Numerical Approach for Catalytic Conversion of CO_2 to Methane over Nickel Base Catalysts

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The study evaluates the performances of the Ni/Al_2O_3-SiO_2 base catalysts prepared by impregnation technique by catalytic hydrogenation of CO_2 to methane on temperature range of 350-550°C under atmospheric pressure. We take into account the important parameters namely reaction temperature, H_2/CO_2 molar ratio. Targeting a very high conversion rate of CO_2 and almost total methane selectivity at up to 400°C catalysts like Ni/Al_2O_3-SiO_2 were proposed. The performances of these catalysts were analysed by table Curve software. The mathematical model corresponding to the characteristic equation provides a good arrangement of the experimental points on the responding surface, simplicity of the characteristic equation and a good determination coefficient that is near unity.

Key words: Ni catalysts, catalytic process, impregnation technique, hydrogenation

The catalytic hydrogenation of CO_2 to methane is of great interest in the scientific world due to the opportunity regarding residual CO_2 utilization as a possible source of energy. In literature there are many papers about catalytical CO_2 hydrogenation to methane [1-9]. Thus, nickel and ruthenium based catalysts catalyse exclusively hydrogenation of CO_2 to methane, while the Pd, Pt, Rh, Mo, Re, Cu, Ag and Au catalyse other reactions too [10]. Also, there are other catalysts with different metals support that are important for the hydrogenation of CO_2 to methane. The support plays an important role on the active site dispersion, activity and stability [11]. Typical supports include silica [12], aluminium oxide [13], lanthanum oxide [14], and composite supports [4], MCM-41 [11], etc. However the nickel based catalysts are the most common studied because of their high activity and low price. In our previous work, Ni-based catalysts supported on alumina-silica was successfully synthesized and tested in a typical hydrogenation reaction [15].

The studies of literature on numerical approach show that mathematical statistics used improve performance, efficiency and quality manufacturing processes [16] as well as the performance of various catalysts [17,18]. One of the methods based on mathematical statistics is Table Curve software which arranges the experimental data in three-dimensional space. This software is able to make a quick graphical and numerical analysis providing the dependency relations between physical quantities that characterize the experimental data obtained, thus providing a mathematical model for the study. The complexity of the software needed to establish use ideal approximation equations and uses around 36,000 approximation procedures which have different equations. There are only few papers which report the numerical analysis in the hydrogenation process of carbon dioxide and from author's knowledge are no studies over nickel base catalysts [19].

Starting from the above considerations the present study is aimed to develop a mathematical model using Table Curve software in order to highlight the performances of the Ni based catalysts prepared by impregnation as in the previous paper [15] and applied in the process of the CO_2 conversion for methane production [20].

Experimental part

The catalytic conversion procedure and the characteristics of the Ni based catalysts prepared by impregnation were presented in the previous paper [15].

All reactions were carried out in a laboratory-scale, using a continuous-flow stainless steel micro reactor (PID Eng&Tech-Microactivity-Reference) system using a tubular reactor specially placed in a cylindrical conventional tubular furnace equipped with an electrical heater operated at atmospheric pressure and fully monitored by computer. The methanation reactions were performed under atmospheric pressure in the temperature range of 300-500°C. The catalysts were activated prior the reaction by heating at 450°C reaction temperature in 5% H_2/Ar, under 30 mL/min H_2, for a period of 4 h and then the reactor was heated to the working temperature. CO_2 and H_2 were continuously fed into reactor together with argon. Mass flow controllers (ALICAT Scientific model) were used to control the flow rates of the feed gases in known proportions prior to reaction. The compositions of the feed gases were varied by changing the molar ratio of CO_2:H_2 between 1:4 and 1:8, while the total flow rate was maintained at a constant 50 mL min^{-1}. The composition of the gaseous phase was measured and continuously monitored by a Hiden HAL VII quadrupole mass spectrometer. Quantitative calibration of H_2, CH_4 and CO_2 compositions was made based on registered partial pressures signals and using standard calibration gas mixtures. Conversions of carbon dioxide and selectivity to methane are defined with the eqs. (1) and (2):

$$CO_2 \text{conversion}\ (\%) = \frac{(Q_{CO_2\_inlet} - Q_{CO_2\_outlet}) \times 100}{Q_{CO_2\_inlet}} \quad (1)$$

$$CH_4 \text{selectivity}\ (\%) = \frac{(Q_{CH_4\_outlet}) \times 100}{(Q_{CO_2\_inlet} - Q_{CO_2\_outlet})} \quad (2)$$

where:

QCO_2_inlet and QCO_2_outlet are the molar flow rates of CO_2 (mol s^{-1}) at the inlet and the outlet, respectively.

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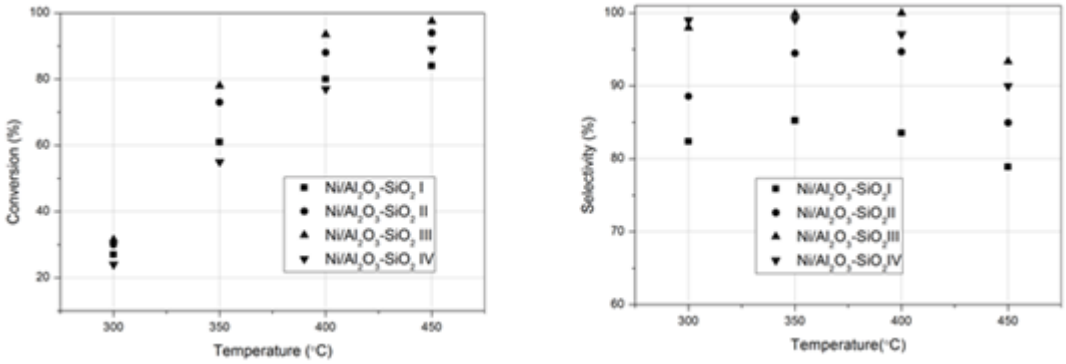

Fig. 1. The catalytic performances of the Ni/Al_2O_3-SiO_2 catalysts in hydrogenation reaction. a). Conversion of the CO_2; b). Selectivity to methane. The reaction conditions: GHSV = 12000 h^{-1}, CO_2:H_2 molar ratio = 1:6.

Catalyst type	Ni/Al_2O_3 - SiO_2 I	Ni/Al_2O_3 - SiO_2 II	Ni/Al_2O_3- SiO_2 III	Ni/Al_2O_3 - SiO_2 IV
Ni (%wt.)	12.21	15.14	18.06	21.13
Ssp. (m^2/g) [a]	136	124	98	92
Vpores (%) [b]	49.32	48.96	47.81	47.29
Crystalline size (Å) [c]	78	83	86	98

Table 1
CHARACTERISTICS OF THE CATALYSTS OBTAINED BY IMPREGNATION

[a]determined by the BET equation; [b]BJH desorption pore volume ; [c]calculated from NiO (200) plane using Scherrer equation from XRD

Results and discussions

The catalytic performance of Ni/Al_2O_3-SiO_2 materials was evaluated in the gaseous phase hydrogenation of CO_2. In figure 1 (a, b) are presented the performances of these catalysts in CO_2 conversion and CH_4 selectivity [20].

In table 1 is presented the characteristics of the catalysts obtained by impregnation [20].

As *key* results of this work, an almost total conversion and high CH_4 selectivity (close to 100%) were achieved at 400°C on the Ni/Al_2O_3-SiO_2 III catalyst, containing 18% wt. Ni. Additionally, the high activity of Ni/alumina-silica was correlated. This led to the high Ni dispersion on the surface of support. According to the literature, high catalytic performances in the hydrogenation reaction can be achieved balancing the interaction effect between metal-support. This means that different catalytic characteristics produce variable performances in regard to the selectivity and conversion. By virtue of present study, one of the potential candidates for a new support for Ni base catalysts is proposed alumina-silica, due to combination effect of their distinctive proprieties such as ordered porous structure, nanosize, adequate surface area, large pore volume and well defined pore size, imperative in sustaining of the intrinsic support proprieties. Further, the catalyst with the best performances in the methanation process, namely Ni/Al_2O_3-SiO_2 III was investigated in different reaction conditions to provide a comprehensive observation in the present study.

The temperature has a significant effect on the CO_2 conversion (fig. 2).

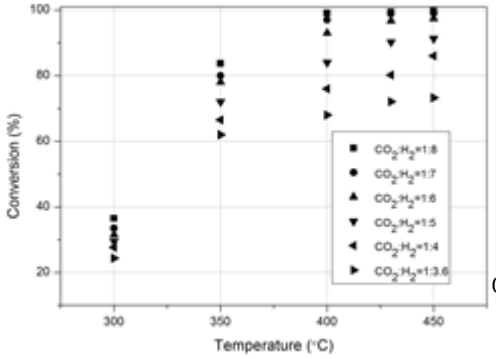

Fig. 2. Conversions of CO_2 as a function of temperature and various CO_2/H_2 molar ratios, GHSV = 12.000 h^{-1}

The conversion was very low (8%, too slow to be practical) at temperatures below 300°C. When we used higher reaction temperatures, the conversion increased continuously, indicating an obvious behaviour, but CO formation drops over 450ÚC and by-products appear. Higher reaction temperatures over 450°C decrease the formation of CH_4 in hydrogenation, known as exothermic reaction. The optimal condition for this type of reaction seems to be between 400 and 430°C, because in this range, methane is the unique hydrocarbon molecule formed, consequently the selectivity is almost 100%. These results in terms of selectivity and conversion are the highest values yet reported on Ni base catalysts tested in similar reaction conditions.

In literature there are studies focused on the methanation of CO_2 under proper stoichiometric conditions (H_2:CO_2 = 4:1). Only few studies dealt with reaction with a high excess of hydrogen and no one was varying reactants ratios over prepared Ni/Al_2O_3-SiO_2. The effect of CO_2/H_2 molar ratios at different temperatures is examined in range 1:3.6 to 1:8.0. The CO_2 conversions are growing continuously with the rise of H_2/CO_2 molar ratio, the rise being faster between 350-400°C. The likely reason is that the higher H_2/CO_2 molar ratio shift equilibrium from CO (detected in ppm range) to CO_2. CO is more reactive and leads to product loss by transforming into CH_4. It is emphasized that the CO_2 conversion increase with increasing H_2/CO_2 ratio, without distinction of what the reaction temperature is. This substantiates mechanisms were evaluated in recent publications [21]. Mathematical modelling performed with Table Curve 3D program was employed in order to describe the methanation of CO_2, by following steps:

- introduction of experimental data;
- graphical representation of the furnished data;
- choosing of the best mathematical model on the basis of the responding surface by taking into account the best arrangement of the experimental data on the plot, the simplicity of the characteristic mathematical equation and the determination coefficient (r^2) as close as possible to unit.

The determined coefficient represents the ratio between the spreading degree of the experimental points around

Table 2

THE EQUATIONS CORRESPONDING TO THE MATHEMATICAL MODELS MAKING EVIDENT THE METHANATION PROCESS PERFORMANCES.

No.	The equation of the mathematical model	The correlation coefficient
1	z= Chebyshev LnX,Y Bivariate Polynomial Order 4	0.9965440486
2	z= Chebyshev LnX,Y Bivariate Polynomial Order 4	0.994424592

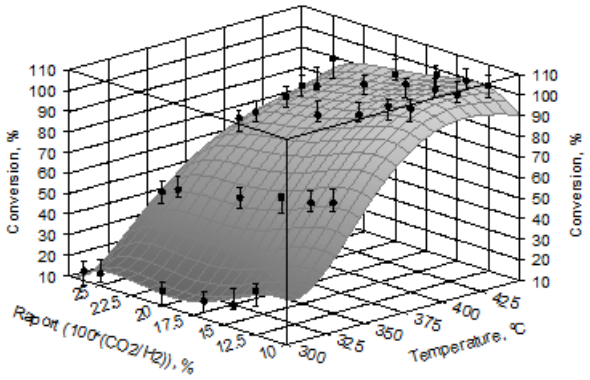

Fig. 3. 3D view-response plot showing the effect of molar ratio and temperature on CO_2 conversion

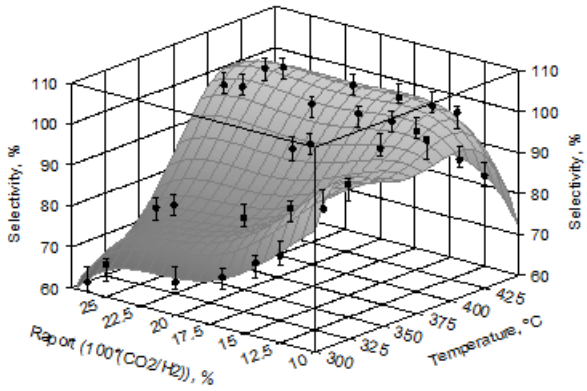

Fig. 4. 3D view-response plot showing the effect of molar ratio and reaction temperature on methane selectivity

the plot of the regression equation and the spreading degree of the same points relative to the arithmetic mean of the own ordinates. Apart from this, a regression function is considered to approximate the best the set of the experimental points when the regression coefficient is as close as possible to the unity.

By taking the above mentioned criteria into account, the number of equations in table 2 decreases very much and the equation corresponding to the best mathematical model is finally obtained. The following symbols were used in the mathematical model:

- in case of the total conversion of CO_2: x-molar ratio (R); y- temperature (T) [°C]; z- total conversion of CO_2 (C) [%].

- in case of selectivity for methane: x-molar ratio (R); y- temperature (T) [°C]; z- selectivity for methane (S) [%].

By processing the obtained experimental data the table Curve software gives a set of equations for the total conversion and for selectivity as a relationship between the experimental results and the values calculated by the equations. After a careful selection and taking the determination coefficient values, simplicity of the equations and the good arrangement of the experimental points of the response surface were taked into account for the equations in order to obtain all performance criterions. The mathematical model was developed on the basis of these equations given in table 2.

In all of above, the x variable refers to the mass ratio and y variable represents the reaction temperature in which the prepared catalysts were tested. The significance of each coefficient was determined by t-test and p-values. The larger the magnitude of the t-value and the smaller the p-value, the more significant is the corresponding coefficient. This implied that the factor most significant.

This implied that the factor most significant. Coefficients of the model given by the software and ANOVA for response surface fit to the experimental results are presented at the end of this paper in Appendix section.

The results of the response surface fitting in the form of analysis of variables are shown and converge with a very high significance for the regression model. The value for the determination coefficient (r^2) verifies the suitable fit of the model, thus indicating a discrepancy of 0.02% for total variation, which is normally accepted range of the experimental error. The value of the adjusted determination coefficient (adjusted r^2) is also very high indicates a high significance for the model. Figure 3, 4 illustrated 3-D view of the predicted values obtained by the software.

The relationships between actual values and predicted and calculated values of conversion and selectivity are presented. The large r^2 values were evidences for the good relationship which proved that there was no remarkable variation between the experimental and estimated values for performances criterion. All the estimated values were close to each other and showed small variations with the experimental values. The best fit model was proposed by the largest R-square value.

Mathematical models show common characteristics due to the very good placing of the experimental points on the response surfaces and to the determination coefficient close to unity but differing in the shape of the response surface and the equation of the model.

Conclusions

The remarkable values for selectivity (more than 99.8%) were obtained at an unprecedented almost total conversion under moderate hydrogenation conditions from the perspective of methane synthesis, offering without doubt competitive costs for CH_4 obtaining as fuel. The experimental results justify the opportunity and possibility of using Ni/Al_2O_3-SiO_2 catalyst for CH_4 synthesis, due to a high easily obtained conversion in a process appearing as a useful procedure for CO_2 turning to account. For this reason, the tested catalysts could have potential applications in CO_2 conversion. The performances of the nickel based catalysts have been highlighted by a numerical computation developed using the Table Curve software. The characteristic equation of the developed mathematical model describes the dependence of the mass ratio on every performance criterion and on the process temperature. The analysis between the experimental results and the values calculated by the equations, resulted in various performance adjustments such as molar ratio in terms of process temperature, and had large r-square value meaning that there was no remarkable variation in the actual and calculated values.

Models given by the software and the equations derived in this study gave close estimated values to the experimental results. The best fit model was proposed by the software which possessed the largest r-square value.

APPENDIX section

Rank 1 Eqn 423 Chebyshev LnX,Y Bivariate Polynomial Order 4

r2 Coef Det	DF Adj r2	Fit Std Err	F-value
0.9965440486	0.9928412435	2.4234026081	308.95276975

Parm	Value	Std Error	t-value	90.00%	Confidence Limits	P>|t|
a	59.60255599	0.75774725	78.65756822	58.2741869	60.93092507	0.00000
b	40.70209154	1.083362231	37.57015924	38.802903	42.60128009	0.00000
c	-9.83901045	0.686448636	-14.3332071	-11.0423895	-8.63563143	0.00000
d	-6.1948031	0.708292711	-8.74610596	-7.43647589	-4.95313031	0.00000
e	-3.52647819	0.932969414	-3.7798433	-5.16202055	-1.89093582	0.00182
f	0.136373942	0.632275237	0.215687622	-0.97203639	1.244784272	0.83214
g	-4.44782679	0.895028616	-4.96947998	-6.01685703	-2.87879656	0.00017
h	1.951442072	0.749066152	2.605166533	0.638291387	3.264592757	0.01989
i	-2.93784473	0.824142169	-3.56473051	-4.38260745	-1.49308201	0.00282
j	-1.66897428	0.68152905	-2.44886741	-2.86372903	-0.47421954	0.02710
k	2.386151684	1.152746396	2.069971064	0.365329204	4.406974164	0.05613
l	1.619250509	0.776466687	2.085408861	0.258065307	2.980435711	0.05453
m	-0.08989977	0.739002227	-0.1216502	-1.38540789	1.205608349	0.90479
n	0.258248933	0.884012996	0.292132507	-1.29147037	1.807968231	0.77419
o	-1.13609756	0.544019469	-2.08833989	-2.08979108	-0.18240404	0.05423

Procedure GaussElim

r2 Coef Det	DF Adj r2	Fit Std Err
0.9965440486	0.9928412435	2.4234026081

ANOVA for response surface fit to the experimetal results for CO_2 conversion

Source	Sum of Squares	DF	Mean Square	F Statistic	P>F
Regr	25402.196	14	1814.4426	308.953	0.00000
Error	88.093203	15	5.8728802		
Total	25490.29	29			

Rank 1 Eqn 423 Chebyshev LnX,Y Bivariate Polynomial Order 4

XYZ *	X Value	Y Value	Z Value	Z Predict	Residual	Residual%	Weights
1	450	26.31	73.3	76.81518	-3.51518	-4.795607	1
2	450	25	89.1	84.546866	4.5531336	5.1101387	1
3	450	20	91.3	93.344551	-2.044551	-2.239377	1
4	450	16.66	97.4	96.664791	0.7352089	0.7548346	1
5	450	14.28	99.1	99.302389	-0.202389	-0.204227	1
6	450	12.5	99.7	99.226223	0.4737774	0.475203	1
7	430	26.31	72.1	72.08551	0.0144903	0.0200975	1
8	430	25	80.2	79.984246	0.215754	0.2690199	1
9	430	20	90.2	90.095468	0.1045321	0.1158893	1
10	430	16.66	96.7	95.07908	1.6209197	1.6762355	1
11	430	14.28	98.9	99.388739	-0.488739	-0.494175	1
12	430	12.5	99.4	100.86696	-1.466957	-1.475812	1
13	400	26.31	68	66.707305	1.2926947	1.9010216	1
14	400	25	73.7	74.184973	-0.484973	-0.658036	1
15	400	20	81.6	83.715021	-2.115021	-2.591938	1
16	400	16.66	88	89.51711	-1.51711	-1.723988	1
17	400	14.28	97	95.163081	1.8369191	1.893731	1
18	400	12.5	99.1	98.11251	0.9874898	0.9964579	1
19	350	26.31	42.7	42.139088	0.5609119	1.3136109	1
20	350	25	46.1	47.641748	-1.541748	-3.344355	1
21	350	20	52	51.368772	0.6312279	1.2138998	1
22	350	16.66	58	55.381959	2.6180408	4.5138634	1
23	350	14.28	60	61.07502	-1.07502	-1.7917	1
24	350	12.5	63.7	64.893412	-1.193412	-1.873489	1
25	300	26.31	14.4	13.480297	0.9197028	6.3868247	1
26	300	25	15.7	17.125316	-1.425316	-9.078448	1
27	300	20	16.8	15.508474	1.2915255	7.6876518	1
28	300	16.66	18.3	18.135142	0.164858	0.9008636	1
29	300	14.28	21.1	24.255345	-3.155345	-14.95424	1
30	300	12.5	31.5	29.295425	2.2045749	6.9986505	1

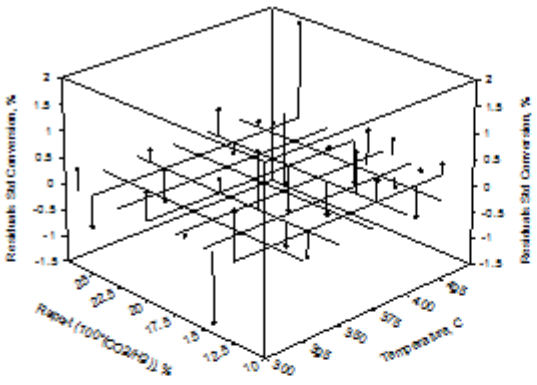

Fig. A1. ANOVA for response surface fit to the experimetal results for CO2 conversion

Rank 1 Eqn 423 Chebyshev LnX,Y Bivariate Polynomial Order 4

r2 Coef Det	DF Adj r2	Fit Std Err	F-value
0.994424592	0.9884509405	1.2492073653	191.09900387

Parm	Value	Std Error	t-value	90.00%	Confidence Limits	P>|t|
a	85.79627355	0.390600985	219.6519642	85.11153035	86.48101674	0.00000
b	10.68721947	0.558447892	19.13736199	9.708232189	11.66620674	0.00000
c	-5.23089738	0.353848217	-14.7828847	-5.85121113	-4.61058364	0.00000
d	-4.57550888	0.365108327	-12.5319215	-5.21556216	-3.9354556	0.00000
e	4.648724734	0.480923912	9.666237455	3.805640899	5.49180857	0.00000
f	0.746094125	0.325923097	2.289172297	0.174734523	1.317453726	0.03699
g	-5.45230717	0.461366318	-11.81774	-6.26110556	-4.64350879	0.00000
h	-0.3975542	0.386126082	-1.02959685	-1.07445266	0.279344268	0.31952
i	-1.8866823	0.424826013	-4.44107057	-2.6314237	-1.14194091	0.00048
j	-0.58029309	0.351312286	-1.65178706	-1.19616121	0.035575041	0.11935
k	-4.5934272	0.594213807	-7.73025997	-5.63511393	-3.55174048	0.00000
l	-2.52318548	0.400250417	-6.30401711	-3.22484461	-1.82152634	0.00001
m	-0.92893284	0.380938364	-2.43853843	-1.59673698	-0.26112871	0.02766
n	1.042236518	0.455688024	2.287171184	0.243392465	1.841080571	0.03713
o	-0.4866452	0.280429312	-1.73535782	-0.97825191	0.004961506	0.10317

Procedure GaussElim

r2 Coef Det	DF Adj r2	Fit Std Err
0.994424592	0.9884509405	1.2492073653

ANOVA for response surface fit to the experimetal results for methane selectivity

Source	Sum of Squares	DF	Mean Square	F Statistic	P>F
Regr	4174.9909	14	298.21363	191.099	0.00000
Error	23.407786	15	1.560519		
Total	4198.3987	29			

Rank 1 Eqn 423 Chebyshev LnX,Y Bivariate Polynomial Order 4

XYZ*	X Value	Y Value	Z Value	Z Predict	Residual	Residual%	Weight
1	450	26.31	76.3	76.265115	0.0348854	0.0457213	1
2	450	25	78.5	78.627222	-0.127222	-0.162066	1
3	450	20	82.1	83.023007	-0.923007	-1.124248	1
4	450	16.66	87	85.136407	1.8635925	2.1420604	1
5	450	14.28	84.4	85.001196	-0.601196	-0.712318	1
6	450	12.5	82.1	82.347052	-0.247052	-0.300916	1
7	430	26.31	98.5	98.165346	0.3346543	0.3397506	1
8	430	25	99.9	99.472042	0.4279581	0.4283865	1
9	430	20	100	100.20537	-0.205374	-0.205374	1
10	430	16.66	100	100.95857	-0.958566	-0.958566	1
11	430	14.28	100	100.79942	-0.799418	-0.799418	1
12	430	12.5	100	98.799256	1.2007445	1.2007445	1
13	400	26.31	98.1	98.550714	-0.450714	-0.459444	1
14	400	25	98.8	99.345201	-0.545201	-0.551823	1
15	400	20	99.2	98.195915	1.0040848	1.0121823	1
16	400	16.66	99.8	98.969688	0.8303115	0.8319755	1
17	400	14.28	100	100.10911	-0.109111	-0.109111	1
18	400	12.5	99.3	100.02937	-0.72937	-0.734511	1
19	350	26.31	74.4	74.097002	0.3029985	0.407256	1
20	350	25	76.2	76.123251	0.076749	0.1007205	1

21	350	20	77.6	78.164585	-0.564585	-0.727558	1
22	350	16.66	82.8	81.977832	0.8221681	0.9929566	1
23	350	14.28	84.9	86.944136	-2.044136	-2.407698	1
24	350	12.5	92.5	91.093194	1.4068056	1.5208709	1
25	300	26.31	62.4	63.233103	-0.833103	-1.335101	1
26	300	25	67.8	66.525623	1.2743775	1.8796128	1
27	300	20	67.9	69.00306	-1.10306	-1.624536	1
28	300	16.66	72.3	71.813703	0.4862975	0.6726106	1
29	300	14.28	77.8	76.838368	0.9616318	1.2360306	1
30	300	12.5	81.2	81.986144	-0.786144	-0.968158	1

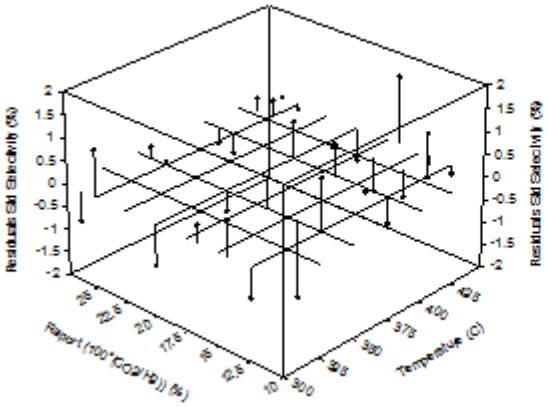

Fig. A2. ANOVA for response surface fit to the experimetal results for methane selectivity

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