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Optimization of direct conversion of methane to liquid fuels over Cu loaded W/ZSM-5 catalyst

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Abstract

The optimization of methane conversion to liquid fuels over copper loaded W/ZSM-5 catalyst was studied by utilizing experimental design from 'Statsoft Statistica' version 6.0 software. Response surface methodology was employed to determine the optimum methane conversion and C_5^+ selectivity. Numerical results indicated the optimum methane conversion of 29.4% with the corresponding C_5^+ selectivity of 57.2% were achieved at 12.3 vol% of O_2, 203.9 ml/min of total feed flow rate, and %W doped of 3.2 wt%. The optimum C_5^+ selectivity of 70.2% was attained at 7.6 vol% of O_2, 208.9 ml/min of total feed flow rate, and 3.2 wt% of W content with the corresponding methane conversion of 26.7%. By means of variance analysis and additional experiments, the adequacy of this model is confirmed.

Keywords: Optimization; Direct conversion; Methane; Liquid fuels

1. Introduction

Methane, the principal component of natural gas, can be converted to produce liquid fuels and chemicals of commercial importance. However, the commercialization of the direct conversion process remains a challenging goal as the engineering and chemistry involved are quite complex. In general, there are two routes for converting methane to liquid fuels: indirectly or/and directly. The indirect route is a two-step process whereby natural gas is first converted into synthesis gas (a mixture of H_2 and CO), and then into gasoline range. The direct route is a one step process in which the natural gas is reacted with oxygen (or another oxidizing species) to give the desired product directly.

Many researchers studied the applicability of HZSM-5 and modified ZSM-5 zeolite to the direct conversion of methane to liquid hydrocarbons [1–9], but the conversion and selectivity remained low making the process not lucrative economically. The direct partial oxidation of methane to liquid hydrocarbons was reported by Han et al. [1,2]. They found that liquid hydrocarbons could be produced from the reaction between CH_4 and O_2 over metal loaded ZSM-5. However, low conversion of methane was obtained due to a high formation of CO_x as side products. They concluded liquid hydrocarbons could be produced from the reaction between CH_4 and O_2 if CH_4 or C_2H_6 dehydrogenation and olefin oxidation functions of the metals in the metal–ZSM-5 catalysts are in balance. Different reactor configuration could also be used to achieve a better catalytic result as demonstrated by Pak et al. [9]. In their study, a high yield of liquid hydrocarbons (80%) was achieved using a two-reactor system with recycle, one for oxidative coupling of methane and the other for oligomerization reactor.

Previous studies on the conversion of methane to higher hydrocarbons generally accepted that CH_4 in the absence of O_2 reacted to form ethylene as an intermediate product on metal active sites by dehydrogenation, then followed by the formation of liquid hydrocarbons by oligomerization over acid sites of the catalyst. Recently, it has been shown that Mo supported on HZSM-5 are active and selective for conversion of methane to aromatics [10–17]. Wang et al. [16] studied the conversion of methane to aromatics over Mo/HZSM-5 based catalysts under non-oxidative condition and found that Mo species is transformed to Mo carbide species which is an active phase for methane transformation to higher hydrocarbons. Liu et al. [17] reported that methane

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is dissociated on Mo active sites (Mo_2C) to form CH_x, which oligomerized on ZSM-5 support having proper acidity to produce aromatic hydrocarbons. Cu loaded ZSM-5 catalyst prepared by acidic ion exchange method showed a promising performance in the conversion of methane to liquid hydrocarbons where the methane conversion and the composition of gasoline range (C_{5-10}) in liquid hydrocarbons were 15.6 and 80.2%, respectively [18]. However, the infrared study of the catalyst indicated that it was not resistant to high temperature. Li et al. [19] found that introduction of Cu by ion exchanged into Mo/HZSM-5 catalysts could improve the stability of the catalysts to some extent at reaction temperature of 750 °C.

Results from two recent studies [20,21] found the W/HZSM-5 catalyst to be suitable for methane reaction in a non-oxidative environment reaction at temperatures as high as 800 °C over which a much higher methane conversion (18–23%) and yields of aromatic hydrocarbon (48–56%), without the loss of W component, were obtained. The result from the TPR-H_2 analysis revealed the temperature needed for the reduction activation of the W/HZSM-5 catalyst was moderate (600–720 °C) and the catalyst was stable even at 800 °C.

In our previous study on the direct conversion of methane to liquid fuels [22], the FT-IR and TPR-H_2 analysis revealed the W loaded Cu/ZSM-5 catalyst was thermally stable at the reaction temperature. 3.0 wt% of W in 3.0 wt% of Cu/ZSM-5 catalyst demonstrated a longer lifetime than 3.0 wt% of W/ZSM-5; 12 and 8 h, respectively. The 3.0W/3.0Cu/ZSM-5 showed potential of catalysing the direct conversion of CH_4 to liquid fuels (C_5^+), over which the methane conversion and C_5^+ selectivity were reported to be 21 and 34%, respectively. With the encouraging performance plus its thermal stability, the combination of Cu and W species loaded onto the ZSM-5 catalyst has potential to be used in the methane oxidation reaction to produce liquid fuels.

Response surface methodology (RSM) is a method to determine the optimum condition of a process. RSM has similarity with regression analysis. In regression analysis, empirical mathematical model are derived from the experiment data. RSM is a set of technique designed to find the optimum value of the response and the influencing factors. RSM technique has been successfully applied in the field of quality experimental work [23–26].

A new combination of tungsten first and then copper loaded onto the ZSM-5 catalyst was developed and tested for the direct conversion of methane to liquid fuels. The catalyst developed was to elucidate the role of tungsten in enhancing the thermal stability of the ZSM-5 catalyst. Previous works found that some aspects such as percent of metal loading, percent volume of O_2 in feed and feed flow rate affected the catalytic performance of methane conversion to higher hydrocarbons. In this paper, the optimization of those variables for direct conversion of methane to gasoline over 3% Cu loaded W/HZSM-5 catalyst was studied to obtain maximum methane conversion and selectivity to C_5^+ products by utilizing experimental design.

2. Experimental

2.1. Preparation of catalysts

ZSM-5 zeolite with a SiO_2/Al_2O_3 mole ratio of 30 was supplied by Zeolyst International Co. Ltd, The Netherlands. The surface area of the zeolite is 400 m^2/g. The 3.0 wt% of Cu loaded with variable percentage of W doped into the W/HZSM-5 catalyst was prepared by first impregnating a certain amount of the HZSM-5 zeolite carrier with a calculated amount of tungsten hydrate in aqueous solutions. The tungsten hydrate solution was prepared by dissolving a certain amount of ammonium tungsten hydrate ($(NH_4)_6{\cdot}W_{12}{\cdot}O_{40}{\cdot}H_2O$) in deionized water. A small amount of H_2SO_4 was added to regulate the pH value of the solution to 2–3 followed by drying at 120 °C for 2 h and calcining at 400 °C for 4 h. The sample was subsequently impregnated with a calculated amount of H_2SO_4 acidified copper nitrate aqueous solution (pH 2–3). Finally, the sample was dried at 120 °C for 2 h and calcined at 500 °C in air for 5 h. The sample is designated as 3.0Cu/W/ZSM-5 zeolite catalyst.

2.2. Apparatus

The direct conversion of methane reaction over the catalyst was carried out in a continuous flow quartz reactor (ID = 9 mm). The catalysts were pretreated in situ in a flow of nitrogen at 550 °C for an hour. The feed was a mixture of pure methane and oxygen. The reaction was performed at 753 °C, atmospheric pressure and the amount of catalyst used was 500 mg. The reactor effluent gases were analyzed by an on-line Hewlett Packard Agilent 2000 gas chromatograph using Porapak-N columns.

2.3. Experimental design

The low, middle and high levels of all the independent variables were wt% of W doped into the 3.0Cu/W/ZSM-5, X_1; vol% of O_2, X_2; and flow rate of feed gases, X_3. Accordingly, 1.5, 3.0 and 4.5 wt% were chosen for variable X_1; 5, 10 and 15 vol% O_2 for X_2 and 100, 200 and 300 ml/min for X_3 (Table 1). Allowances for extreme

Table 1
Experimental range and levels of independent variables

X Variables	Variable level			Step change value, ΔX
	$-\alpha$	0	α	
X_1 (% tungsten)	1.5	3.0	4.5	1.5
X_2 (% oxygen)	5.0	10.0	15.0	5.0
X_3 (flow total)	100.0	200.0	300.0	100.0

measures are designated as $-\alpha$ and $+\alpha$ in the central composite design.

The optimization method based on RSM involved three major steps: design of experiment using statistical approach, coefficient estimation based on mathematical model and response prediction and finally model adequacy check. The equation model is tested with analysis of variance (ANOVA) with 99% degree of confidence. The RSM output such as contour and 3D graphic surface plots provide the optimum and most influential variable for methane conversion and C_5^+ selectivity. According to central composite design, the total number of experiment combinations is $2^k + 2k + n_o$, where k is the number of independent variables and n_o is the number of experiments repeated at the center point [27,28]. In this case, $n_o = 2$.

The variables X_i were coded as x_i according to Eq. (1). The basis to form a polynomial equation is given in Eq. (2)

$$x_i = (X_1 - X_o)/\Delta X; \qquad i = 1, 2, 3 \ldots k \tag{1}$$

$$Y_u = \beta_o + \sum_{i=1}^{k} \beta_i X_{ui} + \sum_{i=1}^{k} \beta_{ii} X_{ui}^2 + \sum \sum_{i<j}^{k} \beta_{ij} X_{ui} X_{uj} \tag{2}$$

with Y_u, predicted response u; β_o, offset term; β_i, linear term; β_{ii}, squared term; β_{ij}, interaction term; x_i, dimensionless value of an independent variable; X_i, real value of an independent variable; X_o, real value of an independent variable at center point; ΔX, step change and $u = 1, 2, \ldots, n$.

In this work, the number of independent variables are three and therefore, $k = 3$. Eq. (2) becomes:

$$Y_u = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \tag{3}$$

Table 2
2^{3-1} Fractional factorial central composite design three variable with the observed responses and predicted values for CH_4 conversion

Run	X_1	X_2	X_3	Y_o	Y_p	$(Y_o - Y_p)$
1	1.50	5.00	100.00	12.0	11.62506	0.37494
2	1.50	5.00	300.00	14.0	13.90390	0.09610
3	1.50	15.00	100.00	21.0	20.50652	0.49348
4	1.50	15.00	300.00	25.0	22.28535	2.71465
5	4.50	5.00	100.00	13.0	15.24927	−2.24927
6	4.50	5.00	300.00	15.0	15.02810	−0.02810
7	4.50	15.00	100.00	23.0	22.63072	0.36928
8	4.50	15.00	300.00	22.0	21.90955	0.09045
9	0.48	10.00	200.00	17.0	18.96329	−1.96329
10	5.52	10.00	200.00	23.0	21.69486	1.30514
11	3.00	1.59	200.00	11.0	9.70159	1.29841
12	3.00	18.41	200.00	21.0	22.95656	−1.95656
13	3.00	10.00	31.82	19.0	18.17416	0.82584
14	3.00	10.00	368.18	18.0	19.48399	−1.48399
15	3.00	10.00	200.00	28.0	28.44354	−0.44354
16	3.00	10.00	200.00	29.0	28.44354	0.55646

X_1, wt% of tungsten; X_2, % oxygen; X_3, flow total (ml/min), Y_o observed CH_4 conversion; Y_p, predicted CH_4 conversion.

The actual experimental design for optimization is shown in Table 2. From Eq. (3), it was found that a total of 16 runs were needed to optimize the methane conversion and C_5^+ selectivity. The result for the design of experiment was obtained by using the Design Expert Statsoft software, 'Statistica' version 6.0, 2001.

3. Results and discussion

3.1. Optimization of CH_4 conversion and C_5^+ selectivity by regression analysis

The result for methane conversion according to the experimental design is given in Table 2. The application of RSM yielded the following regression equation, which is an empirical relationship between methane conversion and the test variable in coded unit as given in Eq. (4)

$$Y = -28.5459 + 9.5251x_1 + 4.4146x_2 + 0.1549x_3 - 0.0500x_1x_2 - 0.0042x_1x_3 - 0.0003x_2x_3 - 1.2751x_1^2 - 0.1713x_2^2 - 0.0003x_3^2 \tag{4}$$

The fitting of the model can be checked by several criteria. The ANOVA tabulated in Table 3 pertains to the response of the methane conversion. The determination of coefficient $R^2 = 0.94$ indicates that only 6% of the total variation did not fit the model. The adequacy of the fitted model was tested by Eq. (4) using static Fisher (F). The value of F is compared to the table value $F_{(p-1,N-p,\alpha)}$, which is the upper 100 α percent point of the F distribution with $p-1$ and $N-p$ degrees of freedom, respectively. Since the value $F = 10.4632$ exceeded the table value $F_{(9,6,0.01)} = 7.9761$, the Fisher test also demonstrated the regressions model fitted fairly well with the observed values. Each of the observed values, Y_o is compared with the predicted value, Y_p calculated from the model, as depicted in Fig. 1.

The significance of each coefficient was determined using the Student t-test and p-value in Table 4. The corresponding variables will be more significant if the absolute t-value becomes larger and the p-value becomes smaller. It can be seen that the variable with the largest effect was the linear term of vol% of O_2, (X_2), followed by the quadratic of vol% of O_2, (X_2X_2), and the quadratic of total flow of feed gases, (X_3X_3). The factor t-test value

Table 3
ANOVA for the methane conversion

Source	Sum of squares	Degree of freedom	Mean square	F-value	$F = 0.01$	R^2
S.S. regression	430.508	9	47.834	10.4632	7.9761	0.9401
S.S. error	27.430	6	4.572			
S.S. total	457.938	15				

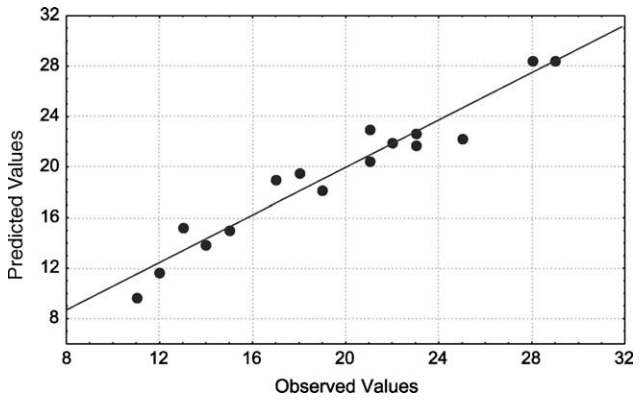

Fig. 1. Comparison between predicted and observed methane conversion.

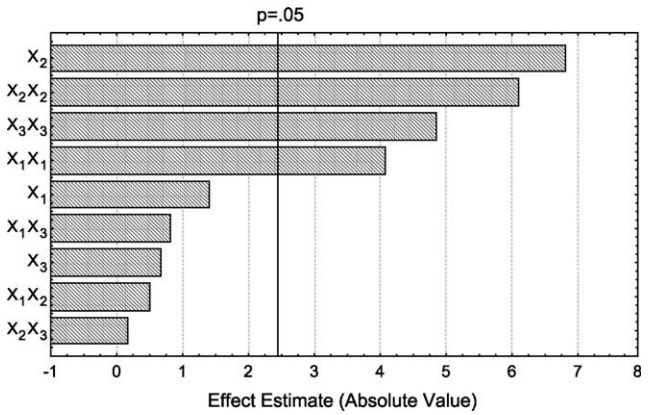

Fig. 2. Pareto chart of standardized effects of methane conversion.

(6.1692) and p-value ($p = 0.000833$) corresponds to X_2, while the t-test values for X_2X_2 and X_3X_3 are smaller at 6.0971 and 4.8389, respectively, but the p values are still significant at $p = 0.00089$ and 0.00288, respectively.

From Fig. 2 (Pareto chart), the most significant parameters are clearly the vol% of O_2 (X_2) and its quadratic effect (X_2X_2). The quadratic of total flow of feed gases and quadratic of wt% of W are significant but less important. The significance of wt% of W, (X_1) and total flow of feed gases, (X_3) as well as the interactions between wt% of W-total flow, (X_1X_3) and wt% of W–vol% of O_2, (X_1X_2) are negligible. The interaction between the vol% of O_2 and the total flow of feed gases, (X_2X_3) did not seem to have affected the methane conversion.

The results for gasoline range (C_5^+) selectivity according to the experimental design are given in Table 5. The application of RSM yielded the following regression equation, which is an empirical relationship between C_5^+ selectivity and the test variable in coded unit given in Eq. (5)

$$Y = -67.0195 + 32.0514x_1 + 8.1699x_2 + 0.5304x_3 + 0.0833x_1x_2 - 0.0008x_1x_3 - 0.0012x_2x_3 - 5.1206x_1^2 - 0.5386x_2^2 - 0.0012x_3^2 \quad (5)$$

Table 4
Significance of regression coefficient for methane conversion

Variables	Regression coefficient	Computed t-value	Significance level, p-value
Constant	−28.54597	−3.72491	0.009795
X_1 (%W)	9.5251	3.99322	0.007174
X_2 (%O_2)	4.4146	6.16916	0.000833
X_3 (Flow)	0.1549	4.32823	0.004938
X_1X_1	−1.2751	−4.08397	0.006473
X_2X_2	−0.1713	−6.09715	0.000886
X_3X_3	−0.0003	−4.83891	0.002884
X_1X_2	−0.0500	−0.49607	0.637492
X_1X_3	−0.0042	−0.82678	0.439996
X_2X_3	−0.0003	−0.16536	0.874095

The fitting of the model can be checked by several criteria. The ANOVA tabulated in Table 6 pertains to the response of the C_5^+ selectivity. The determination of coefficient $R^2 = 0.94$ indicates that only 6% of the total variation is not explained by the model. The fitted model was tested with Eq. (5) using static F for model adequacy check. The value of F is compared to the table value $F_{(p-1,N-p,\alpha)}$, which is the upper 100 α percent point of the F distribution with $p - 1$ and $N - p$ degrees of freedom, respectively. Since the value $F = 11.5647$ exceeded the table value $F_{(9,6,0.01)} = 7.9761$, the Fisher F test demonstrated that the experimental results fitted the model well. Each of the observed values Y_o is compared with predicted value Y_p calculated from the model, as shown in Fig. 3.

The significance of each coefficient was determined using the Student t-test and p-value in Table 7. It can be seen that the variable with the largest effect was the quadratic of vol% of O_2, (X_2X_2) with the absolute

Table 5
2^{3-1} Fractional factorial central composite design five variable with the observed responses and predicted values of C_5^+ selectivity

Run	X_1	X_2	X_3	Y_o	Y_p	$(Y_o - Y_p)$
1	1.50	5.00	100.00	36.0	37.43430	−1.43430
2	1.50	5.00	300.00	49.0	42.78187	6.21813
3	1.50	15.00	100.00	15.0	11.40692	3.59308
4	1.50	15.00	300.00	19.0	14.25449	4.74551
5	4.50	5.00	100.00	43.0	42.41859	0.58141
6	4.50	5.00	300.00	49.0	47.26616	1.73384
7	4.50	15.00	100.00	18.0	18.89121	−0.89121
8	4.50	15.00	300.00	28.0	21.23878	6.76122
9	0.48	10.00	200.00	24.0	29.23453	−5.23453
10	5.52	10.00	200.00	37.0	39.29887	−2.29887
11	3.00	1.59	200.00	49.0	50.65303	−1.65303
12	3.00	18.41	200.00	1.0	6.88037	−5.88037
13	3.00	10.00	31.82	30.0	28.53130	1.46870
14	3.00	10.00	368.18	26.0	35.00211	−9.00211
15	3.00	10.00	200.00	67.0	66.85374	0.14626
16	3.00	10.00	200.00	68.0	66.85374	1.14626

X_1, wt% of tungsten; X_2, % oxygen; X_3, flow total (ml/min); Y_o, observed C_5^+ selectivity; Y_p, predicted C_5^+ selectivity.

Table 6
ANOVA for the C_5^+ selectivity

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	$F = 0.01$	R^2
S.S. regression	4866.406	9	540.712	11.56472	7.9761	0.945496
S.S. error	280.532	6	46.755			
S.S. total	5146.938	15				

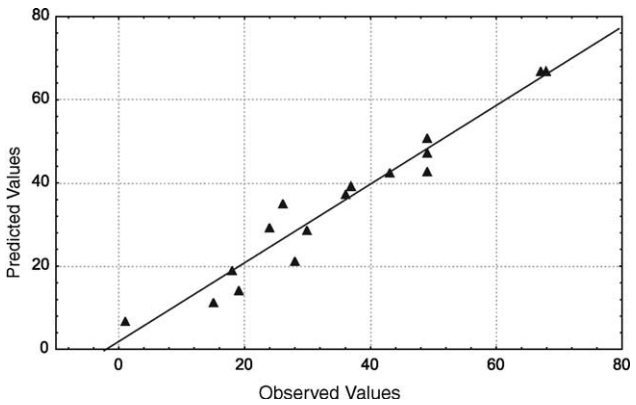

Fig. 3. Comparison between predicted and observed C_5^+ selectivity.

t-value = 5.9940 and a significant *p*-value of 0.0009. This is followed by the quadratic of total flow of feed gases, (X_3X_3) and the quadratic of wt% of W, (X_1X_1). The quadratic of total flow of feed gases and quadratic of wt% of W have smaller *t* values, 5.5219 and 5.1285, respectively, and the *p* values of 0.001484 and 0.0002160, respectively, seemed to be significant.

From Fig. 4 (Pareto chart), the most significant parameters are clearly the vol% of O_2, (X_2) and its quadratic effect, (X_2X_2). The quadratic of total flow of feed gases, (X_3X_3) and quadratic of wt% of W, (X_1X_1) are significant but less important. The significance of wt% of W (X_1) and total flow of feed gases (X_3) as well as the interactions

Table 7
Significance of regression coefficient

Variables	Regression coefficient	Computed *t*-value	Significance level, *p*-value
Constant	−67.0195	−2.73460	0.033978
X_1 (%W)	32.0514	4.20165	0.005675
X_2 (%O_2)	8.1699	3.57000	0.011784
X_3 (Flow)	0.5304	4.63575	0.003556
X_1X_1	−5.1206	−5.12846	0.002160
X_2X_2	−0.5386	−5.99403	0.000970
X_3X_3	−0.0012	−5.52190	0.001484
X_1X_2	0.0833	0.25853	0.804639
X_1X_3	−0.0008	−0.05171	0.960442
X_2X_3	−0.0012	−0.25853	0.804639

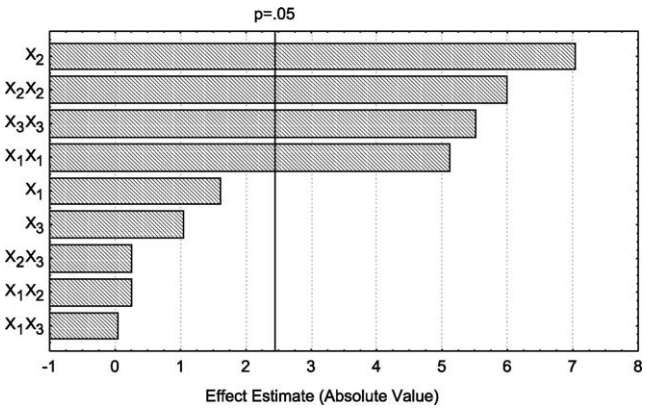

Fig. 4. Pareto chart of standardized effects of C_5^+ selectivity.

between vol% of O_2 and total flow of feed gases, (X_2X_3) and wt% of W–vol% of O_2, (X_1X_2) appeared low. The interactions wt% of W–total flow, (X_1X_3) can be safely ignored for this study.

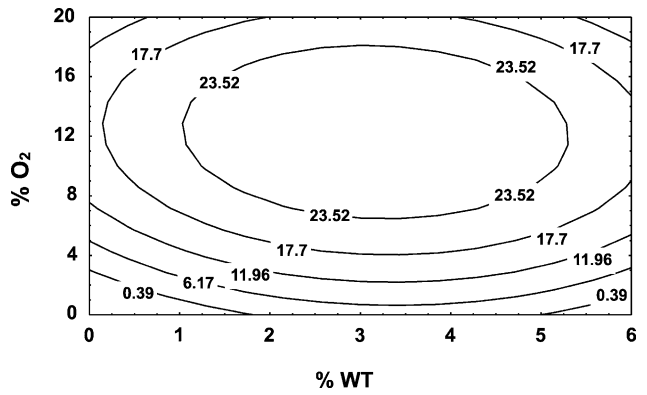

Fig. 5. Contour surface plot of CH_4 conversion as a function of vol% of O_2 and wt% of W.

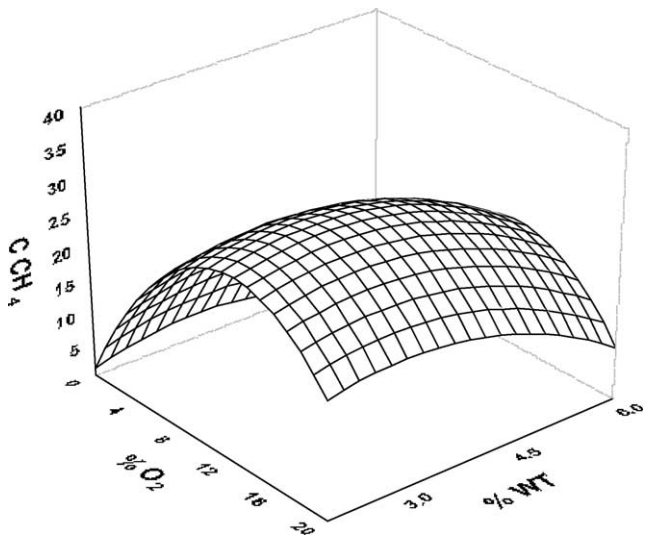

Fig. 6. 3D graphic surface optimization of CH_4 conversion versus wt% of W and vol% of O_2.

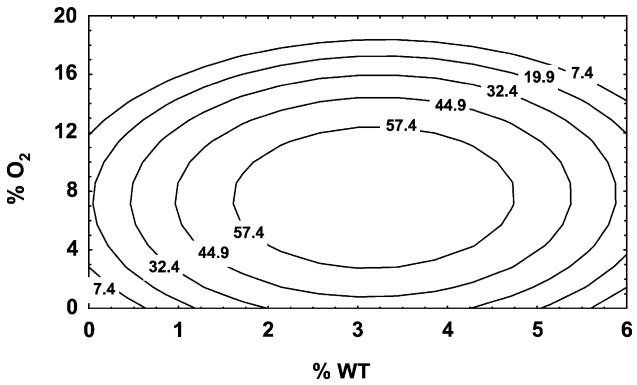

Fig. 7. Contour surface plot of C_5^+ selectivity as a function of vol% of O_2 and wt% of W.

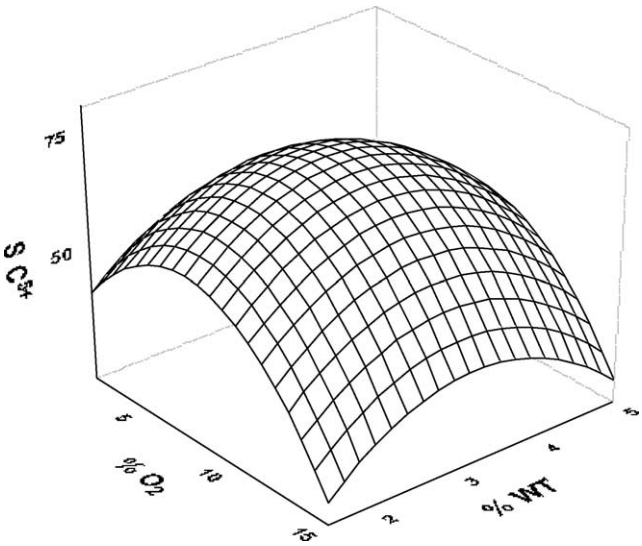

Fig. 8. 3D graphic surface optimization of C_5^+ selectivity versus wt% of W and vol% of O_2.

3.2. Optimisation of CH_4 conversion and C_5^+ selectivity by analysing the response surface contour plots

The CH_4 conversion and C_5^+ selectivity can also be predicted from the respective contour plots. Each contour curve represents an infinite number of two test variables

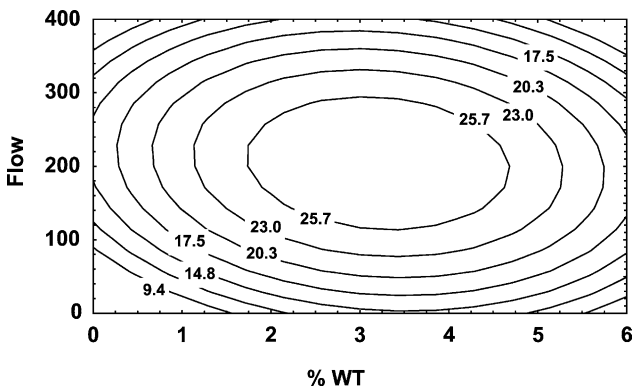

Fig. 9. Contour surface plot of CH_4 conversion as a function of total flow of feed gases and wt% of W.

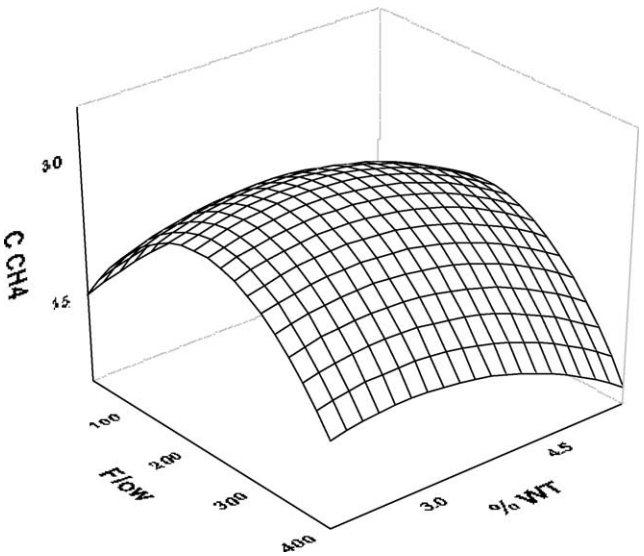

Fig. 10. 3D graphic surface optimization of CH_4 conversion versus wt% of W and total flow of feed gases.

and others are maintained at their respective zero level. The maximum predicted conversion is indicated by the surface confined in the smallest ellipse in the contour diagram [29,30].

It is evident from the plot that CH_4 conversion reached its maximum at a combination of coded level 8–16 vol% of O_2 and 2.5–4.0 wt% of W doped. The model predicted a maximum CH_4 conversion of 25.6% within this range (Figs. 5 and 6). Similar operating parameters between 4 and 12 vol% of O_2 and 2.5–4.0 wt% of W will produce C_5^+ selectivity above 57.4% (Figs. 7 and 8).

Figs. 9 and 10 depict the relationship between total flow of feed gases and wt% of W doped. Methane conversion above 25.7% could be obtained when W doped is 2.5–4.0 wt% of W and total flow is 150–250 ml/min. The same factors will lead to C_5^+ selectivity above 57.2% at 2.5–4.0 wt% of W and 150–250 ml/min (Figs. 11 and 12).

The results from RSM using Statistica software are tabulated in Table 8. The optimum point for methane conversion is 29.4% when wt% of W doped = 3.2%, vol% of O_2 = 12.3%, and total flow of feed gases = 203.9 ml/min.

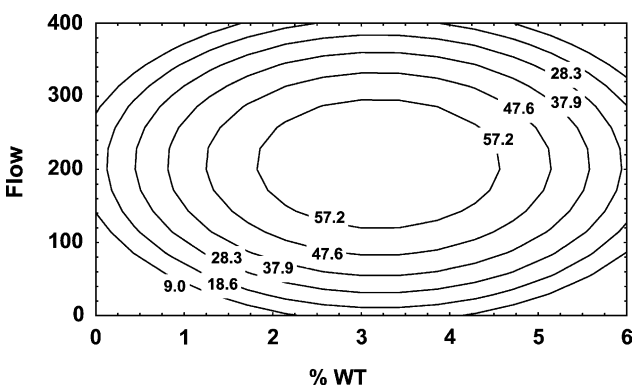

Fig. 11. Contour surface plot of C_5^+ selectivity as a function of total flow of feed gases and wt% of W.

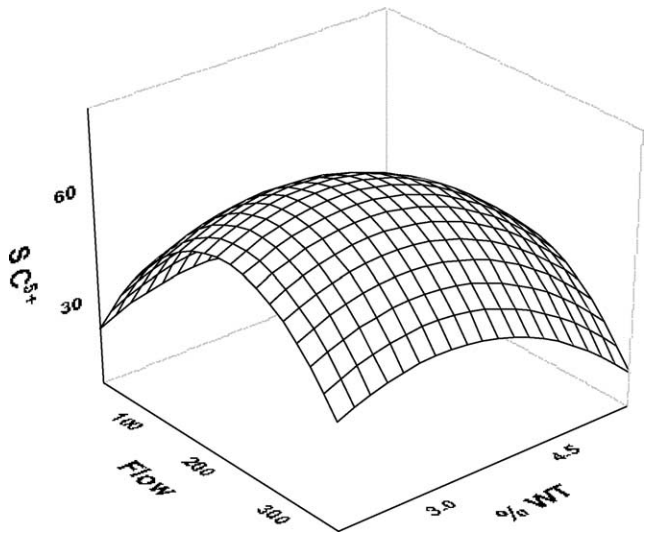

Fig. 12. 3D graphic surface optimization of C_5^+ selectivity versus wt% of W and total flow of feed gases.

Table 8
Optimization results using response surface method

	Optimal CH_4 conversion	Optimal C_5^+ selectivity
wt% of W doped	3.2	3.2
vol% of O_2	12.3	7.6
Total flow of feed gases (ml/min)	203.9	208.9

The highest C_5^+ selectivity is 70.2% when wt% of W doped = 3.2%, vol% of O_2 = 7.6%, and total flow of feed gases = 208.9 ml/min.

The results in Table 9 pertain to the catalytic reaction test at the optimized reaction condition to compare with the modeling result. The experimental values are 27 and 69% for CH_4 conversion and C_5^+ selectivity, respectively. The results in Table 9 also indicated to achieve a high C_5^+ selectivity the percentage of O_2 in the feed gas is very critical; otherwise the oligomerization activity will be suppressed. Meanwhile the % error between the predicted and experimental results for CH_4 conversion and C_5^+ selectivity are 8 and 2%, respectively. The discrepancies between the predicted and experimental results are probably due to the characteristic of the catalysts, which have not been taken into account by the statistical model. Nevertheless, the differences are within the acceptable limit. From these results, it is verified that the statistical model is useful for the accurate prediction of C_5^+ selectivity and CH_4 conversion.

Table 9
Comparison between predicted and observed optimized values

	% of W doped	% vol of O_2	Total flow of feed gases	Predic -ted (%)	Observed (%)	% Error
CH_4 conversion	3.2	12.3	203.9	29.4	27.0	8.0
C_5^+ selectivity	3.2	7.6	208.9	70.2	69.0	2.0

Table 10
The RON and composition of liquid fuels over 3.0Cu loaded 3.2W/ZSM-5 catalyst

Composition of liquid fuels	%
Gasoline range (C_{5-10})	82.8
C_{11}^+ range	18.2
Composition of gasoline range	%
n-Paraffins	9.0
Iso-paraffins	22.0
Olefins	52.0
Aromatics	17.0
RON	86.1

The composition of liquid fuels and research octane number (RON) over 3.0Cu–3.2W/ZSM-5 catalyst is shown in Table 10. The RON was estimated [31] to be 86.1. The gasoline composition has a low *n*-paraffin and high aromatics content, at 9 and 17%, respectively, while the majority is olefins at 52% as indicated in Table 10.

4. Conclusions

The direct conversion of methane was optimized over Cu–W/ZSM-5 catalyst using 'Statsoft Statistica' version 6.0 software. The three independent variables involved in the optimisation are wt% of W doped, vol% of O_2, and total flow of feed gases. The Student *t*-test, *p*-value and Pareto chart indicated that the variable with the largest effect was vol% of O_2 (X_2) and its quadratic effect (X_2X_2). This is followed by flow total of feed gases (X_3), wt% of W doped (X_1) and its quadratic effects (X_3X_3 and X_1X_1). The interactions between any two of the independent variables can be neglected. From the RSM results the optimal methane conversion and C_5^+ selectivity of 29.4 and 70.2%, respectively, were obtained. The adequacy of this model is confirmed by means of variance analysis and additional experiment.

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