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Study of process data in autothermal reforming of LPG using multivariate data analysis

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Abstract

Autothermal reforming of LPG was studied in a fixed-bed reactor by varying controlled parameters, such as reforming temperature, steam-to-carbon ratio (S/C), oxygen-to-carbon ratio (O/C) and catalyst. The conditions tested were two nickel-based catalysts, at 680–820 °C, with S/C of 0.30–1.9 and O/C of 0.64–1.4. In addition to controlled variables, it was found vapor composition of LPG withdrawn were not constant at different levels of tank exhaustion. The fuel vapor contained more heavy components and odorant—ethyl mercaptan as the bottle approached empty. Multivariate data analysis method, projections to latent structures (PLS), provided quantitative analysis of the effects of temperature, S/C, O/C, fuel composition and catalyst activity on reformate gas composition. Temperature, S/C and O/C were found to be the most important parameters for fuel conversion and avoiding carbon deposition. Sulfur poisoning by odorant was the main cause of catalyst deactivation. Composition of hydrocarbons in LPG vapor was shown to affect the autothermal reforming process, but the influence was less significant. Under test conditions, reformate gas composition generally approached equilibrium. The kinetically controlled methane reduction was well predicted by a PLS regression model.

Keywords: Autothermal reforming; Hydrogen; LPG; Vapor composition; Multivariate analysis; Sulfur

1. Introduction

Hydrogen production, storage, distribution, and utilization are current areas of major research focus. Using fuel cells, electricity can be generated from hydrogen with high efficiency and almost no environmental impacts. Due to the lack of naturally occurring H_2 resources, successful fuel cell implementation will require H_2 production based on highly efficient fuel processing, in which fuels are converted to hydrogen and contaminants and pollutants are removed. In the near term, conventional hydrocarbon fuels can be potential sources of hydrogen, serving as transition fuels toward future production of H_2 from renewable sources. Liquefied petroleum gas (LPG) is a mixture of ethane to butane hydrocarbons that exist as liquids under modest pressures at ambient temperatures [1]. LPG is easily transported and stored on-site [2] and may be attractive in remote areas or for residential use.

Fuel processing converts LPG into hydrogen and carbon dioxide. Small amounts of methane, carbon monoxide, and potential contaminants for polymer electrolyte membrane (PEM) fuel cell, such as sulfur compounds are removed. Typical fuel processing steps are desulphurization, reforming, water–gas shift, and CO removal. Desulphurization removes sulfur compounds, frequently mercaptans that have been added as odorants and can poison catalyst and fuel cell electrode materials. Reforming is the key step to convert hydrocarbons to H_2, CO_2, and CO. Small amounts of methane and other higher hydrocarbons may also be present. The water–gas shift is a reversible reaction converting CO and H_2O to CO_2 and H_2. CO removal is necessary if the reformate is to be used in PEM fuel cells. Generally, there are three methods to produce hydrogen from hydrocarbons: steam reforming, catalytic partial oxidation, and autothermal reforming [3]. Propane is normally the major component (>80%) of LPG and the reactions involved in propane reforming include [4]:

- Steam reforming

$$C_3H_8+3H_2O(l) \rightarrow 3CO+7H_2, \quad \Delta H^{\circ}_{298}=629.757\ \text{kJ/mol} \tag{i}$$

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Nomenclature

A	number of PLS or PCA dimensions
$\mathbf{B}$	regression coefficient
$\mathbf{C}$	matrix of loadings for $\mathbf{Y}$
$\mathbf{D}$	diagonal matrix of correlation coefficients
$\mathbf{E}$	residual matrix of predictors
$\mathbf{F}$	residual matrix of responses
$\mathbf{G}$	residual matrix of responses
$\mathbf{H}$	matrix of the residual of the inner correlation fit
J	number of time points
K	number of variables
N	number of batches (e.g. experiments)
$\mathbf{P}$	matrix of loadings for $\mathbf{X}$
t	score vector for $\mathbf{X}$
$\mathbf{T}$	matrix of scores for $\mathbf{X}$
u	score vector for $\mathbf{Y}$
$\mathbf{U}$	matrix of scores for $\mathbf{Y}$
$\mathbf{X}$	matrix of predictor variables
$\mathbf{y}$	vector of a response variable
$\mathbf{Y}$	matrix of response variables

- Partial oxidation (O/C = 1)

$$C_3H_8+\frac{3}{2}O_2 \rightarrow 3CO+4H_2, \quad \Delta H^{\circ}_{298}= -227.747\ \text{kJ/mol} \tag{ii}$$

Autothermal reforming is a combination of steam reforming (reaction (i)) and partial oxidation (reaction (ii)).

- The water–gas shift reaction described earlier is

$$CO + H_2O(g) \rightarrow CO_2 + H_2, \quad \Delta H^{\circ}_{298} = -41\ \text{kJ/mol} \tag{iii}$$

Several researchers have reported their work on production of hydrogen from LPG by steam reforming, autothermal reforming and catalytic partial oxidation [2,5–7]. Autothermal reforming is likely the most suitable one for LPG–PEM combination for residential use. Compared with steam reforming, autothermal reforming is easily operated for a small system, has better temperature control, and less coking tendency [8]. Without steam, partial oxidation has the advantage of fast response, however, conversion efficiency is lowered as the heat released by combustion is not completely used [6].

Ayabe et al. [6] studied activity of metal-supported catalysts in autothermal reforming of methane and reported a ranking of metal activity as Rh > Pd > Ni > Pt > Co. The result is similar to that summarized by Rostrup–Nielsen determined from steam reforming ethane and toluene, Rh > Ru ≫ Pd > Pt > Ni > Co [9]. Despite differences in activity, Ni is less expensive than precious metals and greater amounts of Ni can be loaded to provide the same overall activity as Rh catalyst [2].

LPG vapor can generally be used in place of natural gas but some adjustment of conditions, e.g. air/fuel ratio are needed [1]. Compared with methane, the larger molecules of LPG usually require higher temperature to obtain complete conversion to hydrogen, carbon dioxide and carbon monoxide. As expected due to the greater carbon number, propane fuel was found to cause more carbon deposition than methane fuel [6]. Another source of catalyst deactivation is sulfur poisoning by odorant, such as ethyl mercaptan, which is commonly added to LPG.

The present study was performed to investigate LPG reforming reaction conditions and the effect of the composition of LPG vapor on conversion, carbon deposition on catalyst, and sulfur poisoning. Controlled variables included reforming temperature, catalyst amount, steam-to-carbon ratio (S/C) and oxygen-to-carbon ratio (O/C). The temperature profile in the reactor was dependent on reactor temperature set point, gas velocity, S/C and O/C. In addition, LPG vapor composition withdrawn from tanks was not constant. The concentration of hydrocarbons and sulfur odorant was monitored as fuel in the tank decreased. The effects of fuel composition and controlled parameters were explored by a multivariate data analysis method that is good at examining dependent and noisy variables.

2. Materials and methods

2.1. Materials

Fig. 1 shows a lab-scale fixed-bed catalytic reactor. The reactor is made from 316 stainless steel and is 45.7 cm in length and 1.93 cm internal diameter. The reactor is heated by an electrical furnace with a heating length of 30.5 cm. Two, G-90-type steam reforming catalysts, C11-NK (#1) and G-91 EW (#2) from Süd-Chemie, were tested. G-91EW was designed for natural gas and LPG, and C11-NK was for naphtha.

The composition of LPG vapor is determined by the equilibrium of liquid and vapor in LPG bottle. Lighter hydrocarbons with higher saturation vapor pressures vaporize first. When the vapor is withdrawn from the bottle, both the amount and the composition of the liquid in the bottle will change. The pressure of the bottle gradually decreases, and the fractions of higher hydrocarbons increase. When the bottle pressure begins to decline, the remaining liquid is enriched in heavier hydrocarbons. As a result, the composition of vapor obtained from the head space of an LPG bottle depends on the composition of liquid in the bottle, the amount of liquid left in the bottle, and the bottle's refill history. In the experiments, three propane based fuels were tested; (1) LPG in an 8.3 kg tank (Tank A) that had been refilled several times, i.e. history undocumented, (2) LPG in a newly purchased, 8.2 kg tank (Tank B), and (3) Grade 5.0 propane (Propane). The LPG is a commercial product from GasPro, Hawaii sold as a motor grade or high-octane propane. The composition of LPG was stated to be 90–100% propane/propylene, 0–2% ethane, 0–10% butane and 40 ppm ethyl mercaptan. Auto ignition temperature was in the range of 360–450 °C. In all tests, vapor was withdrawn from the head space of the tank.

2.2. Methods

The experiments were conducted by varying predictor variables at two levels (Table 1). Initially, a full factorial design for

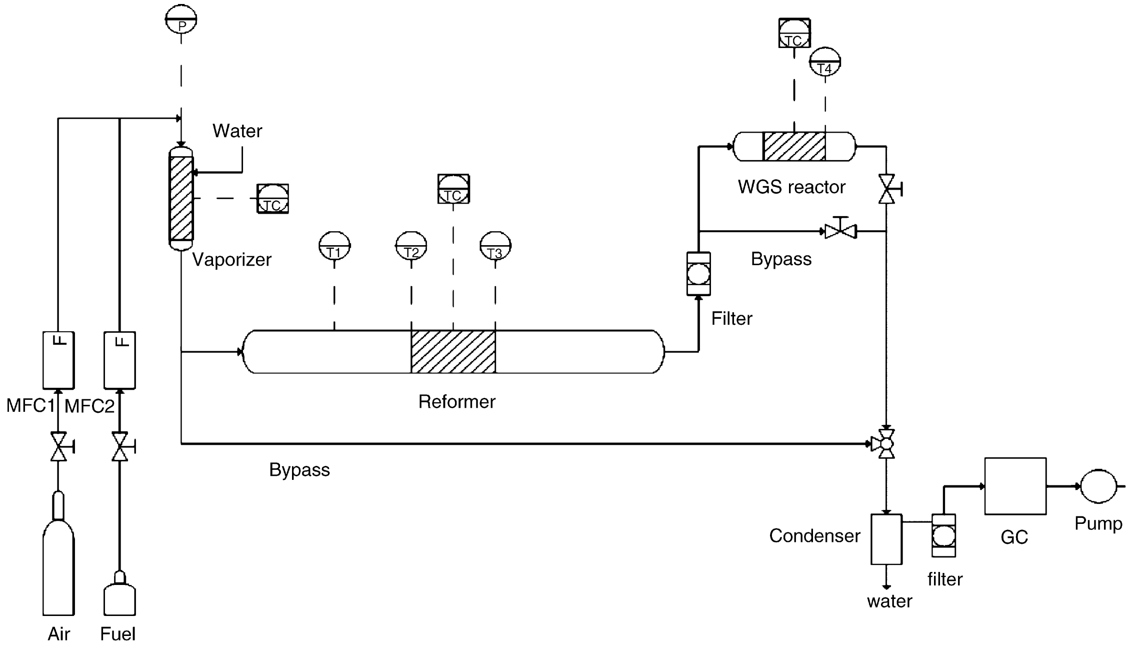

Fig. 1. Schematic diagram of the fixed-bed reactor.

Table 1
Levels of the predictor variables

	T_{sp}	S/C	O/C	Catalyst	GHSV	Sulfur
−1	620–680	0.3–0.6	0.6–0.8	C11-NK	7,700	Tank B
1	770	1.5–1.8	1.2–1.4	G91-EW	15,000	Tank A

Table 2
Summary of experimental conditions

	Variables	Abbreviation	Unit	Minimum	Maximum
Predictor variables, **X** block					
1	Catalyst	Cat		C11-NK	G91-EW
2	Furnace set point	T_{sp}	°C	620	770
3	T_1	T_1	°C	414	912
4	T_2	T_2	°C	575	963
5	T_3	T_3	°C	676	818
6	Gas hourly space velocity v/Vcat	GHSV	h^{-1}	7000	18,500
7	Steam to carbon ratio	S/C		0.30	1.93
8	Oxygen to carbon ratio	O/C		0.64	1.38
9	Sulfur in LPG	Sulfur	ppm	Low (1–15)	High (15–150)
10	C_2H_6 in LPG	C2H6f	%	0	4.19
11	C_3H_6 in LPG	C3H6f	%	0	3.33
12	C_3H_8 in LPG	C3H8f	%	87.5	100
13	C_4H_{10} in LPG	C4H10f	%	0	10.9
14	Time on stream	TOS	h	0.05	43.5
15	Lagged CH_4	CH4L	%	0	3.29
16	Lagged C_2H_4	C2H4L	%	0	4.55
Response variables, **Y** block					
Product gas composition on dry basis					
1	H_2	H2	%	19.1	44.5
2	N_2	N2	%	30.8	63.2
3	CO	CO	%	4.32	15.3
4	CH_4	CH4	%	0	3.29
5	CO_2	CO2	%	4.56	14.5
6	C_2H_4	C2H4	%	0	4.55
7	Mass balance of carbon	MBC	%	54.1	109

three variables, namely reactor temperature, steam-to-carbon ratio and oxygen-to-carbon ratio, was performed with replicates. The results led to proper reforming conditions, under which hydrocarbon fuels were nearly completely converted to gas phase products. Then impacts of the catalyst type, and gas velocity were examined by varying one variable at a time. Finally the influence of the sulfur content was studied. Ranges of the controlled variables, uncontrolled process variables and characterization variables of LPG vapor are listed in Table 2. Temperature in the reactor was controlled by the furnace set point (T_{sp}). The 20–40 g catalyst bed was located in the constant temperature zone in the reactor. Temperatures in the reactor were measured at three locations, 7.5 cm in front of the catalyst bed (T_1), just before the catalyst bed (T_2) and just after the catalyst bed (T_3). Usually during autothermal reforming the temperatures in the reactor were not uniform due to the occurrence of exothermic partial oxidation and endothermic steam reforming reactions. A set point of 770 °C was equal to around 800 °C at the end of the catalyst bed. Gas hourly space velocity (GHSV) was determined on the basis of catalyst volume. Oxygen-to-carbon ratio of one is equivalent to 30% of the oxygen required for complete combustion of propane. The parameter CH4L and C2H4L are defined as lagged methane and ethylene concentrations obtained from the previous measurement. Methane is an indicator of catalyst activity in that increasing methane content indicates that the catalyst activity is decreasing [9,10]. Ethylene usually is related to coke formation. Mass balance of carbon (MBC) was calculated using the flow rate and composition of LPG entering the reactor and the flow rate and composition of the reformate exiting the reactor.

During the experiments, air and LPG were introduced from gas bottles and were controlled by mass flow controllers (Fig. 1). Mixed air and LPG passed a vaporizer where water was heated to 100 °C before entering the reactor. After the reactor, water was separated from product gas in a condenser. Water was further removed by silica gel or a coalescing filter. The dry effluent gas was analyzed by a Shimadzu GC 14A. Gas was separated on a Supelco Carbonex 1000 45/60 (1.5 m × 0.32 mm) packed column and analyzed using a thermal conductivity detector (TCD). The gas components quantified were H_2, N_2, CO, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, and C_3H_8. Test durations ranged from 3.6 to 43.5 h. Reactor operating conditions were monitored and recorded on a 1 min interval. Composition of the gas exiting the reactor was usually determined every 30–35 min. LPG vapor was characterized using the Shimadzu GC equipped with an Alltech HayeSep D 100/120 (3.05 m × 0.32 mm) packed column and TCD. Sulfur concentrations in the fuels were determined on a Varian 3800 GC equipped with a pulsed flame photometric detector (PFPD) and a Varian CP-Sil 5 CB capillary column (50 m × 0.32 mm).

2.2.1. Multivariate data analysis

In this work, an advanced data reduction method, projections to latent structures (PLS) [11], was used to evaluate the parameters. The PLS method is an approach that represents an extended type of multiple linear regression model. PLS is flexible and can be applied where traditional multiple linear regression is severely limited. For example the PLS analysis can handle collinear and noisy variables and when the number of observations is fewer than predictor variables.

The PLS method is based upon the use of projections [11,12]. Through projecting sample points to PLS components, reduced spaces in both **X** and **Y** are defined. The approach approximates as closely as possible the original data, while providing stable results and low predictive error by maximizing covariance between the two reduced spaces.

In the PLS, the **X** matrix (predictors) and the **Y** matrix (responses) are decomposed separately into score matrices and loading matrices (Eqs. (1) and (2)). The **X** and **Y** blocks are linearly related by inner relation (Eq. (3)) through the score vectors of a common PLS component.

$$\mathbf{X} = \mathbf{T}\ \mathbf{P}' + \mathbf{E}\ (\mathbf{X}\ \text{blocks}) \tag{1}$$

$$\mathbf{Y} = \mathbf{U}\ \mathbf{C}' + \mathbf{G}\ (\mathbf{Y}\ \text{blocks}) \tag{2}$$

$$\mathbf{U} = \mathbf{T}\ \mathbf{D} + \mathbf{H}\ (\text{inner relation}) \tag{3}$$

T and **U** are matrices of the score vectors, **P**′ and **C**′ are the transposed matrices of the loading vectors. The inner relationship is denoted by **D**, which is a diagonal matrix. **E**, **G** and **H** are the matrices of the residuals.

An overall PLS regression (PLSR) model of a response variable can be written as:

$$\mathbf{y} = \mathbf{X}\mathbf{B} + \mathbf{F} \tag{4}$$

B is a vector of PLS-regression coefficients. **y** is a vector of one response variable.

The multivariate analysis was conducted by SIMCA-P (Umetrics AB).

3. Results and discussion

3.1. Fuels

During the experiments, compositions of vapor from Tanks A and B were monitored by the GC with TCD. Results of the analysis are presented in Fig. 2. As shown, the LPG vapor composition varied with time, the result of differing vapor pressures of the constituent species. Generally the lighter components (ethane, propylene, and propane) were in higher concentration when the bottle was full. As gas was withdrawn from the bottle, the concentration of these components was reduced and the heavier component, butane increased. Although the liquids in the two tanks were not sampled and analyzed, by integrating the discharged gas composition curve it is evident that Tank A that had been refilled several times (Fig. 2a) had more propylene and butane and less ethane than the new Tank B that had only been filled once (Fig. 2b). Tank A was almost empty as the total tank weight approached 8 kg (Fig. 2a). Tank B was pressurized with N_2 before filling with LPG, and this is evident in Fig. 2b. N_2 concentration decreased rapidly at the beginning of usage (Fig. 2b). Since the liquid LPG contained mostly propane, the vapor composition of hydrocarbons was nearly constant, except for the first and the last kilogram of LPG in the bottle.

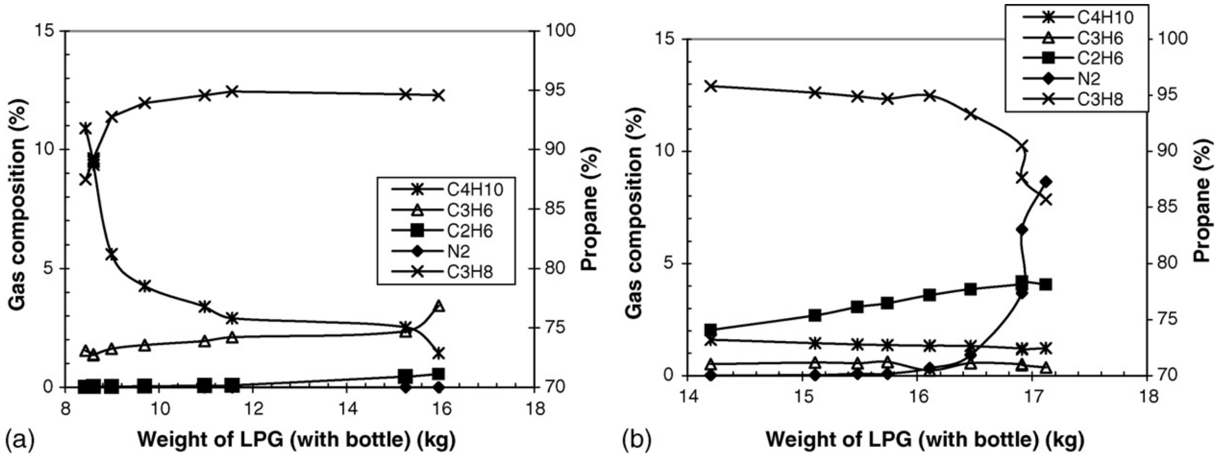

Fig. 2. LPG composition vs. the total weight of LPG bottles. (a) Tank A and (b) Tank B. Empty bottle weight is about 8.2 kg.

Table 3
Sulfur in LPG vapor

Tank		Weight (kg)	Ethyl mercaptan (ppm)
A	Full	16.7	6.9
A	Half	12.5	14
A	Empty	8.7	140
C	Full	16.5	1.5
C	Half	12.2	14
C	Empty	8.5	170

To monitor the change of sulfur level in LPG vapor, Tank A was filled again and another new tank (Tank C) was filled at the same time. The sulfur content of the gas stream metered from the LPG tanks was measured by the GC with PFPD at three points, full tank, half tank, and near empty (Table 3). The difference between the new bottle and used bottle was not found to be significant. Although the LPG was reportedly dosed with 40 ppm ethyl mercaptan on average, mercaptan found in the vapor varied greatly increasing drastically when the bottle was nearly empty. During the experiments, Tank A use was predominantly in the weight range from 13.5 to 8.3 kg, and Tank B was used from 17.1 to 13.8 kg. As shown in Table 3, the sulfur concentrations in vapor from Tank A and B were classified as high (15–150 ppm) and low (1–15 ppm), respectively.

3.2. *Autothermal reforming*

Effects of experimental parameters (Table 2) on autothermal reforming of LPG were studied over a total of 29 conditions. The composition of reformate gas from a typical autothermal reforming test is presented in Fig. 3. Equilibrium gas compositions were calculated using FACTSage^{TM} 5.1 (from Thermfact/CRCT, Montreal, Canada and GTT-Technologies, Aachen, Germany) and are shown as lines in the figure. The gas concentrations for hydrogen, nitrogen, carbon monoxide and carbon dioxide approached equilibrium because water–gas shift reaction (reaction (iii)) was not rate limited at the reaction temperature, nominally 800 °C. Methane was higher than the equilibrium value, indicating methane reforming was kinetically controlled. The observed trend of increasing methane concentration implies decreasing catalyst activity over time.

Experiments performed over ∼40 h time on stream were plotted to study catalyst activity (Fig. 4). Propane, LPG from Tank

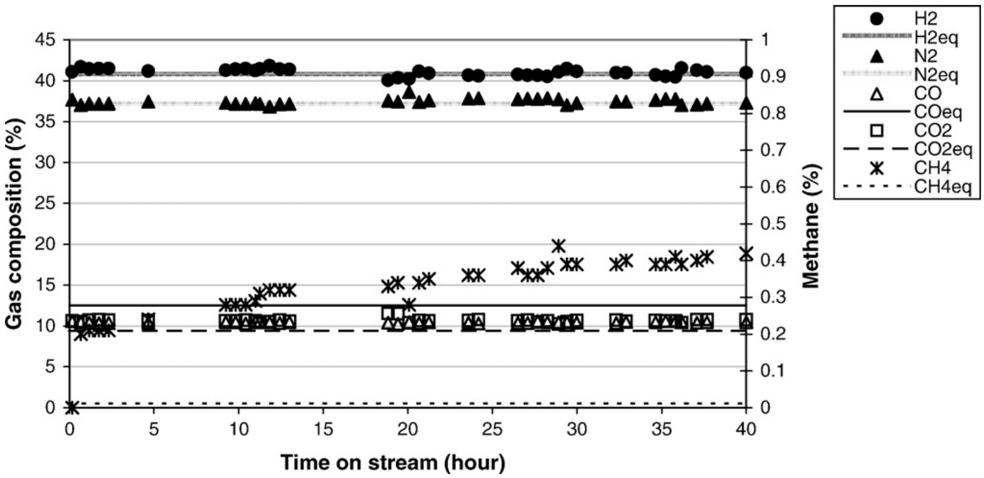

Fig. 3. Gas composition (dry basis) from autothermal reforming of LPG from Tank B. G91-EW, 20 g, 800 °C, S/C = 1.8, O/C = 0.9. Equilibrium gas compositions are calculated by FACTSage and are shown as lines.

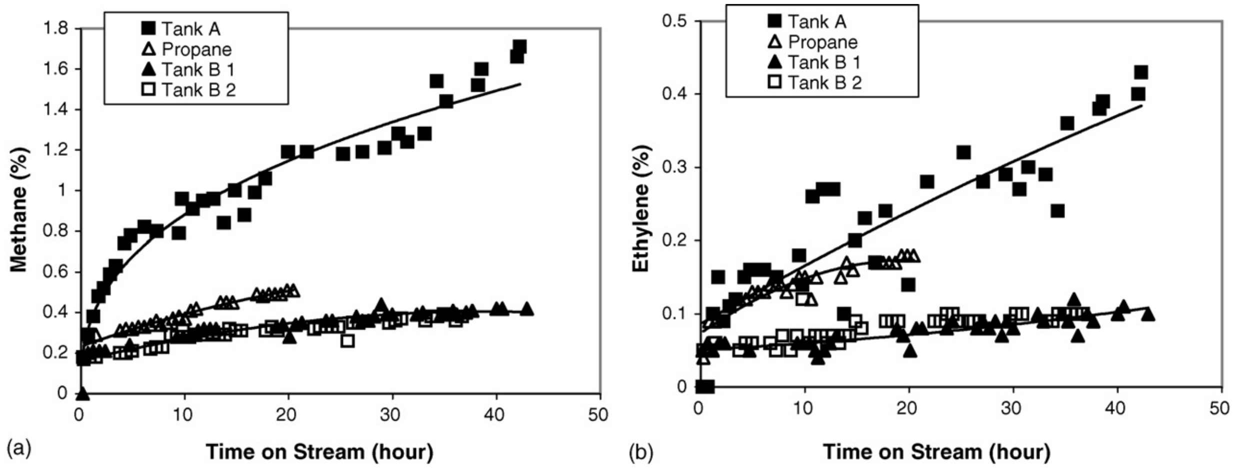

Fig. 4. Methane (a) and ethylene (b) concentrations after autothermal reforming of different fuels. G91-EW, 20 g, 800 °C, S/C = 1.75–1.80, O/C = 0.90–1.13.

A, and LPG from Tank B were tested. Autothermal reforming was conducted on ∼20 g samples of G91-EW, at 800 °C, S/C = 1.75–1.80 and O/C = 0.90–1.13, under which conditions a nearly complete conversion of LPG was achieved. The experiment with LPG from Tank B was repeated. As shown in Fig. 4, initial concentrations of methane and ethylene were almost the same, indicating rate of reactions on fresh catalyst were nearly identical for the fuels. Both methane and ethylene concentrations increased with increasing time on stream. The rate differed for different fuel sources. The weight of Tank A in the test shown in Fig. 4 began at 11.5 kg and ended at 8.6 kg. By GC analysis (Table 3), vapor from Tank A could contain sulfur as high as ∼100 ppm, while vapor from Tank B had sulfur below 15 ppm. In addition, over the range of fuel use from the two bottles, Tank B had more light hydrocarbons and Tank A had more heavy hydrocarbons (Fig. 2).

3.3. Multivariate data analysis

Evaluation of the results indicated that some experimental parameters were correlated, e.g. reactor temperature and S/C or O/C. In addition during one experiment the composition of LPG vapor gradually changed over time both for hydrocarbons and odorant (Fig. 2a and b, Table 3). Consequently, the PLS analysis was employed to explore the effects of each parameter on the experimental results.

As shown in Fig. 4, the reformate gas composition changed with time for each experiment. The data became a three-way matrix of dimension ($N \times J \times K$) for K variables at J time points in N batches (experiments). Wold [13] mentioned an approach to unfold a three-way matrix to a two-way matrix of dimension ($N \times (J \times K)$). However, for the present data, that method cannot be used directly since the length of each experiment was different and the measurements were not evenly distributed over time. For the present work, the data matrix was unfolded to ($N \times J$) rows and K columns. Two lagged predictor variables, CH4L and C2H4L, were added to form an expanded **X** matrix (Table 2).

A total of 256 data points under 29 sets of conditions were analyzed. One long experiment with 40 data points was used as a validation set. The remaining data were used as a training set to develop the model. The **X** block contained 16 predictor variables and the **Y** block contained 7 response variables (Table 2). The data were mean-centered and scaled to unit variance for each variable.

Principal component analysis (PCA) was first applied to examine the distribution within **X** block. Each point represented a condition at one time. Two dense clusters were revealed on the right side (Fig. 5). The clusters included the results from the long experiments. There were a few points located outside the Hotelling T^2 with 95% confidence. The points on the left were from experiments at 620 °C, and the points below the ellipse were the ones with the highest O/C ratio. The points were still kept in the dataset because they represented the extreme conditions. In general, Fig. 5 shows that the conditions were not strongly clustered, and covered a proper experimental range.

Subsequently, PLS analysis of 216 data points in the training set gave a regression model with four significant component ($A = 4$) explaining 71.3% of the **Y**-variance ($R^2Y = 71.3\%$, $Q^2 = 69.2\%$). R^2Y is the relative sum of squares of **Y** fitted by the model, and Q^2 is the relative sum of squares of **Y** predicted by the model in cross validation [11]. The plot of PLS scores u_1 versus t_1 (Fig. 6) showed quite scattered data around the straight line on the lower left side, indicating the fitting was not very good. The scattered data were from experiments with low LPG conversion

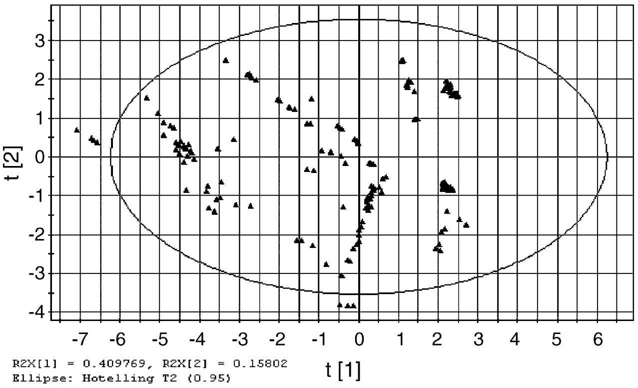

Fig. 5. PCA score plot of pricipal components 1 and 2 for **X** matrix.

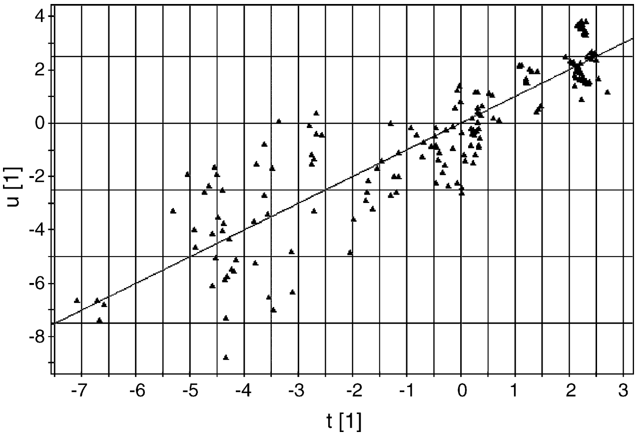

Fig. 6. The score plot of first PLS component of **X** and **Y** blocks.

to hydrogen due to low temperature, low S/C or O/C. The noisy data were probably the result of errors in the experiments. It also indicated a nonlinear feature of the data.

The plot of the first two PLS loadings of **X** and **Y** blocks illustrated (Fig. 7) the correlation between the **X** and the **Y** variables and the correlation within the **X** and the **Y** blocks. Conversion of fuel to fix gases (MBC) was closely correlated to temperatures, catalyst type, and S/C. It was also negatively correlated to fuel composition, e.g., sulfur and C3H6f. O/C was negatively correlated to the concentrations of hydrogen and CO on the vertical axis. The correlations between the hydrocarbons in the LPG vapor were also shown in Fig. 7. Propane was negatively correlated to sulfur, propylene and butane.

The response matrix contains mainly gas composition and mass balance of carbon, which is calculated based on gas composition. Therefore the responses are correlated. The correlation can be seen in Fig. 7 (red ones). For example, methane and ethylene are negatively associated with mass balance of carbon. PLS regression was conducted for each single response to avoid correlation problems. In the PLS regression, the importance of a predictor variable for the modeling of a response variable is evident from its regression coefficient (Eq. (4)). Fig. 8 summarized the effects of predictor variables on H_2, CO, CH_4 and C_2H_4 concentration in the reformate. H_2 (Fig. 8a) was the desired product and CO (Fig. 8b) could be converted to H_2 by the water–gas shift reaction (reaction (iii)). Both methane and ethylene were undesirable products (Fig. 8c and d). Catalyst G91-EW (#2) was more effective in decomposing methane and ethylene than C11-NK (#1). High furnace temperature (T_{sp}) was favorable for H_2, and could reduce CH_4 and C_2H_4 considerably. Note that H_2 was related to T_2, the temperature at the inlet side of catalyst, and CO was related to T_1, the temperature upstream of the catalyst. This indicated that production of hydrogen relied on steam reforming on the catalyst and CO started to form by partial oxidation before the catalyst. At high T_1, the carbon mass balance was improved, implying partial oxidation at high temperature could reduce coking. The effect of gas hourly space velocity through the catalyst bed (GHSV) was generally weak, showing that the amount of catalyst used in the experiments was in excess.

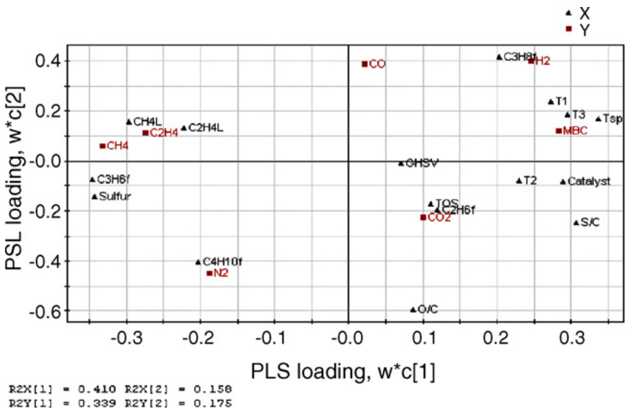

Fig. 7. Plot of the PLS loadings.

As shown in Fig. 8, S/C and O/C had different effects on the gas component concentrations in the experimental range of variables tested. S/C had a great negative impact on CO concentration, suggesting that conversion of CO to CO_2 is sensitive to an increase of steam. O/C was influential for H_2 production. At higher O/C, H_2 concentration decreased both by conversion to H_2O and by dilution with N_2 present in increased air flow rate. In order to help interpret the results, equilibrium calculations were performed over the range of test conditions (Table 4). The results from PLS analysis agreed well with equilibrium calculation. Unlike CO and H_2, methane and ethylene were kinetically controlled. From Fig. 8c and d it is apparent that increasing S/C or O/C was responsible for controlling the levels of methane and ethylene in the product gas.

The effects of fuel composition were shown in Fig. 8 as well. Sulfur had an adverse impact for H_2 production and for methane and ethylene conversion. Sulfur and CH4 were closely correlated in the PLS loading plot (Fig. 6). It is likely sulfur poisoning occurred and caused deactivation of the catalysts. Propane appeared to have positive effect on carbon conversion of LPG and H_2 production. Propylene and butane seemed to have negative impacts. This is partly because the ratio of hydrogen to carbon is lower for butane (2.5) and propylene (2) than for propane (2.67). Concentration of propylene in the fuel gas was found to be related to an increase of CH_4 and C_2H_4.

As it is shown in Fig. 3, methane concentration increased with TOS. The **X**-block was thus augmented with the concentrations of methane and ethylene at the previous sampling time, CH4L and C2H4L, and TOS so that the effect of time would be included. The variable CH4L is an indicator of catalyst deactivation and C2H4L is related to coke formation on the catalyst. Concentrations of CH_4 and C_2H_4 were evidently related to the lagged variables, CH4L and C2H4L. Conversions of methane and ethylene were sensitive to deactivation of catalyst. Comparing Fig. 8c and d, it seemed that increases of methane and ethylene over time were due to different mechanisms. Methane relied more on catalytic steam reforming and sulfur poisoning seemed to have stronger influence as a result. Ethylene, the precursor of coke formation, was reduced by high temperature, oxygen, steam, and catalyst. Both partial oxidation and steam reforming seemed to have influence on reducing levels of ethylene in the reformate.

Finally, methane concentration in the validation set (Fig. 9) was predicted by the two component PLSR model for methane

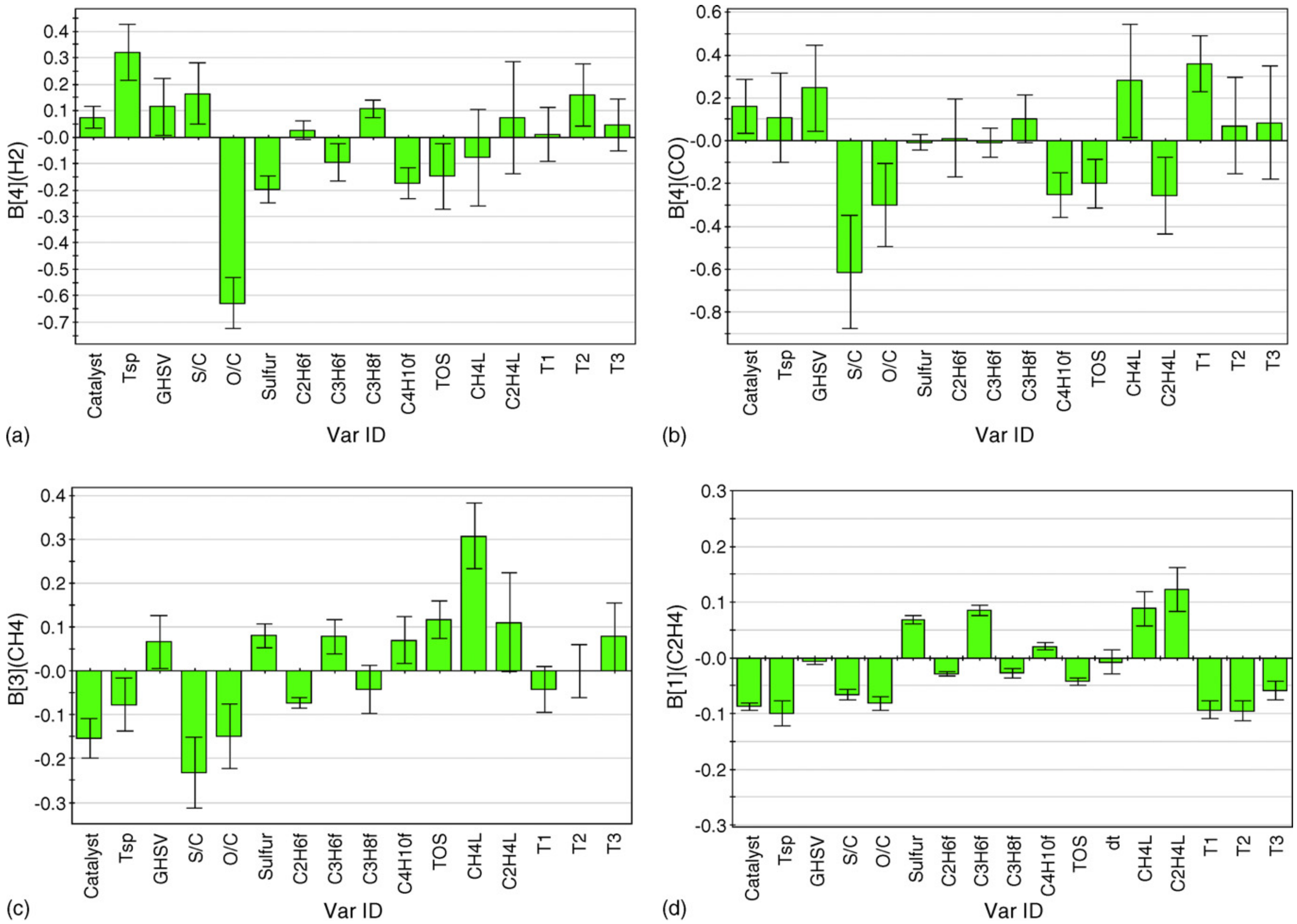

Fig. 8. PLS regression coefficients. (a) Hydrogen, $A = 4$, $R^2Y = 0.904$, $Q^2 = 0.887$, (b) carbon monoxide, $A = 4$, $R^2Y = 0.791$, $Q^2 = 0.738$, (c) methane, $A = 3$, $R^2Y = 0.818$, $Q^2 = 0.808$ and (d) ethylene, $A = 1$, $R^2Y = 0.563$, $Q^2 = 0.551$.

Table 4
Results of equilibrium calculations modeling autothermal reforming of 1 mol propane at 800 °C, 1 atm

	O/C = 1.0			S/C = 1.5		
	S/C = 0.5	S/C = 1.0	S/C = 1.5	O/C = 0.93	O/C = 1.1	O/C = 1.4
% dry basis						
H_2	34.6	36.5	37.8	39.6	34.6	28.7
CH_4 (ppm)	567	224	117	146	75.9	31.1
C_2H_4	0.001	0.000	0.000	0.000	0.000	0.000
N_2	42.5	41.2	40.4	38.3	44.3	51.5
CO	18.6	15.2	12.9	13.5	11.7	9.6
CO_2	4.26	6.98	8.88	8.63	9.34	10.2
Mole of gas						
Mol-H_2	4.54	4.93	5.22	5.37	4.93	4.34
Mol-CH_4	0.00743	0.00303	0.00162	0.00198	0.00108	0.000472
Mol-C_2H_4	1.45E−08	2.26E−09	6.32E−10	8.76E−10	3.29E−10	8.77E−11
Mol-N_2	5.57	5.57	5.57	5.2	6.31	7.8
Mol-H_2O	0.949	2.06	3.28	3.13	3.57	4.16
Mol-CO	2.43	2.05	1.77	1.83	1.67	1.46
Mol-CO_2	0.559	0.94	1.22	1.17	1.33	1.54
Mol-gas	14.1	15.6	17.1	16.7	17.8	19.3

Calculations performed using FACTSage software.

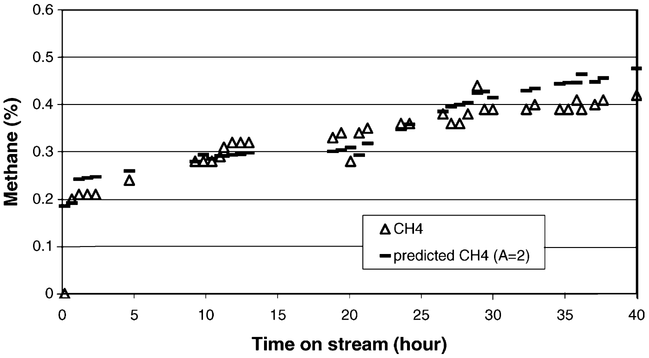

Fig. 9. Comparison of methane concentration obtained by experiments and by two-component PLSR prediction. The experiment data for methane are same as in Fig. 2.

($R^2Y = 80.8\%$, $Q^2 = 81.8\%$). Predicted gas compositions were compared with observations in Fig. 9. The PLSR model prediction of methane concentration in the reformate gas agrees well with the experimental data. Base on limited amount of experiments, the effects of fuel composition and of controlled variables on methane were quantified. The PLS method was shown to be a useful tool for studying process data in autothermal reforming under the test conditions.

4. Conclusion

Autothermal reforming of LPG over nickel-based catalysts was performed in a fixed-bed reactor. Controlled process variables such as temperature, steam-to-carbon ratio, equivalence ratio, catalyst type, and catalyst amount, as well as fuel characterization variables, LPG composition and sulfur in LPG, were studied. In most cases, LPG could be converted completely at temperatures over 800 °C at S/C = 1.5 and O/C = 1.0. It was found that hydrogen, carbon monoxide, and carbon dioxide in the reformate gas approached concentrations predicted by equilibrium. Conversion of methane and ethylene were kinetically controlled.

Changes of composition were reported for LPG vapors withdrawn from the head space of LPG bottles. In general, the vapor composition was quite stable, but contained more light components when the bottle was full and more heavy components as the bottle approached empty. In addition, vapor compositions differed between bottles depending on the residual liquid in the bottle at the time it was refilled and the number of times it was refilled. Ethyl mercaptan concentration in the vapor drawn from the bottle headspace increased by two orders of magnitude, from 1.5 ppm in when the bottle was full to ∼150 ppm as the bottle approached empty.

A multivariate data analysis method, PLS regression, was used to evaluate the experimental results. The PLS analysis accounted for about 70% of the variance in the dataset. By PLSR, the significance of each parameter and the correlations between each variable were clearly revealed. In general, the effects of some controlled variables, i.e. temperature, S/C, and O/C were found to be significant. Temperature affected fuel conversion to fix gases. Carbon deposition was more likely to occur at low temperature. Over the range of conditions tested, S/C was found to shift CO to CO_2 through the water–gas shift and was effective in reducing methane and ethylene concentrations in reformate. At high O/C, H_2 decreased due to oxidation reactions and dilution by nitrogen in air. The fuel compositions were of secondary importance. Sulfur poisoning was the main reason for catalyst deactivation under test conditions.

Using a limited amount of data, the prediction of methane concentration by the PLSR model agreed well with experimental observations.

The PLS method was advantageous in that it statistically analyzed the collinear and noisy data and provided quantitative relations between the response variables and the predictor variables for limited amount of experiments. The PLSR model took into account the LPG vapor composition and could predict kinetically controlled variables, e.g. methane concentration over the test range. Based on the present results, more experiments and analysis are planned to confirm the multivariate analysis results and to improve the accuracy of the PLS analysis.

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