REGRESSION-BASED OPTIMIZATION OF THE PARTIAL OXIDATION OF METHANA ON Ni-MgO/α-ALUMINA MONOLITH CATALYST IN A REVERSE-FLOW REACTER

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Abstract

This study describes the use of statistical optimization techniques on a laboratory scale reverse flow reactor for the catalytic partial oxidation of methane on Ni-MgO/α-alumina monolith catalyst. The effects of initial temperature (T_{ini}), switching time (τ), total flow rate (F), mole fraction of methane (M), and catalyst length on hydrogen yield and methane conversion are investigated using systematic experimental design. In the first experimental phase, the steepest ascent path was established by ridge analysis to determine the stationary point. The optimum operating conditions were determined in the second experimental phase. The following interactions were found to be significant for methane conversion: $M*\tau$, $F*\tau$ and $M*F$. The interaction of $F*\tau$ also affected the hydrogen yield. The third-order interaction of $F*\tau*M$ was also found to be statistically significant. The optimum methane conversion value of 57.36% could be obtained by setting switching time, total flow rate and a mole fraction of methane of 4.24 minutes, 543ml/min and 0.6043, respectively. The optimum value of hydrogen yield of 36.73% was reached by setting total flow rate, mole fraction of methane and switching time of 540ml/min, 0.5845 and 4.15 minutes, respectively. The analysis of reactor operation showed that optimization of the system required changing more than one factor and that there is a complex interplay of the different experimental factors. The influence of the factors may all be interpreted in terms of heat release and heat loss in the system.

Keywords: Experimental design, Monolith catalyst, Optimization, Partial oxidation methane, Reverse flow reactor

Introduction

Hydrogen is commonly produced by steam-reforming natural gas. However, steam reforming is an endothermic process in which an external heat source is always required. This process also releases a large amount of carbon dioxide. In the past few years, there has been an increasingly strong interest in the catalytic partial oxidation of methane (POM). This is motivated by a high demand for compact and low capital-cost reactors for the conversion of natural gas to produce synthesis gas for production of liquids fuel and hydrogen used for fuel cells [1].

The POM, which is a mildly exothermic reaction, can be conducted autothermally in a reverse flow reactor (RFR) wherein the direction of flow is reversed at specified periods of time. The duration of time between flow reversals is called a half-cycle and the period required to complete a half-cycle is called the switching time. The idea behind the

approach is to store and utilize the heat of exothermic reaction within the catalyst bed itself. The RFR has become a promising technology for producing synthesis gas using POM. Thermal energy released from weakly exothermic reactions can be stored by the two inert sections at both ends of the reactor. The temperature of the product is lowered by the outlet section and at the same time the temperature of the feed stream is raised by the inlet section before reaching the catalyst reaction zone. During start-up, the reactor is preheated to establish an initial temperature profile which enables sustained autothermal operation to be achieved. After this initial preheating, all external sources of heat are removed. The partial oxidation of methane in an RFR may have many advantages in saving energy and expenses for investment and operation, since it is not necessary to supply external heat to maintain a high temperature.

The implementation of the partial oxidation of methane in an RFR in the real world is complex because of the inherently unsteady state operation and the many parameters that affect it. Recently published studies have focused mainly on numerical simulation and control strategy, but there have been few published experimental studies. The simulation of a RFR using mathematical models is necessary to determine the parameters which affect the reactor performance [2-4]. However, establishing a mechanistic model which captures all of the complexities of the RFR is an extremely difficult endeavor since each half-cycle involves the solution of a system of partial differential equations.

The determination of the behavior and the characteristics of a real RFR using experimental design tools may give more understanding regarding how to operate the reactor in reality. In this study, the hydrogen yield and conversion of methane of partial oxidation of methane in a real laboratory-scale RFR is optimized using the method of steepest ascent by changing five factors: switching time, total flow rate, the molar fraction of methane; catalyst length and initial temperature.

Literature Review

Partial Oxidation of Methane in a Reverse Flow Reactor

The catalyst in the partial oxidation of methane has an important role. Mitri et al. [5] investigated the catalytic partial oxidation of methane to synthesis gas at high temperature and short contact time conditions over three different noble metal catalysts (Pt, Rh, and Ir). The experimental results showed that reverse flow operation led to strong improvements in synthesis gas yields for all three catalysts, with particularly strong improvements for poorly performing catalysts. Furthermore, as the catalyst temperature increased, resulting in an accelerated deactivation of the unstable catalysts (Pt, Ir), the heat integration completely compensated for this acceleration. Therefore, reverse flow operation has an intrinsic "equalizing" and "self-regulating" effect on catalyst performance and offers a widely applicable reactor engineering approach to compensate for the poor or degrading catalysts in high temperature partial oxidations with noble metal-based catalysts. Hevia et al. [6] also analyzed the role of the catalyst properties, such as the different activities and thermal stabilities of the studied catalysts, on the performance of reverse flow reactors for the combustion of lean methane-air mixtures. The noble-metal catalysts are more appropriate for leaner and stable mixture with closely constant composition; on the other hand, the metal-oxide catalysts are more appropriate for richer mixtures, allowing concentration variations to some extent.

In recent studies, the effect of steam on the partial oxidation of methane in a reverse flow reactor has been mentioned. There are two approaches to demonstrate this influence. In the study of Dobrego et al. [7], steam was mentioned as a positive factor. The hydrogen yield and the methane-to-hydrogen conversion ratio may be increased by the addition of

steam to a working mixture. Bos et al. [8], however, mentioned steam as a catalyst poison, moreover, the presence of steam may assist the steam-reforming process in the reactor.

The optimization of a reverse flow reactor is complex and difficult because it is a combination of the cyclic process and the catalytic reactor. This may be the reason why very few studies mention the optimization of this kind of reactor, especially in experimental optimization. However, some studies tried to analyze the behavior of a reverse flow reactor by modeling and simulation. Litto et al. [9] used simulation method to investigate the operation factors that affect a reverse flow reactor. Thermal properties (including thermal mass and thermal conductivity), interaction between switching time and superficial gas velocity and geometric parameters (which include diameter of reactor and thickness of insulation) were found to have strong effects on the behaviors of reverse flow reactor. Salomons et al. [10], based on the experiments performed from catalytic combustion of lean methane mixture in the reverse flow reactor, found that it is possible to maintain auto-thermal operation of the reactor at methane concentrations as low as 0.22% with feed at ambient temperature. The overall performance of the system is dependent on methane concentration, cycle time and velocity. A large disparity between the peak temperature and the extraction temperature may decrease the efficiency of energy recovery. The study of Salomons et al. [10] also indicated the presence of radial gradients in the reactor. These gradients are expected to affect reactor performance, and must be considered when evaluating the dynamics of the reactor. Litto et al. [9] also confirmed that the primary scaling parameter is the reactor diameter; special care must be paid to this variable, especially in large units where the wall effects are expected to be minimal and the two-dimensional behavior of the reactor cannot be ignored in smaller units.

In general, some parameters of the reverse flow reactor were investigated and have been determined to be the significant factors such as the catalyst [5, 6], the initial flow rate [11], the molar feed ratio [12,13], the switching time[14, 15], the thickness of an insulator, the dimensions (length and diameter) of a reverse flow reactor [9]. However, the optimal values of these factors in a real reverse flow reactor have not been recommended. These optimal values are not only significant to this specific reactor but also to be reused in other studies using the similitude analysis and the dimensionless parameters. Therefore, the optimization of the partial oxidation of methane in a reverse flow reactor is necessary.

Method of Steepest Ascent in the Optimization of a Catalytic Reactor

The method of steepest ascent is a simple, economical and efficient procedure developed to move the experimental region of a response in the direction of the maximum change toward the optimum [16]. If there are many factors in the system, the factors can be screened by the Plackett–Burman design to eliminate the insignificant factors before using this method. Anunziata and Cussa [17] successfully optimized the activation of methane using ethane as co-reactant into higher hydrocarbons on Zn-containing zeolite catalyst using this method. There were four independent variables: time on stream, space velocity of ethane, molar fraction of methane and reaction temperature. The dependent variables were the methane conversion, reducing the operation costs, achieving efficiency and effectiveness of methane activation process. The results indicated that the reaction time, the interactions of the time on stream and temperature significantly affect methane conversion. Reese et al. [18] also used the steepest ascent method to maximize hydrogen production per mole of supplied oxygen in a laboratory-scale catalytic autothermal reformer. Oxygen-to-carbon and water-to-carbon ratios were used as independent variables. Surface response methodology was employed using a 2^2 factorial design. The optimal experimental conditions occurred at the water-to-carbon ratio of 3.00–3.35 and the oxygen-to-carbon ratio of 0.44–0.48.

The results from previous studies have confirmed the validity and capability of the method of steepest ascent in a autothermal reactor. The steepest ascent method seems to be widely used in many fields. However, there have been no published experimental studies about a reverse flow reactor using this method.

Methodology

Reactor Design

The experiments were performed in a reverse-flow reactor system depicted in Figure 1. All experiments were conducted high temperature tubular reactor which uses a 1-m long Inconel tube with a 2-cm diameter (Figure 2). The middle part of reactor was equipped with an electric resistance wire to provide the heat prior to start-up. To reduce heat loss, the reactor was encased in a stainless steel tube with a 60-mm diameter stainless steel shell which was then evacuated with a vacuum pump. The exterior of this shell was insulated using 120-mm thick ceramic wool. The direction of the flow was reversed by two three-way solenoid valves connected to the switching-time controller.

Catalyst Preparation

The catalyst used in this study was Ni-MgO/α-alumina prepared by co-precipitation method. The method was first studied by Doan [19]. This catalyst was made by using ammonia solution (10-15%) slowly poured into a solution of $Ni(NO_3)_2$ (Purity 98%, Analytical Grade) and $Mg(NO_3)_2$ (Purity 99%, Analytical Grade) in the presence of α-alumina (Purity 99.7%, Analytical Grade, powder form) up to pH 11 at low temperature to prevent the evaporation of ammonia. The catalyst was decanted with water six times then dried in air at 80^oC for 4 hours and calcined in air at 900^oC for 4 hours before coating onto monolith surface.

A 15 mm piece of cordierite monolith, obtained from NGK, was coated with NiO-MgO/α-alumina catalyst. The cordierite monolith had a diameter of 20 mm and consists of around 154 channels. This is equivalent to 300 cells per square inch. Each channel had a 1 mm2 square cross-section. The slurry for coating catalyst onto monolith was prepared by vigorously stirring the finely milled mixture of catalyst and α-alumina in PVA (polyvinyl alcohol) solution. The fresh monolith was dipped into the slurry and the excess catalyst suspension was blown out by compressed air before drying. This step was repeated until the needed catalyst loading onto monolith was attained. In these experiments, a Ni catalyst loading of 2% and a catalyst-binder ratio of 2:1 was used. Before using the coated
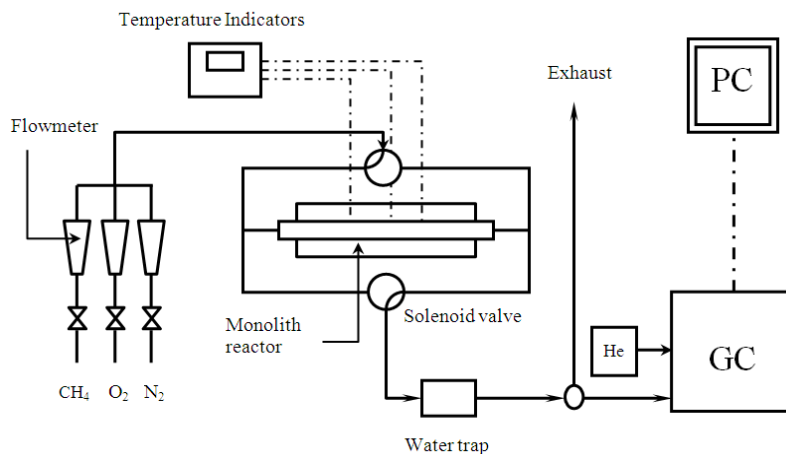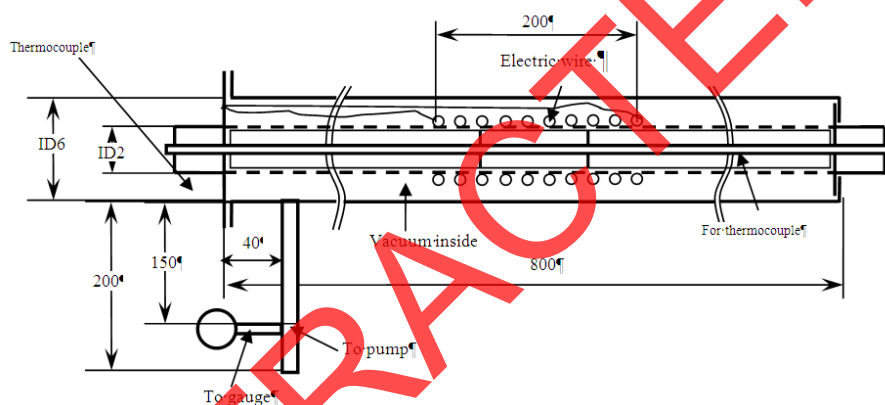
Figure 1. Schematic of experimental setup

Figure 2. Schematic of reverse flow reactor

monolith for reaction, the coated monolith was calcined in air at 900°C for 4 hours and then reduced under hydrogen flowing at 120 ml/min at 900°C for 2 hours to activate the catalyst. The results from X-ray diffraction showed that solid solutions of NiO and MgO were formed. NiO and MgO are completely miscible and form an ideal solid solution because of the similar structures. It was also confirmed that the γ-Al$_2$O$_3$ was changed to α-Al$_2$O$_3$ at 900°C during calcination. The catalyst has a surface area of 35.2 m^2/g and a pore volume of 10.61 m^3/g and pore size of 13.15 nm. Elemental analysis showed that distribution of nickel on coated monolith catalyst was not uniform. The nickel loading of 2% was found in the middle of the monolith catalyst while the ends have significantly different values [20]. However, distribution of magnesium was consistent all throughout the monolith. Based on the temperature-programmed desorption, the catalyst had a large amount of basic sites and seems to be stable in hindering carbon deposition on the surface of the catalyst [20]. Activity testing before and after long periods of use showed that the catalyst was fairly stable within the time frame of the experiments. The total surface area of the catalyst available for carbon deposition is very small compared to the total quantity of gases passed through the system. Hence, it cannot be expected that a mass balance will be able to quantify any carbon deposition.

Coated monoliths were placed to form the desired length of the reacting section. Uncoated monoliths were placed in front of and behind the catalyst coated monolith until a

total length of 1 meter was reached. A 3-mm quartz tube was inserted through the center of the monolith to serve as a channel for the thermocouples in order to monitor the temperature along the reactor axis during operation. The reactor was operated at slightly above atmospheric pressure.

Reactor Operation

Before starting each run, the RFR was preheated with the furnace to establish the initial temperature profile inside the reactor. A typical initial temperature profile is represented in Figure 3. Nitrogen was fed for one minute to purge the reactor during start-up. The electrical heating was then discontinued after required initial temperature profile was achieved. The highest temperature within this initial temperature profile is represented as T_{ini} and is used to represent the entire profile. Once the desired T_{ini} was achieved, the feed of nitrogen and heating were terminated. The reactor was activated by feeding methane followed by oxygen. The reactor feeds were kept at room temperature in all experimental runs. All gases used in experiments were 99.9% purity. Only methane and oxygen were fed to the reactor during the experiments. Therefore, an increase of the mole fraction of methane decreases the mole fraction of oxygen and vice-versa.
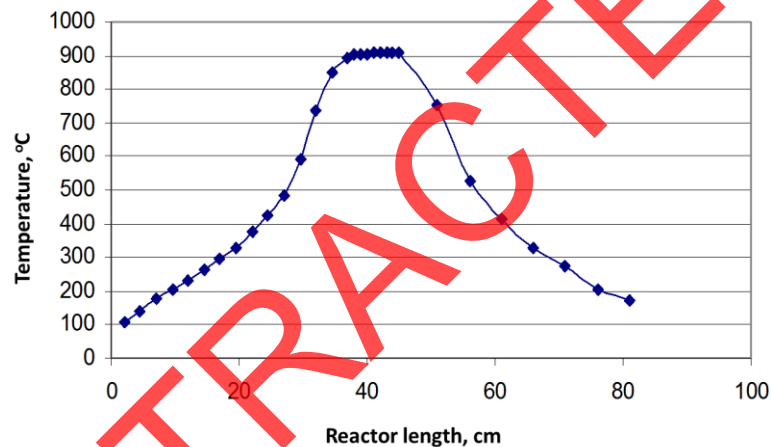

Figure 3. Initial temperature profile before operating the reverse-flow reactor

During the experiment, the temperatures were recorded by a type K thermocouple which was placed at the middle of the reactor axis. The water in the effluent was removed by an ice trap before entering the gas chromatograph (Trace GC Ultra) where the gas compositions were analyzed. A typical temperature record of the reactor in cyclic steady state wherein a measurable conversion is achieved is shown in Figure 4. The yield and conversion were computed using the equations (1) and (2).

$$X_{CH_4} = 1 - \frac{\% \, moles \, of \, CH_4}{\% \, moles \, of \, CO + \% \, moles \, of \, CO_2 + \% \, moles \, of \, CH_4} \tag{1}$$

$$Y_{H_2} = \frac{\% \, moles \, of \, H_2}{2 \cdot \left(\% \, moles \, of \, CO + \% \, moles \, of \, CO_2 + \% \, moles \, of \, CH_4 \right)} \tag{2}$$

The Method of Steepest Ascent

In this study, the method of steepest ascent was used to optimize the system. In this method, a steepest ascent path is determined by ridge analysis in the initial experimental phase. The succeeding experiments are conducted along the path until the stationary point is reached.
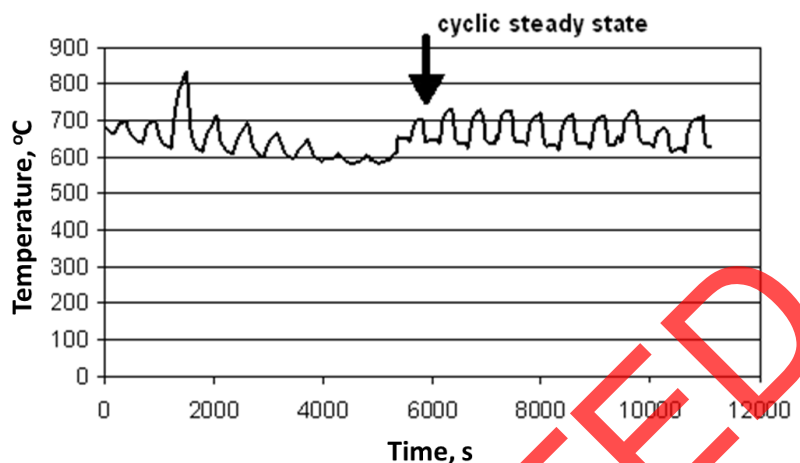

Figure 4. The temperature record at the middle of the reactor, at initial temperature of 750°C, CH$_4$/O$_2$ of 300/150 ml/min, 4-minute switching time of and 180-mm catalyst length

The responses of the stationary point are the largest compared to the other the path. The second experimental phase consists of a design established around the stationary point. The nature of the stationary point and a new steepest ascent path are determined by canonical analysis and ridge analysis, respectively, in the second experimental phase. This process is repeated until the stationary point is determined as a maximum point [21]. In this study, two experimental phase and one steepest ascent path were established to determine the maximum point. Ridge, canonical and regression analysis was done by SAT/STAT® using REG and RSREG procedures.

The Factor Space Boundaries

According to Neumann [18], partial oxidation of methane in a reverse flow reactor should be operated at minimum initial temperature of 400°C. Operation below the temperature can cause extinction of the reaction. However, it is not recommended to operate the reactor at the initial temperature higher than 900°C. The insulator materials can lose effectiveness under the thermal stress of such a temperature. In the interest of safety, the initial temperature should be lower than 900°C. The resolution of temperature in this study is 4°C. This is derived from the error in the thermocouple reading.

The total flow rate of reactants can be established from 150ml/min to 1500ml/min. The values are limited by the capacity of the flow meters. These limits are determined by assigning the superficial gas velocity from 0.5 to 5 cm/s. The velocities in this range ensure adequate residence time for reaction. In this study, the flow rate of methane and oxygen were measured separately. The errors of the methane and oxygen flow meters are 10 ml/min and 5 ml/min respectively. Since the total flow rate is determined by adding methane flow rate and oxygen flow rate, the error of total flow rate is 15ml/min.

Mitri et al. [5] recommended that molar feed ratio between methane and oxygen should be higher than 1.2. According to stoichiometry, the partial oxidation of methane to produce synthesis gas should be done at the molar feed ratio of two. However, the conversion of

methane is decreased when there is an increase of the molar feed ratio between methane and oxygen [13]. Therefore, the molar feed ratio was investigated from the values of 1.2 to 2 which are equivalent to the mole fraction methane of 0.54545 to 0.6666.

According to the simulation of Dang [22], the switching time of a reverse flow reactor should be changed within the range from two to five minutes. The reactor was designed based on the simulation of Dang [22]. Therefore, this range is chosen as the boundary of switching time. In this study, the minimum difference between two set values of switching time is 15 seconds. As previously mentioned in the section on catalyst preparation, the monoliths were prepared as small segments, each of length 15mm. In the reactor, the monoliths were placed in pairs because the reactor was symmetrically operated. The number of monoliths in the reactor was even. Therefore, the catalyst length was investigated in discrete steps of 30 mm. The maximum catalyst length was 270mm, the length of the heating zone. The factor space boundaries are summarized in Table 1.

Table 1. Summary of Boundary Conditions of Independent Factors

Factors	Lower limit	Upper limit	Type of variable
Initial temperature (^{o}C)	400	900	continuous
Catalyst length (mm)	30	270	Discrete step 30mm
Switching time (minute)	2	5	continuous
Mole fraction of methane	0.5454	0.6666	continuous
Total flow rate (ml/min)	150	1500	continuous

Results and Discussion

The First Experimental Phase

In the initial experimental design, the effects of total flow rate, mole fraction of methane, switching time, initial temperature and catalyst length were investigated. The initial design is asymmetrical and the initial temperature was investigated at two levels. Therefore, the quadratic effect of the initial temperature cannot be determined and the quadratic effects and the interaction effects also cannot be analyzed simultaneously. The statistical analysis shows that there are four significant interactions which affect both methane conversion and hydrogen yield. These are the interaction of initial temperature and catalyst zone (T_{ini}*L); the interaction of total flow rate and molar fraction of methane (F*M), The interaction of molar fraction of methane and switching time (M*τ) and the interaction of switching time and total flow rate (τ*F).

The results from the experiments are shown in Table 2 and the statistical analyses are summarized in Table 3. The resulting equations are shown as Equations (3) and (4)

$$X_{CH_4} = 167.32 + 4.54*10^{-4}T_{ini}L - 75.67*M*\tau + 0.1047*\tau*F - 0.6325*F*M \quad (3)$$

$$Y_{H_2} = 55.59 + 2.34*10^{-4}T_{ini}L - 26.72M*\tau + 3.68*10^{-2}\tau*F - 0.2297F*M \quad (4)$$

It is interesting to note that the main effects are insignificant whereas the interaction effects are insignificant. This result is a true indication of the complex interaction of all of these effects together. In other words, the reactor performance cannot be predicted just by adjusting one parameter alone. Other parameters must be considered.

Interaction between Initial Temperature and Catalyst Length

The effects of the interaction between initial temperature and catalyst length on the methane conversion and the hydrogen yield are statistically significant. This means that when the catalyst zone is short (runs 1-10), the initial temperature does not affect both responses very strongly. Indeed, this can easily be seen even without statistical analysis because the conversion and yield are always zero. The reaction does not ignite when there is a short catalyst zone. In preliminary experiments not reported here, the reactor also never ignited when the catalyst zone was short. This result makes sense because the reactor does not ignite when the initial temperature is high, then it cannot be expected to ignite when the initial temperature is low.

Table 2. Experimental Results in the Initial Design

Run	T_{ini} (°C)	L (mm)	τ min	M	F ml/min	X_{CH_4} (%)	Y_{H_2} (%)
1	900	90	2	0.667	450	0	0
2	900	90	3	0.667	450	0	0
3	900	90	5	0.667	450	0	0
4	900	90	6	0.667	450	0	0
5	900	90	4	0.667	300	0	0
6	900	90	4	0.667	375	0	0
7	900	90	4	0.667	525	0	0
8	900	90	4	0.667	600	0	0
9	900	90	4	0.667	750	0	0
10	900	90	5	0.667	450	0	0
11	750	180	3	0.667	450	47.8	29.4
12	750	180	4	0.667	450	30.5	16.7
13	750	180	4	0.625	480	63.9	23.0
14	750	180	4	0.606	495	61.5	28.6
15	750	180	4	0.588	510	68.2	28.5
16	750	180	5	0.667	450	0	0
17	750	270	3	0.667	450	56.2	24.5
18	750	270	4	0.667	450	51.0	31.8
19	750	270	4	0.667	525	58.8	23.7
20	750	270	4	0.667	600	59.5	22.9
21	750	270	4	0.667	675	50.9	30.2
22	750	270	5	0.667	450	54.6	36

Table 3. Statistically Significant Regression Coefficients in the First Experimental Phase

Regression Coefficients	$T_{ini}*L$	$M*\tau$	$\tau*F$	$F*M$	R^2
Methane conversion	4.54×10^{-4} **	-75.67818 **	0.104651 **	-0.632478 **	0.926
Hydrogen Yield	2.34×10^{-4} **	-26.71772 **	0.036825 **	-0.229696 **	0.864

** - Significant at level of confidence of 99%

On the other hand, when the catalyst zone is long(runs 11-16, runs 17-22), the responses become sensitive to the initial temperature. The reason for this effect is that when the catalyst zone is short, the active area may be not enough to sustain the reactions. Therefore, the reactor was extinguished at any value of initial temperature. This means that the initial temperature does not affect the responses when the catalyst zone is short.

However, when the catalyst zone is long, the low initial temperature may not supply enough heat to ignite the reaction but high initial temperature does. When the catalyst zone is long, the active area is increased as increase of initial temperature; hence, the responses are improved. In other words, the responses are sensitive to the initial temperature when the catalyst zone is long.

The interaction of initial temperature and catalyst length is actually the product of these two factors which may be an indicator of the total amount of heat that is available in the reactor prior to feeding the gases. Since there is a larger amount of heat, then the feed gases are easily raised to a higher temperature and therefore the temperature at which the reaction is ignited is reached.   Since monitoring of surface temperature was impossible, it is difficult to give a precise number for this temperature.

Interaction between Mole Fraction of Methane and Total Flow Rate

The effects of the interactions between mole fraction of methane and total flow rate on the methane conversion and the hydrogen yield are statistically significant. It appears that the responses are more sensitive to the total flow rate when the mole fraction of methane is high and vice-versa. At a high mole fraction of oxygen (low mole fraction of methane), the reactions are partially shifted toward the complete combustion of methane which generates more heat. An increase of heat generation causes an increase of the thermal mass and the reactor temperatures [23]. Therefore, at a low mole fraction of methane, the heat loss may not greatly affect the system [24]. The high total flow rate can cause the heat loss by quenching the reactor [25]. That means the total flow rate has no strong effect on the reactor at low mole fraction of methane.

Moreover, the high heat generation increases the temperature of the reactor. The rate of reactions is increased at a high temperature. This causes a decrease of the required residence time. Therefore, the allowance of the total flow rate is increased and the total flow rate can be widely adjusted at a low mole fraction of methane. At a high mole fraction of methane (low mole fraction of oxygen), the heat generation is low because the rate of the complete combustion of methane decreases. The system is hence more sensitive to the heat loss. Therefore, the effect of the total flow rate is more significant in this case.

However, a decrease of the mole fraction of methane more easily explains an increase of methane conversion than an increase of hydrogen yields because a decrease of mole fraction of methane (i.e., an increase of mole fraction of oxygen) causes the complete combustion of methane which produces carbon dioxide and water, not hydrogen.

However, this interaction is also significant to the hydrogen yield. The reason may be the increase of the reactor temperature because of the higher heat generation. The high temperature shift reactions toward the partial oxidation of methane which produces hydrogen [13]. An increase of hydrogen yield is this condition is very limited. In the first experimental phase, the effort to maintain the reactor in operational status was more significant than the other objectives. When the density of the active sites on the catalyst is small, the concentration of the reactants may not significantly affect the hydrogen yield.

The interaction of total flow rate and mole fraction of methane is actually the product of these two factors which is the flow rate of methane was fed into the reactor. An increase of flow rate of methane may cool down the reactor, shorten the contact time between methane and the catalyst and decrease the residence time for mass and heat transfer between methane and the other gases in the reactor, hence adversely affecting the responses.

Interaction between Mole Fraction of Methane and Switching Time

The effects of the interactions between mole fraction of methane and switching time on both the methane conversion and the hydrogen yield are statistically significant. That means the effect of the switching time is more significant at a higher mole fraction of methane. The reason for this interaction may be similar to the previously mentioned explanation. At a high mole fraction of methane (a low mole fraction of oxygen), the system is more sensitive to the heat loss. Heat loss of the system may be affected by the switching time [15].

An inappropriate switching time causes excessive heat loss from the system. When the switching time is increased, the operation of the reactor reaches the quasi-steady state of "thermal resonance." If the switching time is extremely large, the reactor behavior is quite similar to the once-through operation which increases the temperature of the outlet bulk gas flow [15]. Litto [9] also confirmed that an increase of the switching time is one of the reasons of heat loss in a reverse flow reactor. When the sensitivity of the reactor from the heat loss is high, the effect of the switching time on the responses is also high. In other words, the effect of the switching time is more significant at a high mole fraction of methane.

As previously mentioned, using a low mole fraction of methane (a high mole fraction of oxygen) does not always good for the reactor. Drastically increasing the mole fraction of oxygen may decrease the hydrogen selectivity and may activate the undesired reaction [13].

Interaction between Total Flow Rate and Switching Time

The effects of the interactions between total flow rate and switching time on the both responses are statistically significant. It appears that the responses are more sensitive to switching time when the total flow rate is high and vice versa because of the effect on the residence time. At high flow rate (or low residence time), the system may not have enough time to recover the heat loss caused by the long switching time.

The residence time which is determined by the total flow rate has a distinct influence on the conversion unless the reaction rate has zero order [15]. An increase of the residence time may increase both the conversion and the yields by increasing the contact time between the catalyst and the reactants, between the cool feed and the inert hot zone. The inert zones at either end of the reactor play a significant role in the heat recovery because they store the excess heat which is used for the next half cycle [25]. The residence time thus has a significant effect on both mass transfer in the catalyst zone and heat transfer in the inert zone. The long residence time (low flow rate) increases the effectiveness of the heat and mass transfers, hence improves the methane conversion and hydrogen yield.

The switching time and residence time are significant in determining the operation regime of the reactor. When switching time is short compared to the residence time, the reactor approaches relaxed steady state or "sliding" regime [15]. In this regime, there is dead volume in the reactor. This dead gas volume which oscillates around the middle of the reactor never reaches the reactor outlet. This may cause decrease of the conversion. A low switching time also decreases the flushing time of the reactor. Therefore, the contact time between fresh reactants and catalyst is shortened. Furthermore, the effectiveness of heat and mass transfer is decreased; hence, lowering the conversion and yields. At a high switching time, as compared to the residence time the responses also decrease. In this condition, the effectiveness of reverse flow operation is decreased because there is no the captured heat. The high outlet temperature may cause a decrease of the responses and the extinction of the reactions. This results means that switching time should be specified based on the residence time.

The interaction of total flow rate and switching time is actually the product of these two factors, which is the total volume of the gases was fed into the reactor in a half cycle. That value indicates the total amount of materials which is supplied to the reaction. Since there is a larger amount of materials, the reactions easily occur and the effectiveness of the system increases.

The Experiments on the Steepest Ascent Path

The experiments are done on the steepest ascent path which is derived from equation 3 and 4. The results are presented in Table 4. The stationary point may be reached at the constraints of the initial temperature and the catalyst length. The initial temperature for the reactor was limited to 900°C. The catalyst zone could not be made longer than the heating zone whose length was fixed at 270 mm. Therefore, these two factors should be eliminated from the next experimental phase.

Table 4. Results on the Steepest Ascent Path

T_{ini} (^{o}C)	L (mm)	τ (min)	M	X_{CH_4} (%)	Y_{H_2} (%)
853	120	2.96	0.660	00.00	00.00
863	180	2.98	0.645	44.78	21.88
878	240	3.36	0.627	51.14	26.92
888	270	4.21	0.608	56.60	35.43

The Second Experimental Phase

A faced-center central composite design (CCD) was established around the stationary point. The initial temperature and catalyst length was fixed at values of 888°C and 270mm, respectively, based on previous experiments. The total flow rate, switching time and mole fraction of methane were included in the second experimental phase with three levels. The results are presented in Table 5. The regression analysis was done on the CCD and the results are shown in Equations 5 and 6 and Table 6. The R^2 value of the second regression model of hydrogen yield (equation 6) is 88.2% as compared to R^2 value of methane conversion (equation 5) of 96.9%. The model of the hydrogen yield seems less reliable than the model of the methane conversion.

Table 5. Experimental Results for the Second Experimental Phase (T$_{ini}$=888°C and L=270 mm)

No	F (ml/min)	τ (min)	M	X$_{CH_4}$ (%)	Y$_{H_2}$ (%)
1	480	3.42	0.545	34.50	28.50
2	620	3.42	0.545	46.45	28.29
3	480	5	0.545	48.06	21.40
4	620	5	0.545	36.40	15.10
5	480	3.42	0.655	48.90	15.90
6	620	3.42	0.655	37.10	17.95
7	480	5	0.655	41.32	21.15
8	620	5	0.655	45.48	24.63
9	480	4.21	0.608	53.20	32.64
10	620	4.21	0.608	50.66	26.48
11	550	3.42	0.608	51.50	21.89
12	550	5	0.608	51.61	30.39
13	550	4.21	0.545	52.52	30.28
14	550	4.21	0.655	51.94	31.35
15	550	4.21	0.608	62.43	38.89
16	550	4.21	0.608	61.11	37.71
17	550	4.21	0.608	57.87	37.21
18	550	4.21	0.608	58.90	36.27
19	550	4.21	0.608	60.46	36.37
20	550	4.21	0.608	56.60	35.43

$$X_{CH_4} = -34.99 + -1.14*10^{-5}F^2 - 17.52M^2 - 0.0952*\tau^2 + 0.056*F + 60.67*M$$
$$+ 6.33*\tau - 0.071123*F*M - 9.047*M*\tau - 9.96*10^{-3}\tau*F + 0.0163\tau*F*M \tag{5}$$

$$Y_{H_2} = -4.09 - 1*10^{-5}F^2 - 3.149M^2 - 0.134\tau^2 + 0.011F + 1.181\tau$$
$$- 1.028*10^{-3}\tau*F + 1.538*10^{-3}\tau*F*M \tag{6}$$

The R^2 value for the hydrogen yield (Equation 6) is less than the R^2 value for the methane conversion (Equation 5). This may be indicative of the fact that the hydrogen yield computation is dependent on two measurements (hydrogen and methane) whereas the methane conversion is only dependent on one. Thus there may be more measurement error carried over.

Quadratic and Linear Effects on Methane Conversion

Based on equation 5, the quadratic and linear effects of total flow rate, mole fraction of methane and switching time are statistically significant but are of opposite signs. This means that in a certain range there can be an increase expected with increasing value of the factors but only until a critical value is reached. A decrease of the responses is expected when arbitrarily increasing the value of factors after the critical value has been reached.

An increased total flow rate improves the thermal mass and the rate of reaction but it may quench down the reactor, shorten the residence time and the effectiveness of the system. An increase of the mole fraction of methane improves hydrogen selectivity and

lessens the production of steam which poisons the catalyst, but decreases the oxygen concentration which causes decrease of the methane conversion. An increase of the switching time avoids the dead volume in the reactor and improves the heat capture but it leads the reactor to approach the once-through operation which has no heat capture and recovery [8].

Table 6. Regression Analysis in the Second Phase

Regression Coefficients	Maximum Methane Conversion	Maximum Hydrogen Yield
F^2	-1.14E-05**	-1.00E-05*
M^2	-17.51609**	-3.148664**
τ^2	-0.095190**	-0.133509**
F	0.055833**	0.011372*
M	60.66961**	X
τ	6.333174**	1.181018**
F*M	-0.071226**	X
M*τ	-9.046967**	X
τ*F	-0.009959**	-0.001028**
F*M*τ	0.016302**	0.001538**
R^2	0.969	0.882

** - Significant at level of confidence of 99%
* - Significant at level of confidence of 95%
X – Not significant

Quadratic and Linear Effects on Hydrogen Yield

Based on Equation 6, the linear and quadratic effects of total flow rate and switching time are also statistically significant. This means that the hydrogen yield increases when the total flow rate or switching time increases. The explanation of these opposing effects has been discussed previously. The negative quadratic effect of mole fraction of methane is statistically significant. It means that the hydrogen yield decreases with an increase of mole fraction of methane. An increase of the mole fraction of methane decreases the rate of complete combustion which supplies heat to the partial oxidation of methane.

Meaning of Interaction Effects

In the second experimental phase, the interactions effects on the methane conversion is still the same as in the initial experimental design, except for the sign of the interaction between switching time and total flow rate. The interaction effects in the initial experimental phase are either negative or positive. Therefore, it may lead to a wrong claim that simply increasing (positive interaction) or decreasing (negative interaction) both factors in the interaction can improve the responses. This claim does not reflect that the factors cannot be set arbitrarily to high or low levels. In the initial experimental phase, the opposing interactions cannot be indicated because the design is asymmetrical. In the second experimental phase, there are three negative interaction effects and one positive third-order

interaction which can be considered a combination of three positive interaction effects. In other words, there are opposing interactions in one model and the interactions may not always have the same sign. Therefore, the models in the second phase are more general than the models in the initial phase.

In the second experimental phase, the interaction of switching time and mole fraction of methane (τ*M) and the interaction of total flow rate and mole fraction of methane (F*M) are not significant. These two interactions were negative and statistically significant in the first experimental phase. If these two interactions had been significant, decreasing two interactions would have improved the two responses. Simultaneously decreasing these two interactions can be done by decreasing the mole fraction of methane. Therefore, the insignificance of these two interactions means that a high mole fraction of oxygen (a low mole fraction of methane) may not be always a good condition in the region of parameters covered by the second experimental phase. As previously mentioned, in the initial experimental phase, an increase of mole fraction of oxygen can improve hydrogen yield because of high heat generation and high temperature. In the initial experimental design, the molar feed ratio between methane and oxygen varied from 1.43 to 2. It may not be low enough to reveal some disadvantages of a low mole fraction of methane (a high mole fraction of oxygen). In the second experimental phase, this molar feed ratio was changed from 1.2 to 1.9. It can be seen that arbitrarily decreasing mole fraction of methane (increasing the mole fraction of oxygen) produces much steam instead of hydrogen, hence, decreasing the hydrogen yield. Therefore, these two interactions (M*F and M*τ) are significant in the initial experimental phase but they are not significant in the second experimental phase.

The Third-Order Interactions

Three factors are included in the second experimental phase. Therefore, there is only one third-order interaction. In this study, the term "third-order interaction" represents the interaction of mole fraction of methane, switching time and total flow rate. The physical meaning of the third-order interaction can be similarly explained as the second-order interactions by fixing the value of one factor. It means that there are three second-order interactions in one term of the third interaction. The positive third-order interaction also statistically confirms the positive effect of a high mole fraction of methane. An increase of mole fraction of oxygen does not always improve the hydrogen yield and the methane conversion.

Moreover, based on the third-order interaction, it can be said that the nature of the interaction of two factors is determined by the factor that is held constant. If equation 5 is rewritten as Equation (7), it can be seen from the last term that the sign of the interaction between switching time and total flow rate depends on the mole fraction of methane. At a low mole fraction of methane, the interaction is negative. Increase of both switching time and total flow rate decrease the methane conversion. The sign of the interaction can be changed from negative to positive by alternation of mole fraction of methane. At high mole fraction of methane, the interaction between switching time and total flow rate positively affects the response.

$$X_{CH_4} = -34.99 + -1.14*10^{-5}F^2 - 17.52M^2 - 0.0952*\tau^2 + 0.056*F + 60.67*M$$
$$+ 6.33*\tau - 0.071123*F*M - 9.047*M*\tau + \left(0.0163*M - 9.96*10^{-3}\right)\tau*F \qquad (7)$$

The interaction between switching time and total flow rate is actually the total volume of gases which was fed into the reactor in a half cycle. The optimum of this value may depend on the mole fraction of methane. At a low mole fraction of methane, an increase of

the total volume of gases in a half cycle negatively affects the responses because of the disadvantages of a low mole fraction of methane as previously mentioned. At a high mole fraction of methane, the total volume of gases in a half cycle positively affects the responses by increasing the amount of materials which was supplied to the reactor and the effectiveness of the system.

Moreover, the third-order interaction of total flow rate, switching time and mole fraction of methane is actually the product of these three factors which is the volume of methane was fed into the reactor in a half cycle. An increase of this value may increase the materials and rate of the partial oxidation of methane; hence positively affect the responses. It seems to be difficult to increase the effect of the third-order interaction. In order to increase this interaction, either the flow rate of methane (F*M) or the switching time should be increased. It was previously mentioned, both of these two solutions negatively affect the responses. Therefore, the opposing effects should be considered during control and optimization of a reverse flow reactor. The optimum point is a trade-off from all these opposing effects.

Canonical Analysis and Optimum Point

Canonical analysis was done on the experimental data to determine the nature of the stationary point and the result is shown in Table 7. The maximum points of hydrogen yield and methane conversion are different. There is a trade-off between these optimum points. A loss of hydrogen yield of 0.48% is compensated by increase of methane conversion of 0.83%. Figures 5(a) and 5(b) represent the contour plot of methane conversion and hydrogen yield, respectively. The plot of the methane conversion is more circular than the hydrogen yield. This indicates the effects of factors on methane conversion are symmetrical. There are opposing effects such as: (1) three negative quadratic effects and three positive linear effects, (2) the three negative second-order interactions and one positive third-order interaction which is equivalent to three positive second-order interactions. The plot of hydrogen yield is elliptical because of the insignificance of positive linear effect of mole fraction of methane and the two interactions which also relate to the mole fraction of methane (F*M, τ*M).

Table 7. Optimum Points from Canonical Analysis

Factors	Maximum Methane Conversion	Maximum Hydrogen Yield	Δ
F (ml/min)	543.23	540.55	
M	0.6043	0.5845	
τ (min)	4.24	4.15	
Predicted Methane Conversion	57.36%	56.53%	-0.83%
Predicted Hydrogen Yield	36.73%	37.21%	0.48%

Conclusions

In this study, we report on the performance of a reverse-flow reactor for the partial oxidation of methane. The reactor uses a Ni-MgO/α-alumina catalyst that was also developed by our research team. After start-up, no reactor heating or feed preheating was utilized. While the catalyst, the reverse-flow reactor and the use of regression-based optimization are not completely novel by themselves, the combination of both is the unique contribution of this paper. It has been demonstrated that the production of syngas utilizing

this catalyst in a reverse-flow reactor if feasible, though there are improvements that can still be made.
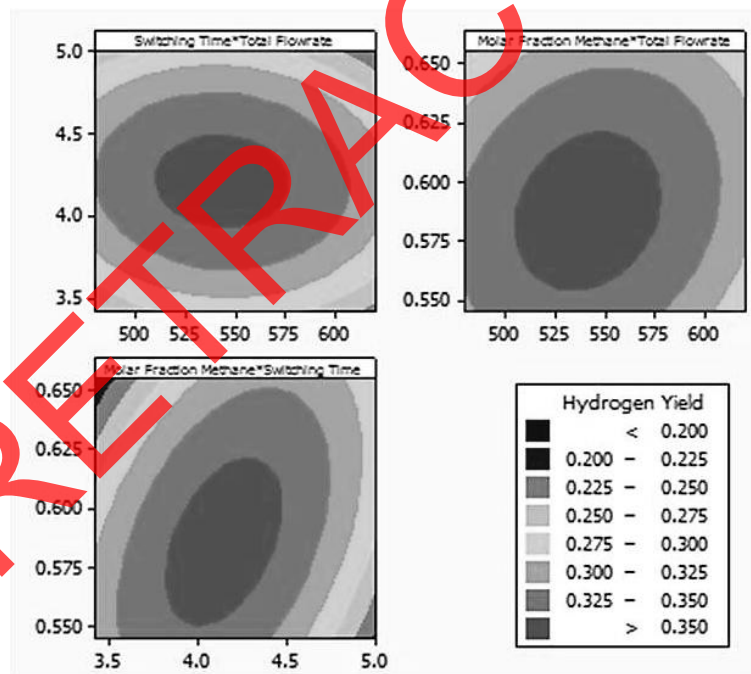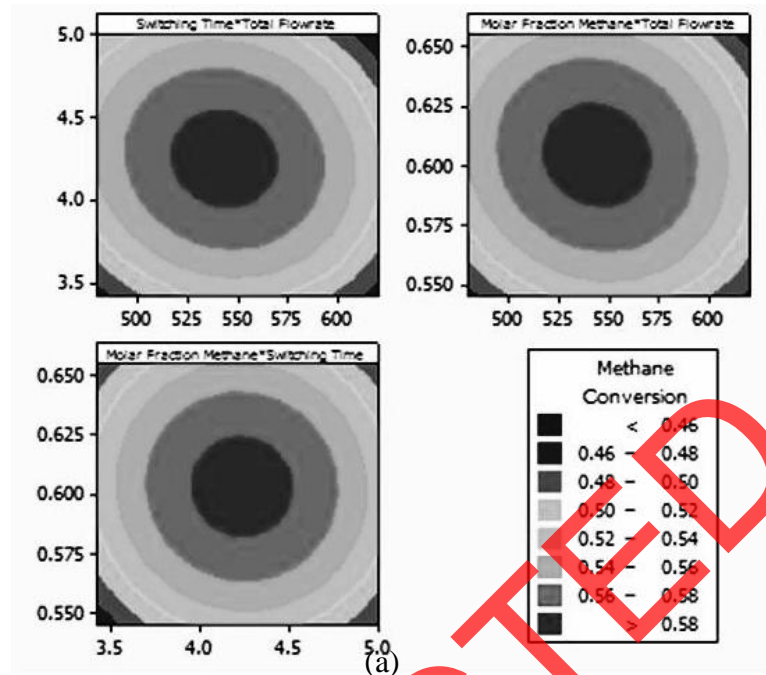

Figure 5. (a) Contour plots for methane conversion (b) Contour plots of hydrogen yield

Such reactors are very complex and a complete mathematical model would involve the repeated solution of a system of nonlinear partial differential equations. The use of an experimental design tool, the method of steepest ascent, has been demonstrated as an effective and relatively simple tool for the optimization of a reverse-flow reactor. Such tools can be very useful in extremely complex systems which are difficult to

accurately model mechanistically. In the course of the experiments, key insights about the importance of key parameters and their complex interactions were found.

The interaction of the significant factors determined during each experimental phase all showed that an optimum does exist and that the optimum conversion could be achieved not just by adjusting one factor but by a combination of factors. The statistical analysis showed that the achievement of adiabatic operation is critical to the overall improvement of conversion and yield. There is little doubt that a higher conversion and yield could have been achieved if adiabatic conditions could have been achieved. The achievement of adiabatic conditions is more easily achieved in a larger reactor to which the insights from this study are still applicable.

Nomenclature

T_{ini}	Initial temperature (°C)
F	Total flow rate (ml/min)
M	Mole fraction of methane
τ	switching time (min)
L	Catalyst length (mm)
X_{CH_4}	Methane conversion (%)
Y_{H_2}	Hydrogen yield (%)

Acknowledgement

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