An Experimental Design Study for CH_4, C_2H_6 and C_2H_4 Adsorption and C_2s/CH_4 Selectivity on 10X Zeolite

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Abstract

CH_4, C_2H_6 and C_2H_4 are the most important outlet gaseous of oxidative couple methane (OCM) reaction and this process is a new technology for conversion of natural gas to ethane and ethylene products. In this study, adsorption of OCM outlet hydrocarbons over 10X zeolite has been examined at equilibrium conditions. Temperature and pressure are the most effective operational parameters in the batch adsorption process. The central composite design was used for evaluating the effect of the operational conditions and optimization of adsorption process. The effect of temperature, pressure, their binary interaction and quadratic effects on adsorption capacity and selectivity of C_2s/CH_4 over 10X zeolite was determined to realize the optimal condition for enhancement of ethane and ethylene separation from methane. Optimization of the effective parameters was carried out by the statistical approach and the maximum predicted value of C_2s' selectivity over CH_4 was calculated 15.6, using the quadratic model at temperature of 308.15 K and atmospheric pressure. Finally, dynamic adsorption was carried out for the mixed gases at optimal conditions. Significant difference was observed between the breakthrough times of methane, ethane, and ethylene. It is concluded that 10X zeolite would be an efficient adsorbent for the separation of methane from the ethane and ethylene.

Keywords: Adsorption capacity, selectivity, 10X zeolite, experimental design, OCM reaction

Introduction

Ethane and ethylene are the main feed for petrochemical industry and the basic components for polymers production. One of the new technologies for production of ethylene is OCM process, but in the best operational conditions, the yield of C_2s products is only around 25%. Therefore, a process of gas separation is affordable, at downstream, to separate the products (ethane and ethylene) from methane and return unreacted methane to the reactor [1-4].

In this research, adsorption process has been suggested as a productive and economic method for separation methane from other products. Operational conditions of the adsorption process and the type of adsorbent would be the important factors in separation efficiency. Selection of a proper adsorbent is a critical step in effective adsorption processes. Different adsorbents such as zeolites and zeotype materials, activated carbons and carbon molecular sieves have been studied in separation of light hydrocarbons processes, among which zeolites have the largest usage. Nowadays, commercial zeolites due to their unique pore diameters are widely used for adsorption process, but studies in concern with OCM products separation, have been rarely carried out [5-11].

Choudhary and Mayadevi had investigated the adsorption of methane, ethane, ethylene, and carbon dioxide on silicalite-1. They found that the order of adsorption for these four different adsorbents on silicalite-1 is $CH_4<CO_2<C_2H_4\leq C_2H_6$ [12].

Triebe et al. studied the potential of H-mordenite, 13X, 10X, 4A and 5A zeolites in adsorption of pure methane, ethane and ethylene. It was concluded that 5A and 10X zeolites yielded better ethylene/methane separation factors compared with others, although efficient separation using 5A and 10X zeolites was only possible at very high temperatures due to the strong affinity of their divalent cations for the ethylene π-bond. [13].

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Macedonia et al. investigated the adsorption of methane, ethane and argon on two different Na-MOR samples with Si/Al ratios of 5 and 9 at ambient conditions. At the best condition, the selectivity of ethane to methane was found 1.6 [14].

In this research, batch adsorption of pure methane, ethane and ethylene on 10X zeolite was examined to determine the potential of this adsorbent in separation of methane from ethane and ethylene. For the first time, a statistical approach, called response surface method (RSM) has been used to derive a proper model for C_2s' selectivity and adsorption capacity as the function of temperature and pressure at equilibrium adsorption. RSM is applied for the experiments design and analysis of the results to find out the significant effects of the variable and introduce a model, including the operating conditions, their binary interaction and quadratic effects to predict the adsorption capacity and selectivity. To realize the efficiency of 10X zeolite in packed bed columns for separation of the gases from their mixture, the dynamic adsorption experiment has been conducted for the mixed gases and the breakthrough curves of methane, ethane and ethylene are obtained at the appropriate conditions.

1. Experimental

1.1. Adsorbent

10X zeolite with a low Si/Al ratio is a kind of X zeolite family, which consists of calcium cations and has the pore size of 10 ? . Ca^{++} exchanged X zeolite is a useful adsorbent for the separation of traces of light hydrocarbons in refinery processes [15]. The calcium form of X zeolite, can exhibit the high capacity for ethylene, mainly due to its high charge density. In this adsorbent the separation can occur according to the differences in molecular size and/or the strength of gas molecule bond. Divalent cations in zeolites are strong adsorptive centers, and ethylene has a strong quadrupole moment. It seems that the interaction between the ethylene π - bond and the cationic site in the zeolite is the reason for the strong adsorption of ethylene on CaX zeolite [13].

Table 1: 10X zeolite properties

Pore size	10 (?)
Bulk density	650 (Kg/m^3)
Adsorbent particle size	1.6-2.6 spherical (mm)
Pretreatment temperature	523 (K)

The sample of 10X zeolite was purchased from Zeochem Company. The information about the zeolite used in this study is given in table 1, and the SEM image of 10X zeolite is shown in Fig.1.

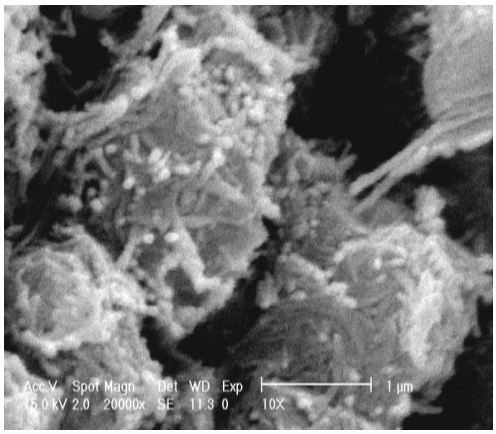

Figure1: The SEM image of the prepared 10X zeolite

1.2. Adsorption process

Temperature and pressure were considered as two influencing variables in equilibrium adsorption. The equilibrium adsorption was measured by a volumetric method at the equilibrium condition. Before each experiment, pretreatment of the adsorbent was carried out in the adsorption cell by N_2 purge gas at 523 K for four hours. The equilibrium adsorption experiments were carried out in a stainless steel setup at moderate temperatures and pressures of the above atmosphere. Selectivity of the adsorbent for C_2s against CH_4 was calculated by the sum of adsorbed equilibrium of ethane and ethylene over methane.

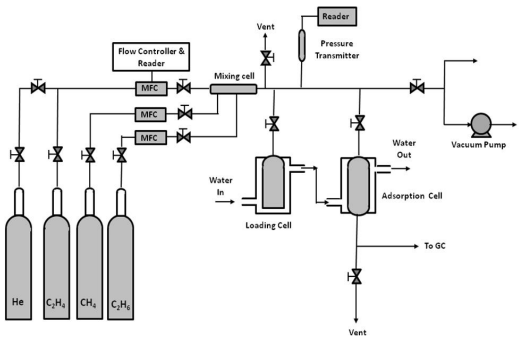

Figure 2: Dynamic adsorption apparatus

The single gas adsorption process was carried out at temperature range of 288.15 to 308.15 K and initial pressure range of 0.1 to 3 MPa. The reason of selecting such a pressure range is regarded to the industrial processes of pressure swing adsorption which takes this range of pressure at adsorption and desorption modes for separation of the gases. The temperature range of 288.15 to 308.15 K was considered to predict the gas separation efficiency of the adsorbent at the temperatures near ambient condition.

To obtain the breakthrough curves and breakthrough times of each component, the dynamic adsorption-desorption experiments were carried out in the packed bed of CaX at atmospheric pressure and 308.15 K. The composition of CH_4, C_2H_6, and C_2H_4 was selected as similar as OCM hydrocarbon products. The experimental conditions of the dynamic adsorption runs are listed in table 2. A schematic diagram of our experimental apparatus is shown in Fig.2 and its detailed illustration is explained elsewhere [8].

Table 2: Dynamic experiments conditions

Bed properties	
Adsorbent Weight	16.33 g
Inside Bed Diameter	1.27 cm
Bed Length	20 cm
Adsorption Conditions	
Feed molar Composition	
CH_4	70%
C_2H_6	15%
$C2H_4$	15%
Feed Flow Rate	20 N ml/min
Temperature	308.15 K
Pressure	1 atm

1.3. Experimental design

This study was carried out according to a kind of RSM experimental design called faced centered central composite design method. Central composite design (CCD) is the most popular response surface method which is useful in response surface methodology, for building a quadratic model for the response variable without needing to use a complete three level factorial experiment. In the other hand, this method can study the effect of the variables at different levels with fewer experiments than those of factorial design. Additionally, it provides an alternative to attain a statistical model and optimize the adsorption conditions [16]. This design method included a total of $2^k + 2k + n$ runs, where k is the number of factors studied (temperature and pressure, k =2), 2^k is the points from a factorial experiment, 2k is the number of points carried out on the axes at a distance of ± α from the center. Two variable central composite design is face centered design if α =1, where n is the number of center points. In this design, the number of center point is equal to 1 (n =1) [17]. Based on the face centered design, 9 experiments were formulated to examine the effect of each parameter, their binary interaction and quadratic.

After performing the experimental runs, the responses were determined as the amount of equilibrium adsorbed at each pressure and temperature, which are reported in table 3. The significant effect of the parameters was analyzed using Design-Expert software (Version 8.0.1) by analysis of the responses variance (ANOVA) and the data were analyzed with multiple regressions. Face centered CCD method was used to define the optimum conditions for adsorption. Initially, the analysis of variance was carried out for linear, 2FI (consist of interaction) and quadratic models. With respect to 95% confidence interval, the model is significant if P-value would be lower than 0.05. After choosing the best regression model, analysis of variance was carried out to investigate the effect of each model parameters.

Table 3: Methane, ethane and ethylene at single equilibrium adsorption according to face centered composite design

Run	Parameters in coded units		Responses ($mmol_{adsorbed}/gr_{adsorbent}$)		
	A (K)	B (MPa)	CH_4 adsorption	C_2H_6 adsorption	C_2H_4 adsorption
1	288.15	0.1	0.28	1.19	1.49
2	308.15	0.1	0.13	0.94	1.28
3	288.15	3.0	1.75	2.01	2.29
4	308.15	3.0	1.51	1.85	2.13
5	288.15	1.55	1.46	1.87	2.15
6	308.15	1.55	1.10	1.71	1.96
7	298.15	0.1	0.20	1.05	1.36
8	298.15	3.0	1.59	1.94	2.25
9	298.15	1.55	1.31	1.78	2.08

Table 4: Analysis of Variance and determination coefficient of the models for CH4, C2H6 and C2H4 adsorption

Source	DF	CH_4 adsorption			C_2H_6 adsorption			C_2H_4 adsorption		
		F-Value	P-Value	R^2_{adj}	F-Value	P-Value	R^2_{adj}	F-Value	P-Value	R^2_{adj}
Linear	2	26.88	0.001	0.87	20.82	0.002	0.83	23.47	0.002	0.85
2FI	3	15.07	0.006	0.84	11.73	0.011	0.81	13.08	0.008	0.82
Quadratic	5	921.5	< 0.0001	0.99	867.36	< 0.0001	0.99	579.07	0.0001	0.99

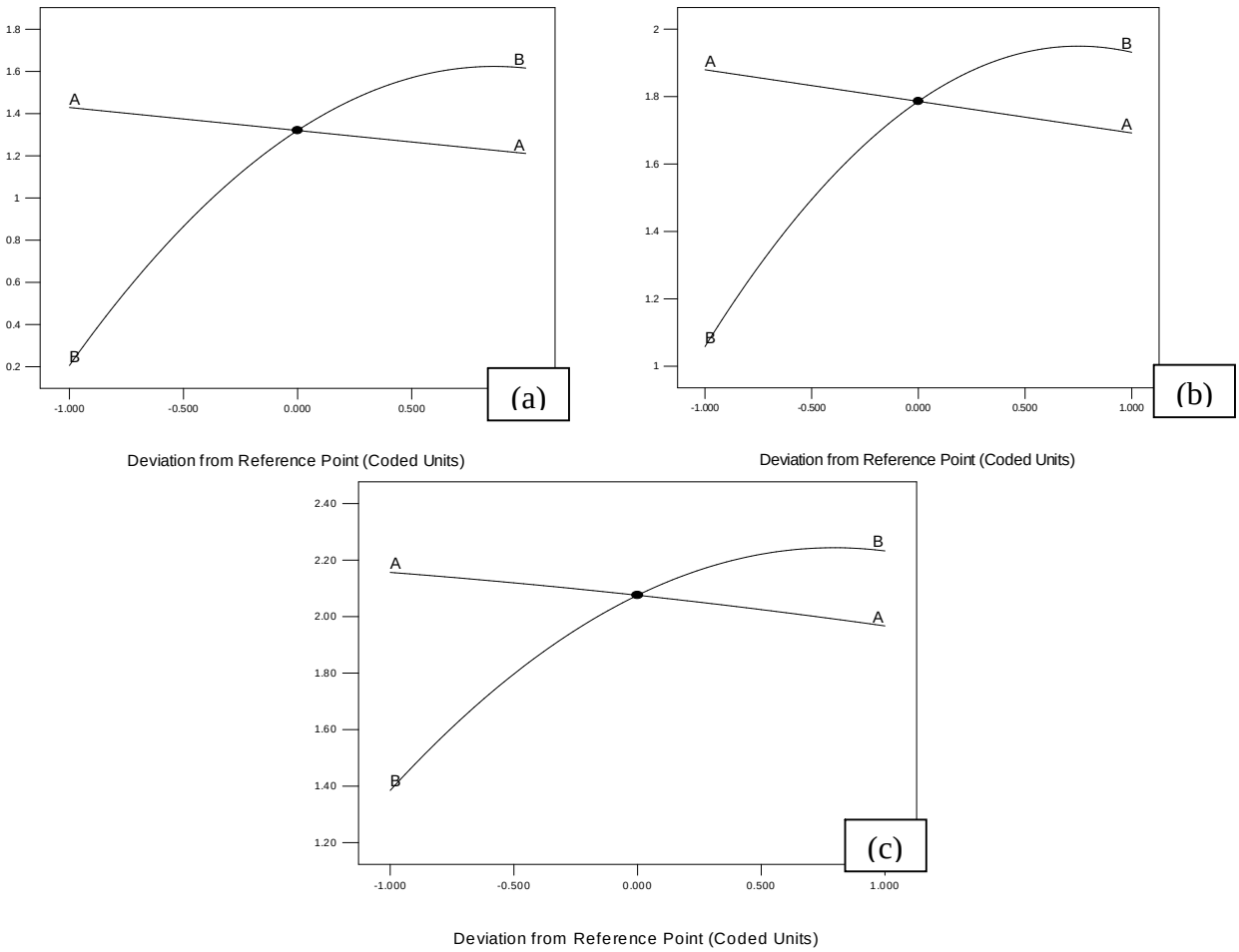

Figure 3: Perturbation plot for a) methane, b) ethane and c) ethylene

2. Result and discussion

2.1. Effects of parameters

The influence of the operating conditions, temperature and pressure, on the equilibrium adsorption was experimentally determined and statistically analyzed. The perturbation plot for methane, ethane and ethylene adsorption versus the experimental levels has been illustrated in Fig. 3. The perturbation plot helps to compare the effect of all the factors at a particular point in the design space. A steep slope or curvature in a factor shows that the response is sensitive to that factor. A relatively flat line shows insensitivity to change in that particular factor [18]. It shows the negative effect of temperature and positive effect of pressure on the adsorption capacity of any gases, so it means that temperature decrease and pressure increase can cause enhancement of adsorption. In addition, quadratic effect of pressure is shown in this figure. The significant effect of temperature, pressure, quadratic relation and their interaction can be determined by analysis of variance.

2.2. Analysis of variance

The theory of analysis of variance (ANOVA) is well discussed by Allus et al. [19]. Using the Fisher variance ratios of the parameter effect dispersion to the error dispersion, called F-test, can demonstrate which parameters are significant or non-significant. In this research, 95% confidence interval has been used for evaluation of the parameters' signification; therefore, a probability value (P-value) of 5% would be the significant level in F-tests for interpretation of the effects [20]. In this method various regression models can be proposed as a function of variables and their interactions, then the best model can be obtained using the residual analysis and dispersion of the responses.

2.3. Regression model

The equilibrium adsorbed capacity of methane, ethane and ethylene according to temperature and pressure are modeled. Three types of models were selected and tested; linear model as a linear relationship of temperature and pressure, 2FI (two factor interaction) model with binary interaction of temperature and pressure, and a quadratic model which has added the second order relationship of the variables to the last model. These models are fitted on the experimental results using the linear least square method. The significance of the model is tested by F-test and the adjusted coefficient of determination (R^2_{adj}) is obtained to recognize the best fitted model. The results are reported in table 4. In this table DF is the degree of freedom of the residual in each model.

As shown in table 4, according to the P-value of different models, the linear and the quadratic models are significant for methane, ethane and ethylene adsorption. Furthermore, because of the higher R^2_{adj} of the quadratic model compared to the other models, it seems that the quadratic model is the most precise model for predicting CH_4, C_2H_6 and C_2H_4 adsorption in terms of temperature and pressure. The general form of the quadratic model is presented as following:

$$Y = \beta_0 + \sum_1^k \beta_i x_i + \sum \beta_i x_i^{\,2} + \sum_{ji} \beta_{ij} x_i x_j \qquad (1)$$

Y is the studied response, x_i and x_j are the variables considered in the study and β_0, β_i and β_{ji} are the estimated coefficients. Proposed model equations for CH_4, C_2H_6 and C_2H_4 adsorption using the face centered approach were given as equations 2, 3 and 4, respectively. The coefficients are in the form of the coded unit.

$$Y_{CH_4} = 21.09 - 0.13A + 1.63B - 0.0002A^2 - 0.19B^2 - 0.002A \times B \qquad (2)$$

$$Y_{C_2H_6} = 5.83 - 0.02A + 0.26B - 0.00001A^2 - 0.14B^2 + 0.002A \times B \qquad (3)$$

$$Y_{C_2H_4} = -7.72 - 0.07A + 0.47B - 0.0001A^2 - 0.13B^2 + 0.0007A \times B \qquad (4)$$

According to the model coefficients, the second order of temperature and interaction has not significant effect on gas adsorption. In the other word, because the

coefficients of pressure are more than other coefficients, pressure has the great effect on the gas adsorption. The coefficients of the above equations should be compared with the residual error of the experiments by analysis of variance to determine the signification of each term in the proposed model. The F-test values and probability values are calculated by DX8 software for each gas and presented in tables 5, 6 and 7. In these tables, SS represents the sum of square of each coefficient in its coded unit, and MSS represents the ratio of SS over DF as the mean square of that coefficient. DF is the degree of freedom of each term. In ANOVA with 95% confidence interval, those P-values with less than 5% show the signification of that parameter.

As shown, A (temperature), B (pressure) and B^2 parameters show P-values less than 0.05. Therefore, temperature, pressure and quadratic function of pressure are the significant terms in adsorption of CH_4, C_2H_6 and C_2H_4, whereas AB (interaction of A and B) and A^2 with high P-values are not significant. As a matter of fact, the calculated F-values of A, B and B^2 are much higher than F_{AB} and F_{A^2}. The high value of the calculated F_i means a great influence of that factor on the experimental outcome. In the present study, the F-value of pressure is much higher than the other factors, and it reveals a great effect of pressure on the adsorption capacity of the three hydrocarbons on 10X zeolite. After deleting non significant parameters, final adsorption models were achieved as equations of 5, 6 and 7. The R^2_{adj} of the final CH_4, C_2H_6 and C_2H_4 adsorption model were 1.00, 0.99 and 0.99, respectively.

$$Y_{CH_4} = 3.35 - 0.011A + 1.09B - 0.19B^2 \quad (5)$$

$$Y_{C_2H_6} = 3.78 - 0.009A + 0.73B - 0.14B^2 \quad (6)$$

$$Y_{C_2H_4} = 4.13 - 0.009A + 0.69B - 0.13B^2 \quad (7)$$

The amount of adsorbed gas has been plotted in Fig.4 as a function of temperature and pressure. As shown in this figure, pressure increase and temperature decrease will enhance the adsorption capacity. In addition, pressure has curvature effect on adsorption capacity.

Table 5: The ANOVA table of CH4 adsorption

Source	SS	DF	MSS	F-Value	P-Value
Model	3.394	5	0.679	921.5	< 0.0001
A	0.071	1	0.0719	96.75	0.0022
B	2.984	1	2.984	4050.6	< 0.0001
A^2	0.001	1	0.001	1.2	0.3554
B^2	0.335	1	0.335	454.0	0.0002
A × B	0.003	1	0.003	3.8	0.1474
Residual	0.002	3	0.001		

Table 6: The ANOVA table of C2H6 adsorption

Source	SS	DF	MSS	F-Value	P-Value
Model	1.368	5	0.274	867.36	< 0.0001
A	0.053	1	0.053	167.01	0.0010
B	1.144	1	1.144	3626.16	< 0.0001
A^2	4.42E-06	1	4.42E-06	0.01	0.9132
B^2	0.169	1	0.169	537.02	0.0002
A × B	0.002	1	0.002	6.53	0.0835
Residual	0.0009	3	0.0003		

Table 7: The ANOVA table of C2H4 adsorption

Source	SS	DF	MSS	F-Value	P-Value
Model	1.28	5	0.26	579.07	0.0001
A	0.054	1	0.054	122.11	0.0016
B	1.08	1	1.08	2447.77	< 0.0001
A^2	0.0003	1	0.0003	0.85	0.4236
B^2	0.143	1	0.1423	323.63	0.0004
A × B	0.0004	1	0.0004	0.98	0.3950
Residual	0.001	3	0.0004		

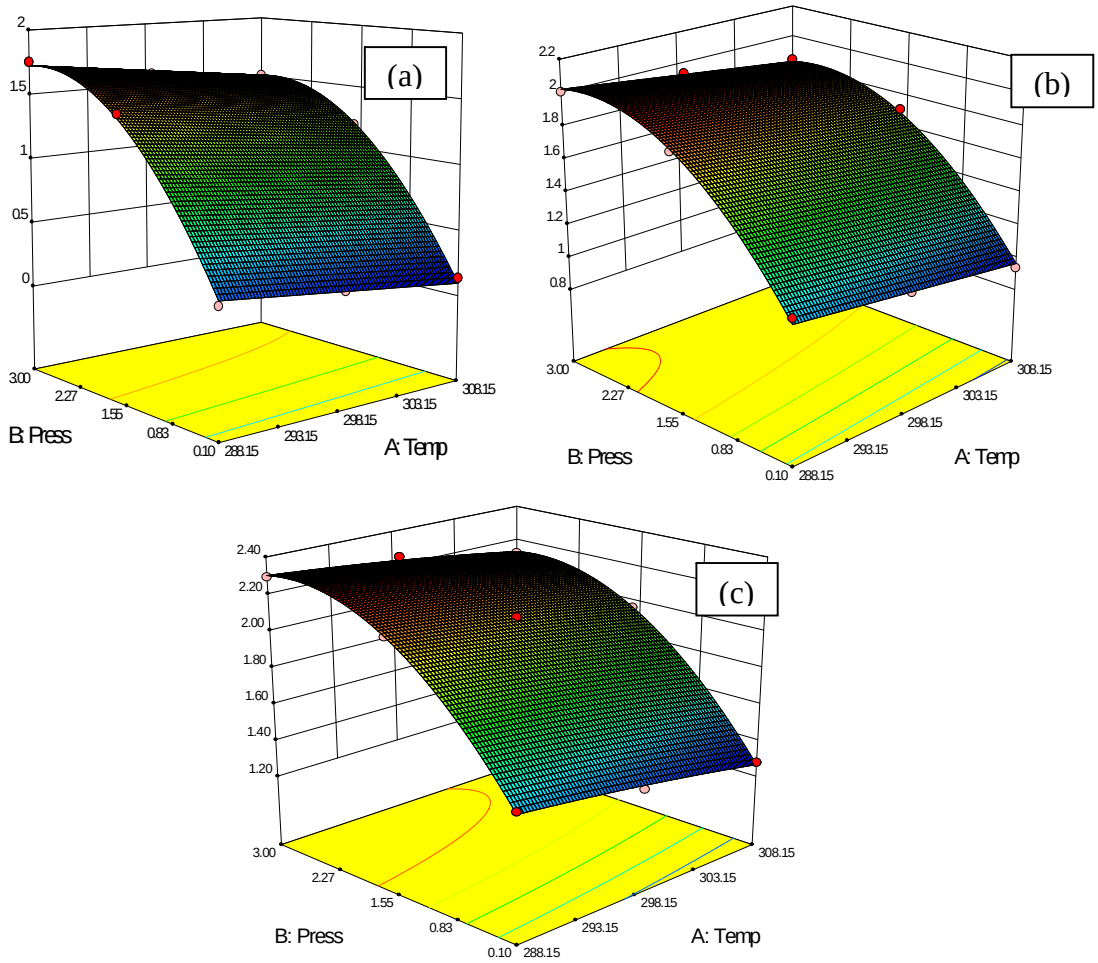

Figure 4: 3D surface plot for a) methane, b) ethane and c) ethylene (•: Design point)

2.4. Selectivity of C_2s

In addition to adsorbed gas capacity, the selectivity of 10X zeolite for C_2s hydrocarbons versus methane is an important response in separation processes by adsorption technology. C_2s selectivity of the adsorbent was calculated by the ratio of equilibrium adsorption of C_2H_6 and C_2H_4 over CH_4. The table of ANOVA is obtained for the C_2s selectivity and shown in table 8.

As shown in table 8, the quadratic of temperature has no significant effect on selectivity. Therefore, it is eliminated in the regression model, and the final model is presented as equation 8.

$$Y_{Selectivity} = -74.43 + 0.30A + 23.28B + 2.22B^2 - 0.11A \times B \quad (8)$$

Fig. 5 is the perturbation plot of C_2s selectivity. The results show the positive effect of temperature (A) and negative and quadratic effect of pressure (B) for enhancement of C_2s selectivity by 10X zeolite.

Contour plot of the binary interactions and 3D surface plot of C_2s selectivity, derived from the model, are shown in Fig.6 and 7. Contour plot demonstrates that the lowest level of pressure and highest level of temperature would be the appropriate conditions to achieve the highest selectivity. Therefore, the response surface model of C_2 selectivity can be employed for predicting the optimal operational conditions to achieve the maximum selectivity. The optimization was performed on model Eq. (8) by the Simplex method and the optimal conditions were determined when the temperature and pressure are 308.15 K and 0.1 MPa, respectively. The maximum predicted value of selectivity is calculated 15.6 by the quadratic model. The optimal point was found with 94% desirability. The desirability provides an overall measure for the goodness of the specific setting [19]. This selectivity is higher than those reported in the literature [12-14]. The pressure has exhibited an inverse effect on the selectivity, and the temperature has shown a forward influence, because methane adsorption is more positively affected by pressure and more negatively influenced by temperature. Therefore, the C_2s selectivity is improved at lower pressures and higher temperatures.

Table 8: The ANOVA table of C2s selectivity

Source	SS	DF	MSS	F-Value	P-Value
Model	214.036	5	42.807	31.63	0.009
A	8.721	1	8.721	6.44	0.085
B	150.874	1	150.874	111.49	0.002
A^2	0.288	1	0.288	0.21	0.676
B^2	43.463	1	43.463	32.12	0.011
A × B	10.690	1	10.690	7.90	0.067
Residua	4.051	3	1.353		

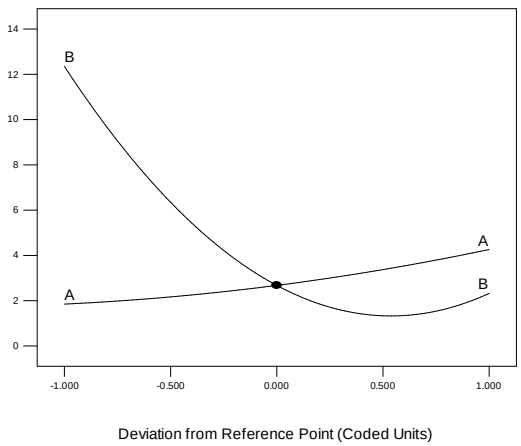

Figure 5: Perturbation plot for C2s selectivity

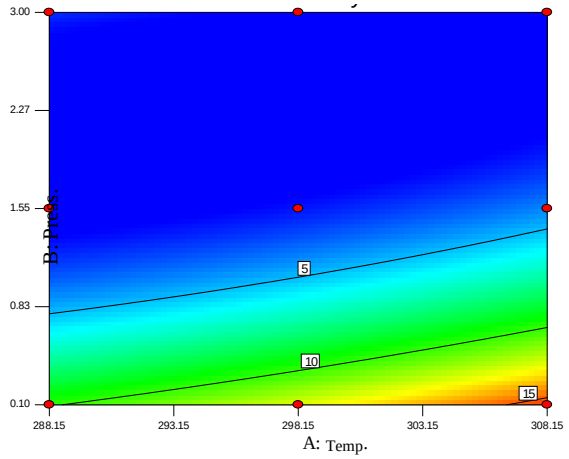

Figure 6: Contour plot for C2s selectivity (•: Design point)

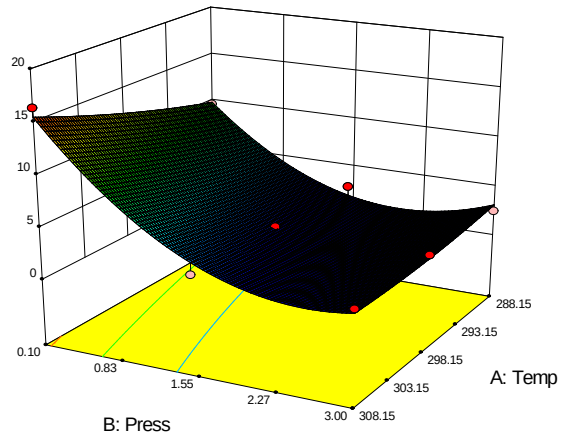

Figure 7: 3D surface plot for C2s selectivity (•: Design point)

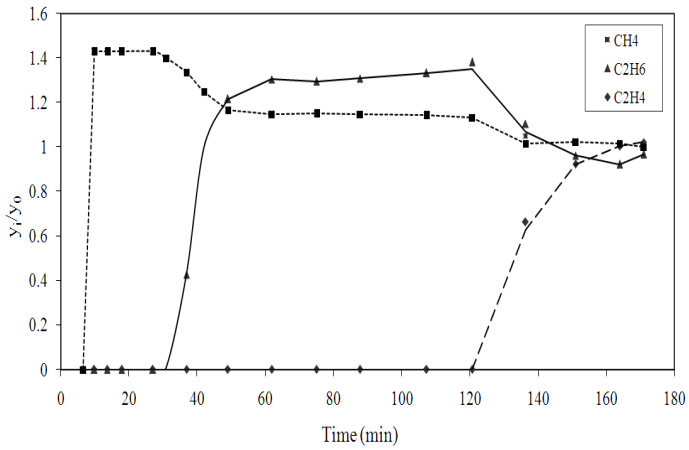

Figure 8: Adsorption breakthrough curves of methane, ethane and ethylene at 308.15 K.

2.5. Dynamic adsorption

After studying the single gas adsorption, capability of separation was evaluated in dynamic adsorption process at optimal condition. The breakthrough curves of methane, ethane, and ethylene were obtained and presented in Fig. 8 as the ratio of outlet molar fraction over inlet composition. The results indicated that methane was passed through the packed

bed very rapidly and appeared at the outlet stream.

The breakthrough time of each component was calculated whenever 1% of inlet molar fraction appeared in the effluent. Methane breakthrough time was observed between 6.6 and 9.8 min, ethane breakthrough time was obtained from 27 to 36.8 min, and ethylene breakthrough time was observed between 120.7 and 136.3 min at the dynamic adsorption experiments. Significant difference between the breakthrough times of methane and ethane reveals that methane can completely exit until the breakthrough time of ethane is appeared.

In addition, Fig. 8 clearly shows a great difference between breakthrough curves of ethane and ethylene which would make a high efficient separation of ethane and ethylene from their mixture.

3. Conclusion

Adsorption of methane, ethane and ethylene on 10X zeolite has been performed and statistical design is applied to predict the significant effects of operational parameters on adsorption capacity and C_2s selectivity. The effect of two numerical variables, temperature and pressure with their interactions were studied in single batch equilibrium adsorption. Quadratic models were suggested with good agreement on the experimental data for adsorption capacity and C_2s/CH_4 selectivity, in the range of 0.1 to 3MPa and 288.15 to 308.15 K. It is concluded that the pressure is the most effective parameter for adsorption capacity and selectivity. The optimal conditions derived from the quadratic models proposed the best experimental temperature and pressure for the highest C_2s selectivity. In this case, decreasing pressure and increasing temperature will improve the C_2s' selectivity for 10X zeolite; therefore the optimal conditions were obtained at temperature 308.15 K and pressure 0.1 MPa. In the optimal conditions, the selectivity of C_2s/CH_4 was determined as 15.6.

The experimental dynamic adsorption of the mixed gases was carried out at optimal conditions and the breakthrough curves were obtained for ethane, ethylene, and methane. The results suggest that separation of methane from ethane and ethylene can be efficiently performed in dynamic adsorption process at atmospheric conditions by 10X zeolite. It is suggested to employ a dynamic adsorption unit at the downstream of OCM process to be used for separation of methane, ethane and ethylene from the outlet gaseous product.

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