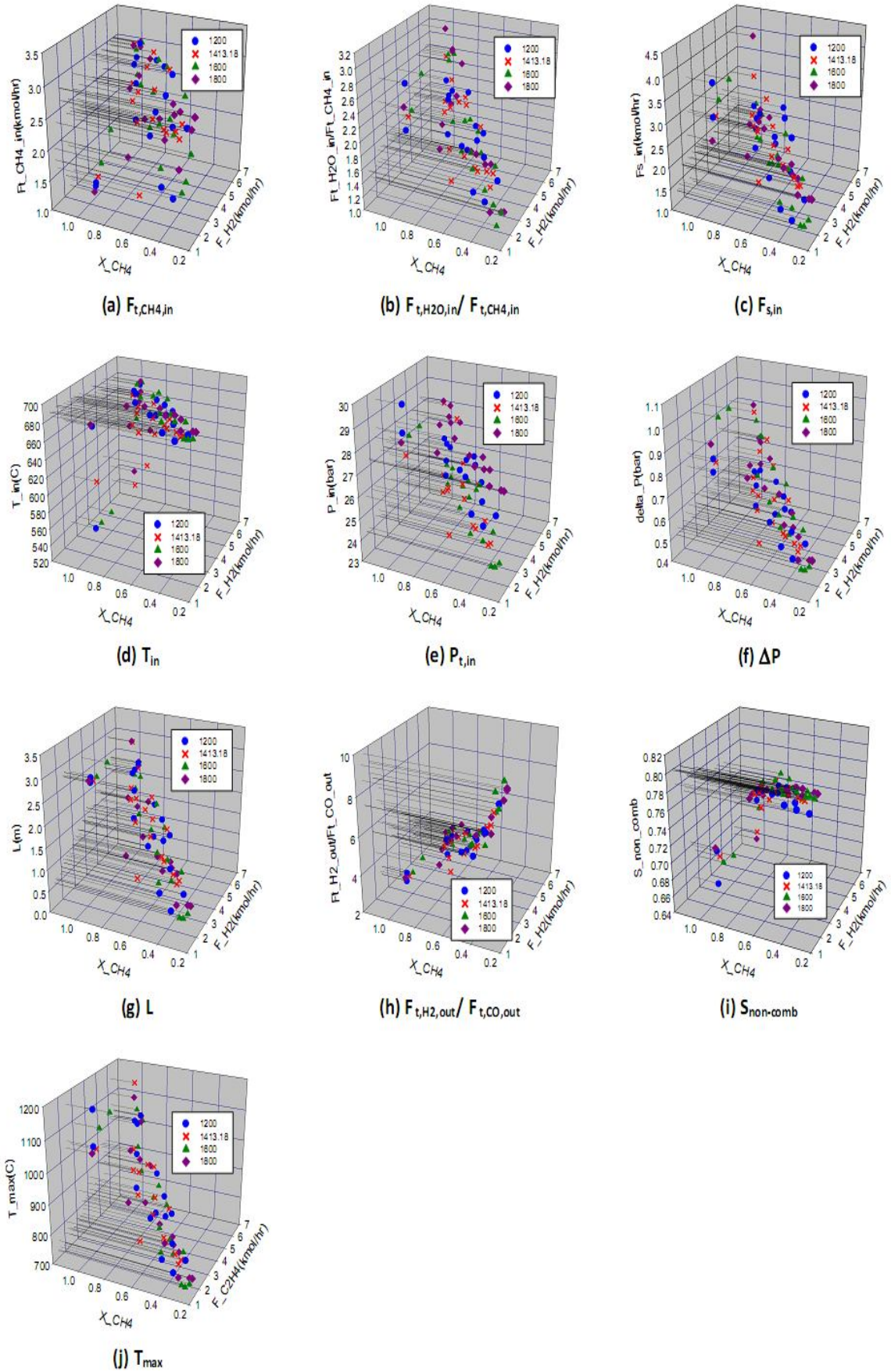



**Fig. 5 Pareto plots for ternary-objective-optimization of MR**

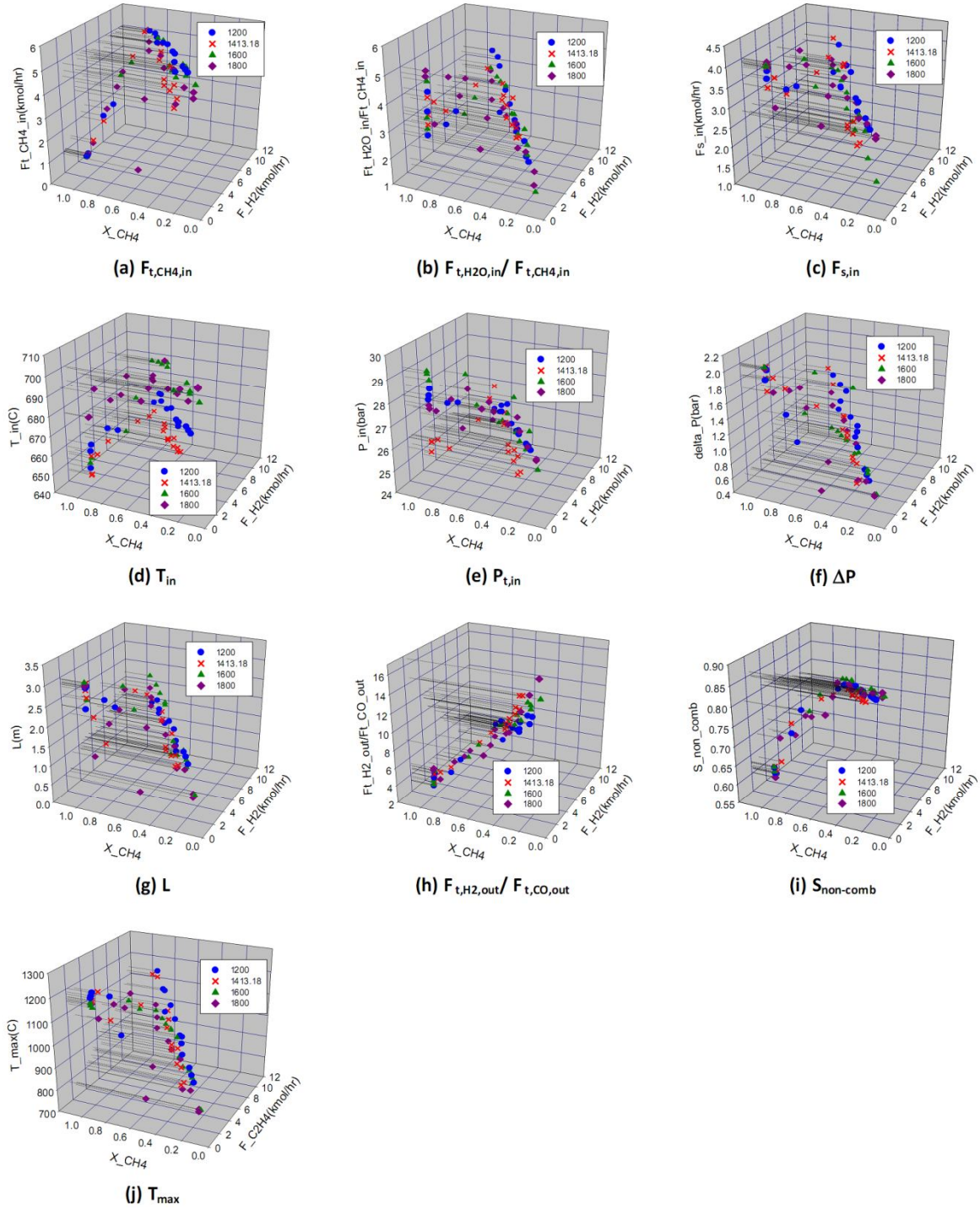



**Fig. 6 Pareto plots for ternary-objective-optimization of MMR**

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