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Original Research Article

Optimization of Carbon Dioxide Hydrogenation to Methanol over Copper-Based Catalyst

N.H. Berahim*[1], A. Abu Seman[1], N.H. Yasin[1], V.C. Quek[1], M.F. Mahmood[2], N.A. Mohd Zabidi[3], N.A. Suhaimi[3]
[1]Carbon Capture Utilization & Storage Department, PETRONAS Research Sdn. Bhd., 43000 Kajang, Selangor, Malaysia
e-mail: hafizah.berahimjusoh@petronas.com, akbar_seman@petronas.com, norhafizah.yasin@petronas.com, quekven@petronas.com
[2]Lab & Pilot Plant Operation, PETRONAS Research Sdn. Bhd., 43000 Kajang, Selangor, Malaysia
e-mail: mfarizal.mahmood@petronas.com
[3]Center of Contaminant Control and Utilization (CenCoU), Institute of Contaminant Management for Oil and Gas, Department of Fundamental and Applied Sciences
Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
e-mail: noorasmawati_mzabidi@utp.edu.my, amirah.suhaimi@utp.edu.my

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ABSTRACT

This study examines the utilization of process optimization as a viable strategy for addressing the issue of global warming through the conversion of carbon dioxide into methanol. In the realm of computational chemistry, the response surface methodology approach has evolved as an alternative for optimizing the reaction parameters through the utilization of statistical models. In the present study, promoted copper/zinc oxide/alumina catalyst was used for carbon dioxide conversion to methanol. The primary objective of the study was to enhance the overall methanol yield by optimizing the various factors in the methanol synthesis. This was accomplished by employing a combination of response surface methodology and one factor at a time techniques. The creation of statistical models was used to optimize the essential factors, and subsequently, one factor at a time. This helps in determining the optimum pressure, temperature, and hydrogen/carbon dioxide molar ratio. Impregnation technique was employed for the synthesis of promoted copper/zinc oxide/alumina catalyst. The analysis of variance results suggested the reduced quadratic model for carbon dioxide conversion, methanol selectivity and methanol yield as responses. The optimum process operating conditions were found to be the hydrogen/carbon dioxide ratio of 10, temperature of 300 °C, pressure of 31 bar and gas hourly space velocity of 2160 mL/g h, in which 28.6% carbon dioxide conversion, 59.2% methanol selectivity and 16.4% methanol yield were achieved. The catalytic performance was then investigated for high pressure range of 40 – 80 bar with other conditions were fixed at optimal value. The carbon dioxide conversion and methanol selectivity were found to increase with increasing pressure. The highest catalytic performance was achieved at 80 bar with carbon dioxide conversion of 68.35%, methanol selectivity of 93%, and methanol yield of 63.57%.

KEYWORDS

Response Surface Methodology (RSM), Carbon dioxide hydrogenation, Methanol synthesis, Process optimization, Copper-based catalyst, Impregnation.

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[*] Corresponding author

INTRODUCTION

With the rapid development of the world's society and economy, particularly in emerging countries, the increasing energy demand is catastrophic. By 2050, global energy consumption is predicted to double [1]. Fossil fuels continue to meet more than 80% of global energy demand because of their abundance and affordability [2]. However, global fossil fuel reserves are decreasing, resulting in various of environmental issues, indicating that new solutions are required [3]. As a result, the necessity for clean, long-term energy is a key component for society [4].

Over the last decade, methanol synthesis processes have gotten much attention. The catalytic hydrogenation reaction uses carbon dioxide and hydrogen as input components. Catalytic hydrogenation of carbon dioxide is now technically competitive with industrial methanol synthesis from syngas [5], [6], and much potential for large-scale applications and carbon dioxide consumption [7], [8].

CO_2 hydrogenation to methanol eliminates the costly synthesis step of the traditional methanol production process [9]. Copper remains the most active catalyst for methanol synthesis when combined with other promoters like zinc, zirconium, cerium, aluminum, and silicon, despite the development and testing of numerous metal-based catalysts. The catalyst $Cu/ZnO/Al_2O_3$ is commonly used in the process of synthesizing methanol [10], [11]. According to Ahadzi *et al.* [12], efficient conversion of CO_2 to methanol requires high Cu loading on the catalyst. The Cu-centers are generally regarded as the main active sites; the presence of ZnO is thought to have a stabilizing impact on the copper, and Al_2O_3 stabilizes and prevents the particles from sintering [13], [14]. Water created during methanol synthesis is said to remain connected to the active sites, which ultimately poisons the catalyst [15]. The $Cu/ZnO/Al_2O_3$ catalyst prevents this by inducing a reverse water gas shift reaction and maintaining a high CO/CO_2 ratio in the reactor feed stream [16]. It is known that the most important factors for CO_2 hydrogenation are temperature, pressure, and feed ratio.

Torcida *et al.* [17] optimized a multibed reactor for producing biomethane and methanol. Parameters such as feed ratio, pressure conditions, and number of beds were shown to have optimal values in the results. The effect of operational factors such as pressure, temperature, and space velocity on the efficiency of CO_2 hydrogenation on fuels were examined by Saeidi *et al.* [18]. Reactor behavior remains unaffected by variations in pressure and space velocity when the temperature rises, as revealed by the sensitivity analysis, which indicates that this mechanism is temperature dependent. Leonzio *et al.* [3] utilized analysis of variance (ANOVA) and a central composite design in their investigation of the process of CO_2 hydrogenation to methanol. The findings indicated that elevated temperatures and recycling parameters were associated with increased production.

The high CO_2 conversion and methanol production observed in commercial $Cu/ZnO/Al_2O_3$ catalysts were found to be facilitated by operating pressure and temperature conditions of 124.1 bar and 240 °C, respectively [19]. An example of this can be seen in the methanol yield of 27.3% reported by Kim *et al.* [20] at an ideal temperature of 247 °C. Additionally, it was observed that a rise in pressure has a beneficial effect on the yield of methanol. At 240 °C, 124.1 bar, and 3300 h^{-1} space velocity, a pilot-scale reactor system achieved 49% methanol rate and 14.3% CO_2 reduction [19]. Methanol yield increased with higher operating pressure, resulting in reduced by-product generation.

Based on the past research, optimization of process variables for CO_2 hydrogenation to methanol was found to be minimal, thus this research focuses on the investigation of the combined effects of the H_2/CO_2 ratio, temperature, pressure, and space velocity (GHSV) toward the CO_2 conversion, methanol selectivity and methanol yield as the response variables for tri-promoted (GVII, GV, GIV) Cu/ZnO catalyst supported on Al_2O_3. The process variables were optimized using face centered (FCCD) along with the RSM method. A model was developed to determine the optimum conditions for methanol synthesis, where the maximum percentage of methanol production was achieved. Under this optimization using RSM method, the pressure range was kept in between 22 – 40 bar (lower pressure range). One significant drawback of RSM models is that their accuracy is limited to a small set of input and process parameters. Additionally, creating higher-order RSM models is more time-consuming, expensive, and requires a large number of tests. Considering this constraint, the present study employed a mix of OFAT and RSM approaches to ascertain the methanol production [21]. Thus, the high-pressure testing range of 40 – 80 bar employed the one-factor-at-a-time (OFAT) method, while the remaining operating conditions, including H_2/CO_2 ratio, temperature, and space velocity, were held constant at their optimal levels determined during testing at lower pressures.

MATERIALS AND METHODS

Prior to the catalytic testing, the bare support and catalyst formulation need to undergo pre-treatment and synthesize. Figure 1 shows the simplified diagram of the catalyst synthesis.

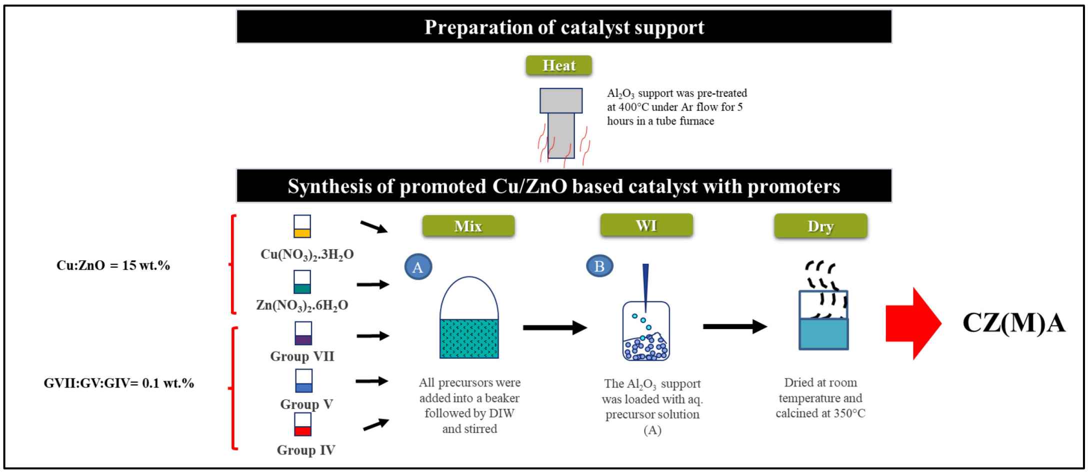


Figure 1. Catalyst synthesis

Preparation of Al_2O_3 as catalyst support

Al_2O_3, which was purchased from Merck, with purity of 98% has been pre-treated under argon flow at 400 °C for 5 h to remove moisture and impurities.

Preparation of Cu/ZnO based catalyst with addition of promoters

Cu/ZnO with fixed metal loading of 15 wt.% and tri-promoters (GVII, GV, GIV) with 0.1 wt.% loading was synthesized using wet impregnation method. The amount of each precursor and promoter added was calculated based on the mass of the prepared catalyst. In order to make an aqueous solution, copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Group VII salt, Group V salt, and Group IV salt were dissolved in deionized water. The solution was stirred at room temperature for 1 h. The prepared aqueous precursor solution was then added dropwise to the beaker containing the Al_2O_3 support. The pH of the mixture was maintained at 7. After stirring for 24 h, the mixture was filtered and rinsed with deionized water. The paste was dried in an oven at 120 °C for 12 h. After drying, the catalyst was placed in a ceramic crucible and calcined for 4 h at 350 °C. The catalyst sample was denoted as CZ(M)A for $Cu/ZnO/GVII/GV/GIV/Al_2O_3$. M represents the tri-promoters (GVII/GV/GIV).

Optimization of methanol synthesis conditions to enhance methanol production

The optimization of CO_2 hydrogenation to methanol was investigated using two different approach which are Response Surface Methodology (RSM) and one factor at a time (OFAT).

Response surface methodology (RSM) analysis for the statistical optimization of methanol production. The process parameters of the synthesized CZ(M)A for CO_2 hydrogenation reaction were investigated using a standard response surface methodology (RSM) design, also known as central composite design (CCD). H_2/CO_2 ratio, temperature, pressure (lower range), and space velocity (GHSV) were studied. Using a second-degree polynomial as in eq. (1), an empirical model was built to correlate the responses CO_2 conversion (X_{CO2}), MeOH selectivity (S_{MeOH}), and MeOH yield (Y_{MeOH}) to the four respective parameters impacting the CO_2 hydrogenation process in methanol synthesis:

$$\gamma = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \quad (1)$$

where γ is the predicted response; β_0 is the constant coefficient; β_1, β_2 and β_3 are the linear coefficients; β_{12}, β_{13}, and β_{23} are the interaction coefficients; β_{11}, β_{22}, and β_{33} are the quadratic coefficients; and *A*, *B*, *C* are the coded values of independent input parameters.

Design Expert Version 13 (Stat Ease, USA) was used to correlate all responses and determine experimental condition with the highest desirability. Analysis of variance (ANOVA) described every change in the statistically obtained model and demonstrated the significance of each model parameter. The significance of the model was assessed using the *F*-test with a 95% confidence level and the lack of fit (LOF) test. When the *F*-value is higher and the *p*-value is lower, the model is considered more significant.

Conventional one factor at a time (OFAT) approach. One factor at a time approach was employed to optimize pressure at higher range with the rest of the variables (H_2/CO_2 ratio, temperature, and GHSV) were fixed from RSM optimization.

Catalyst performance evaluation

Low pressure range testing. The CO_2 hydrogenation reaction to methanol was carried out in a tubular, stainless steel micro-activity fixed bed reactor. Prior to a reaction, (0.2 – 1.0) g of calcined catalyst was activated in H_2 for 2 h. Then, the reaction was performed on the activated catalyst under process conditions listed in **Table 1**. The reactor effluents were analysed using a gas chromatograph equipped with a TCD detector for H_2 and CO_2 analysis and an FID detector for alcohols and other hydrocarbons. CO_2 conversion, MeOH selectivity, and MeOH yield were calculated using eqs. (2–4), respectively.

Table 1. Independent variables in experimental design

Variables	Unit	Levels -1 Low	 0 Medium	 +1 High
H_2/CO_2 (*A*)	-	3	6.5	10
Temperature (*B*)	°C	200	250	300
Pressure (*C*)	bar	22	31	40
GHSV (*D*)	mL/g h	2160	6480	10800

$$\text{CO}_2 \text{ Conversion } (\%) = \frac{\text{moles of CO}_2 \text{ in} - \text{moles of CO}_2 \text{ out}}{\text{moles of CO}_2 \text{ in}} \times 100 \quad (2)$$

$$\text{MeOH Selectivity (\%)} = \frac{\text{moles of MeOH produced}}{\text{total moles of products}} \times 100 \tag{3}$$

$$\text{MeOH yield (\%)} = \frac{\text{CO}_2\text{ conversion (\%)}}{100} \times \text{MeOH selectivity (\%)} \tag{4}$$

High pressure range testing. The catalyst performance for CO_2 hydrogenation to methanol was evaluated using a fixed bed reactor (5 times reactor volume than microactivity fixed bed reactor). The catalyst was reduced in-situ under H_2 flow and atmospheric pressure for 2 h. The pressure was varied in the range of 40 – 80 bar and H_2/CO_2 ratio, temperature, and GHSV were fixed using optimized conditions from low pressure testing range. The product gases were analysed via an on-line gas chromatograph. The catalytic performance was evaluated based on the CO_2 conversion, MeOH selectivity, and MeOH yield calculated as per eqs. (2–4) respectively.

RESULTS AND DISCUSSION

The following results of RSM and OFAT optimization for CO_2 hydrogenation to methanol at low- and high-pressure range testing respectively were discussed.

Low pressure range testing using response surface methodology approach

Regression model equation and analysis of variance (ANOVA). The proposed model should be considered a good starting point for model fitting when identifying the optimal model to employ for the response [22]. **Table 2** shows the reduced quadratic models are suggested for all three responses (X_{CO2}, S_{MeOH}, and Y_{MeOH}) with p-values < 0.05 indicated the models' term are significant. The lack of fit (LOF) values of 0.4349 (X_{CO2}), 1.00 (S_{MeOH}), and 1.47 (Y_{MeOH}) are not significant which imply that the models are a good representation of the responses. The coefficient of determination (R^2) values for X_{CO2}, S_{MeOH}, and Y_{MeOH} were 0.9458, 0.8541, and 0.9342 respectively which means the models explain 95%, 84%, and 93% respectively of the observed variances. The remaining % (that are not explained by the model) can be due to random variability (experimental variability) or to an effect that is not considered by the model or a combination of both, which is almost always the case. The values are considered acceptable because they're not far away from unity indicating how close the chosen models are to the experimental data points. Meanwhile, the adjusted R^2 represents the amount of variance around the mean that the model can explain [23]. The predicted R^2 values of 0.7649, 0.5728, and 0.6955 for X_{CO2}, S_{MeOH}, and Y_{MeOH} are in reasonable agreement with their respective adjusted R^2 of 0.8916, 0.7666, and 0.8785 where the difference is <0.2. In addition, adequate precision which measures the signal to noise ratio shows the ratio of greater than 4 at 15.6177, 10.7154, and 15.4175 respectively for each response. These indicate adequate model discrimination.

Table 2. Analysis of variance (ANOVA) for the process optimization study of CZ(M)A

Model	X_{CO2} Reduced Quadratic	S_{MeOH} Reduced Quadratic	Y_{MeOH} Reduced Quadratic
Standard deviation	2.67	9.20	17363.03
R^2	0.9458	0.8541	0.9342
Adjusted R^2	0.8916	0.7666	0.8785
Predicted R^2	0.7649	0.5728	0.6955
Adequate precision	15.6177	10.7154	15.4175
p-value	<0.0001	<0.0001	<0.0001
F-value	17.45	9.76	16.77
LOF	0.4349	1.00	1.47

Tables 3, 4, and **5** summarize the multiple regression coefficients of a second order polynomial model describing the effect of catalyst CZ(M)A process operating conditions on the values of X_{CO2}, S_{MeOH}, and Y_{MeOH} respectively. The *F*-value and *p*-value were used to assess the significance of each coefficient. If the *p*-value is less than 0.05, it is deemed significant.

If the linear term (*A*, *B*, *C*, *D*) is significant or insignificant, it indicates that there is a significant or insignificant linear relationship between the predictor variable (*A*, *B*, *C*, *D*) and the response variable (X_{CO2}, S_{MeOH}, and Y_{MeOH}). In other words, as the predictor variable changes, the response variable changes in a linear fashion or do not lead to significant changes in the response variable respectively. If the interaction term (*AB*, *AD*, *BC*, *CD*) is significant or insignificant, it suggests that there is a significant or insignificant interaction effect between the two predictor variables. This means that the relationship between one predictor variable and the response variable depends on the value of the other predictor variable or is consistent across different values of the other predictor variable respectively. If the quadratic term (A^2, B^2, C^2, D^2) is significant or insignificant, it indicates that there is a significant or insignificant quadratic relationship between the predictor variable (*A*, *B*, *C*, *D*) and the response variable. This suggests that the relationship between the predictor variable and the response variable is not linear but instead follows a curved pattern or can be adequately explained by a linear model respectively.

The effects of process operating conditions of the catalyst CZ(M)A on X_{CO2} are shown in **Table 3**. The first order effect of *A* (H_2/CO_2) and *B* (temperature) are significant with both *p*-values <0.0001. However, the first order effect of *C* (pressure) and *D* (GHSV) are not significant with *p*-value of 0.1167 and 0.1165 respectively. The interaction effect of *AB* is significant while the interaction effect of *AD*, *BC*, and *CD* are not significant where the *p*-values are >0.0.5. The second order effect of A^2 (H_2/CO_2), B^2 (temperature), C^2 (pressure) and D^2 (GHSV) all are not significant ($p>0.05$). The coefficient estimate values of the regression model are $A = 4.97$ (H_2/CO_2), $B = 7.57$ (temperature), $C = -1.29$ (pressure) and $D = 1.19$ (GHSV). Hence, temperature has the highest effect on the response X_{CO2}, followed by H_2/CO_2, pressure and GHSV, summarized as $B>A>C>D$.

Table 3. Coefficient of regression model and their significance for first response, X_{CO2}

Source	Coefficient Estimate	*F*-value	Prob>*F*	Remark
Reduced quadratic model	-	17.45	<0.0001	significant
A	4.97	42.46	<0.0001	significant
B	7.57	98.63	<0.0001	significant
C	1.29	2.86	0.1167	insignificant
D	–1.19	2.86	0.1165	insignificant
AB	3.72	19.38	0.0009	significant
AD	0.4677	0.3510	0.5646	insignificant
BC	–1.19	1.97	0.1860	insignificant
CD	–1.03	1.72	0.2148	insignificant
A^2	–2.98	3.20	0.0988	insignificant
B^2	2.46	2.18	0.1656	insignificant
C^2	3.24	3.78	0.0757	insignificant
D^2	–0.8987	0.2906	0.5997	insignificant

Effects of catalyst CZ(M)A process operating conditions on the second response, S_{MeOH} are shown in **Table 4**. The first order effect of A (H_2/CO_2), C (pressure), the interaction between the first order effect of AD, the second order effect of A, B, and D are not significant with p-values >0.05. Furthermore, the first order effect of B (temperature), D (GHSV), the interaction between first order effect of AB is significant with p-values <0.01. The coefficient estimate values of the S_{MeOH} regression model are $A = –2.13$ (H_2/CO_2), $B = 16.06$ (temperature), $C = –0.3494$ (pressure), and $D = –9.56$ (GHSV). The highest effect on the S_{MeOH} is the temperature followed by GHSV, H_2/CO_2, and pressure ($B>D>A>C$).

Table 4. Coefficient of regression model and their significance for second response, S_{MeOH}

Source	Coefficient Estimate	F-value	Prob>F	Remark
Reduced quadratic model	-	9.76	<0.0001	significant
A	–2.13	0.6860	0.4205	insignificant
B	16.06	39.08	<0.0001	significant
C	–0.3494	0.0185	0.8936	insignificant
D	–9.56	15.71	0.0012	significant
AB	7.55	7.88	0.0133	significant
AD	2.34	0.8100	0.3823	insignificant
A^2	–8.40	2.33	0.1480	insignificant
B^2	4.24	0.5915	0.4538	insignificant
D^2	11.51	4.37	0.0541	insignificant

Table 5 shows the effect of process operating conditions on Y_{MeOH}. The first order effect of A (H_2/CO_2), B (temperature), interaction effect in between A and B, B and D are all significant with p-values of <0.05. Meanwhile, the first order effect of C (pressure), D (GHSV), interaction effect in between A and D, B and C, and the second order effect of A, B and D are not significant with p-value >0.05. The coefficient estimate values of the regression model are $A = –19225.97$ (H_2/CO_2), $B = 41975.97$ (temperature), $C = 4162.92$ (pressure) and $D = –15022.24$ (GHSV). According to the corresponding p-value, the first order effect of C is the least significant among the variables studied because it has the lowest coefficient estimate. Thus, temperature has the greatest influence on the response Y_{MeOH}, followed by H_2/CO_2, GHSV and pressure ($B>A>D>C$).

Table 5. Coefficient of regression model and their significance for third response, YMeOH

Source	Coefficient Estimate	F-value	Prob>F	Remark
Reduced quadratic model	-	16.77	<0.0001	significant
A	19225.97	15.01	0.0019	significant
B	41975.97	71.56	<0.0001	significant
C	4162.92	0.7038	0.4167	insignificant
D	–15022.24	10.78	0.0059	insignificant
AB	22250.60	16.41	0.0014	significant

AD	–9320.17	3.29	0.0929	insignificant
BC	3186.90	0.3367	0.5717	insignificant
BD	–14782.87	8.27	0.0130	significant
A^2	–13103.51	1.58	0.2308	insignificant
B^2	22046.49	4.47	0.0543	insignificant
D^2	13496.49	1.68	0.2179	insignificant

The responses variables of the design experiment were modeled using the polynomial eq. (5) (CO_2 conversion), eq. (6) (MeOH selectivity) and eq. (7) (MeOH yield).

$$X_{CO2} = 10.54 + 4.97A + 7.57\mathrm{B} + 1.29C - 1.19\mathrm{D} + 3.72AB + 0.4677AD - 1.19BC - 1.03CD - 2.98A^2 + 2.46B^2 + 3.24C^2 - 0.8987D^2 \tag{5}$$

$$S_{MeOH} = 20.44 - 2.13A + 16.06B - 0.3494C - 9.56D + 7.55AB + 2.34AD - 8.40A^2 + 4.24B^2 + 11.51D^2 \tag{6}$$

$$Y_{MeOH} = 23141.21 + 19225.97A + 41975.97B + 4162.92C - 15022.24D + 22250.60AB - 9320.17\mathrm{AD} + 3186.90BC - 14782.67BD - 13103.51A^2 + 22046.49B^2 + 13496.48D^2 \tag{7}$$

Interaction effect of process operating conditions variables. The 3-D curvatures and its respective interaction plots for the optimum responses and the relationship between significant model terms are graphically illustrated in **Figure 2** – **Figure 4**. Since the model of each response is reduced quadratic model, some of the interaction effects of the variables were removed to improve the model. **Figure 2** shows the interaction effect of *AB* on CO_2 conversion. When the temperature (*B*) increased from 200 °C to 300 °C, and the H_2/CO_2 (*A*) increased from 3 to 10, X_{CO2} was increased. Interaction effect of *AB* on MeOH selectivity (S_{MeOH}) are depicted in **Figure 3**. When the temperature (*B*) is at low level of 200 °C, and H_2/CO_2 (*A*) increased from 3 – 10, the S_{MeOH} significantly decreased. Nevertheless, when the temperature (*B*) is at higher level of 300 °C, increasing H_2/CO_2 shows slight increase in S_{MeOH}.

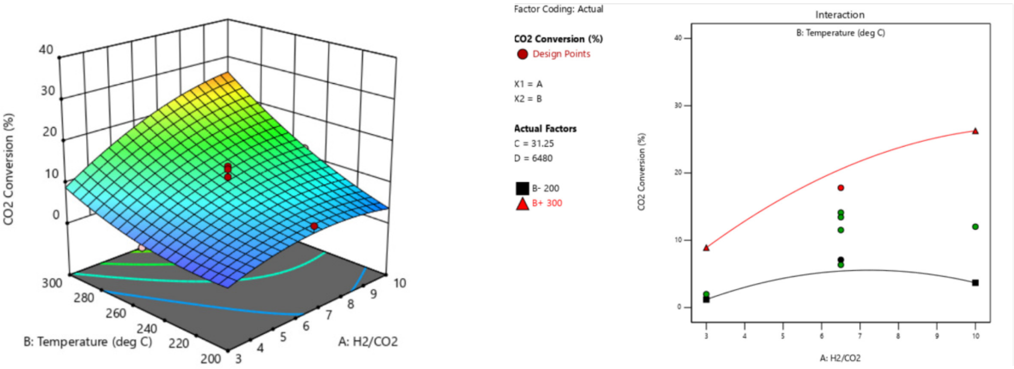


Figure 2. Interaction effect of *AB* on CO_2 conversion (X_{CO2})

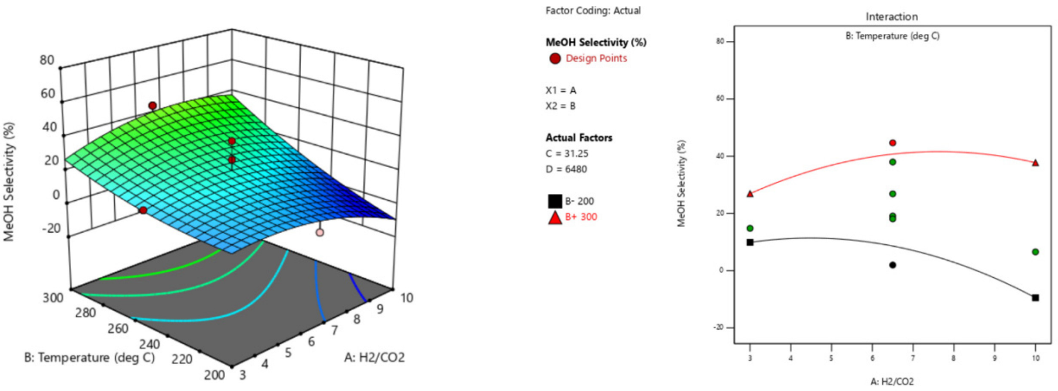
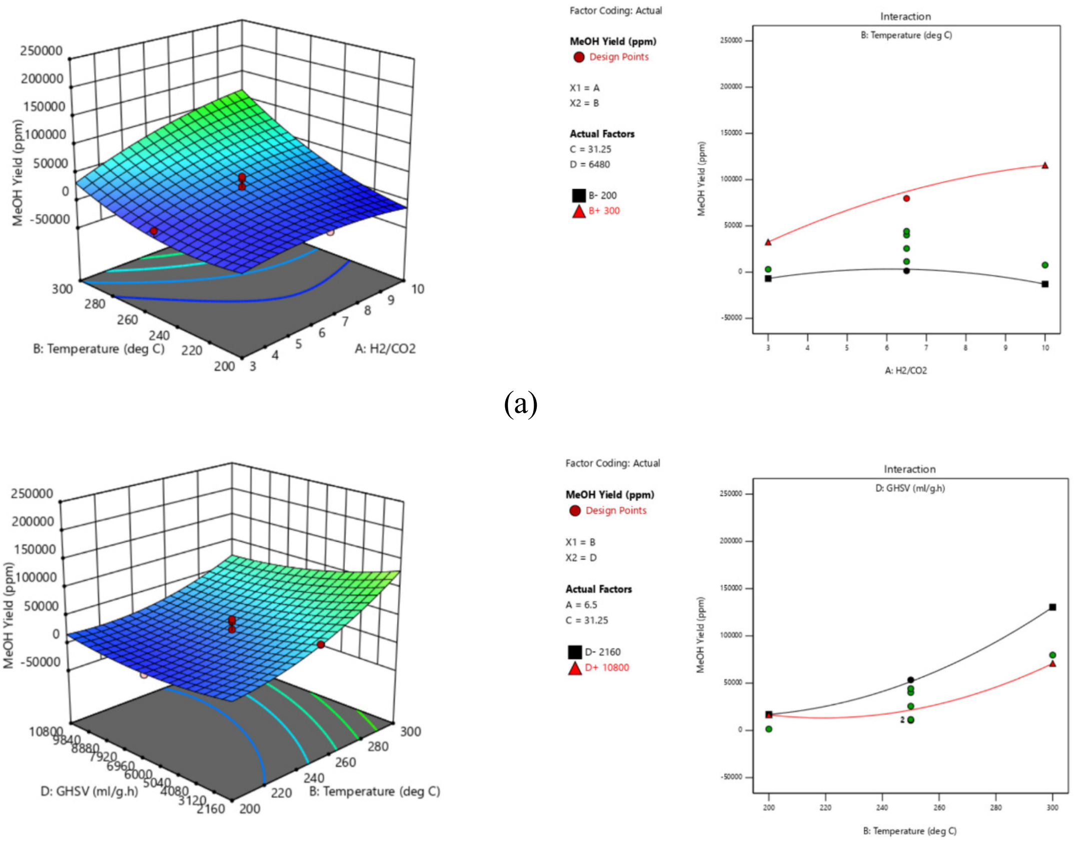


Figure 3. Interaction effect of AB on MeOH selectivity (SMeOH)

Figure 4a and **Figure 4b** show the interaction effect of *AB* and *BD* on MeOH yield (Y_{MeOH}). *AB* has significant influence on Y_{MeOH} which is similar trend as X_{CO2} and S_{MeOH}. The interaction effect in between temperature (*B*) and GHSV (*D*) to Y_{MeOH} is also significant.

When *B* is at low level of 200 °C and decreasing GHSV (*D*) from 10,800 mL/g h to 2160 mL/g h shows an increase by 2.8% (16448.8 ppm to 16928 ppm) in Y_{MeOH}. However, an increase by 46% (70835.4 ppm to 130445 ppm) was observed when the temperature is at high level of 300 °C and GHSV was decreased from 10,800 mL/g h to 2160 mL/g h. The higher the temperature and the lower the GHSV, has increased MeOH yield by 94%.



(a)

(b)

Figure 4. Interaction effect of (a) AB; and (b) BD on MeOH yield

RSM Optimization. The optimum process operating conditions for catalytic activity of the synthesized CZ(M)A catalyst are summarized in **Table 6**. Based on the optimum conditions, the X_{CO2}, S_{MeOH} and Y_{MeOH} were calculated using eqs. (5–7). Three confirmation runs were carried out under the same experimental technique. The calculated and experimental values of X_{CO2} were 28.6% and 30.7% respectively, and 59.2% and 66.3% for S_{MeOH}. While for Y_{MeOH}, 164,000 ppm and 202,000 ppm respectively. The percentage errors between the calculated and experimental values are 7.34% (X_{CO2}), 12.0% (S_{MeOH}) and 23.2% (Y_{MeOH}) which are not within the acceptable range of deviation of 5%. This observation in measured responses could be due to heterogeneity of Cu active sites at atomic scale. Methanol synthesis is a structure sensitive reaction, thus even small variation on distribution of Cu active sites and proportion of low-coordinated surface atoms at atomic scale could lead to significant change in catalytic activity and product selectivity.

Table 6. Optimum process operating conditions for synthesized catalyst CZ(M)A

Variables	Units	Optimum conditions
H_2/CO_2 (A)	-	10
Temperature (B)	°C	300
Pressure (C)	bar	31
GHSV (D)	mL/g h	2160
X_{CO2}, calculated	%	28.6
X_{CO2}, experimental	%	30.7
Percentage error, X_{CO2}	%	7.34
S_{MeOH}, calculated	%	59.2
S_{MeOH}, experimental	%	66.3
Percentage error, S_{MeOH}	%	12.0
Y_{MeOH}, calculated	ppm	164,000
Y_{MeOH}, experimental	ppm	202,000
Percentage error, Y_{MeOH}	%	23.2

High pressure range testing using one factor at a time approach

Le Chatelier's principle indicates that a system at equilibrium will adjust to stress, hence at equilibrium, CO_2 conversion and selectivity to methanol rise with pressure, while CO selectivity declines. The effect of high reaction pressure of 40 − 80 bar on the performance of the CZ(M)A catalyst in CO_2 hydrogenation to methanol was evaluated. The evaluation was carried out in a reactor volume five times bigger than microactivity fixed-bed reactor for low pressure testing in which this reactor can only run at maximum pressure of 40 bar. Meanwhile, the H_2/CO_2, temperature, and GHSV were kept constant using the optimum value from low pressure testing at 10:1, 300 °C, and 2160 mL/g h, respectively.

The catalytic performance in terms of CO_2 conversion is shown in **Figure 5**. The result showed that reaction pressure has a considerable impact on CO_2 conversion, with conversion increasing from 54.80% to 68.35% as reaction pressure was increased from 40 bar to 80 bar. Under a kinetic-controlled regime, increasing the reaction pressure could boost CO_2 conversion by increasing CO_2 and hydrogen adsorption on the catalyst [24].

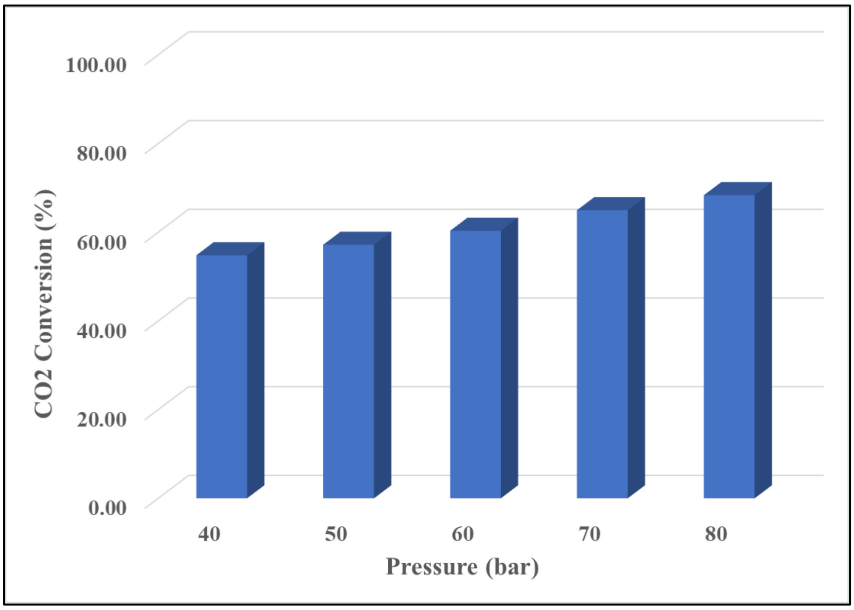


Figure 5. Effect of high reaction pressure of CZ(M)A catalyst on CO_2 conversion

CO production by the RWGS is pressure independent from a thermodynamic aspect [25]. The methanol synthesis from CO_2 hydrogenation, on the other hand, is pressure sensitive due to the reduction of 4 moles of reactants to 2 moles of products during the reaction. This is consistent with Le Chatelier's principle. According to the findings in **Figure 6**, the methanol selectivity increased progressively from 53% to 62% as the reaction pressure increased from 40 to 60 bar. When the reaction pressure was increased from 60 to 80 bar, the selectivity increased dramatically from 62% to 93%. At the greatest reaction pressure, neither CO or methyl formate is formed. Based on the findings, it can be concluded that increasing reaction pressure has a positive effect on methanol production rate by improving CO_2 conversion and, to a lesser extent, increasing methanol selectivity. The highest catalytic performance was achieved at 80 bar with CO_2 conversion of 68.35%, MeOH selectivity of 93%, and MeOH yield of 63.57%.

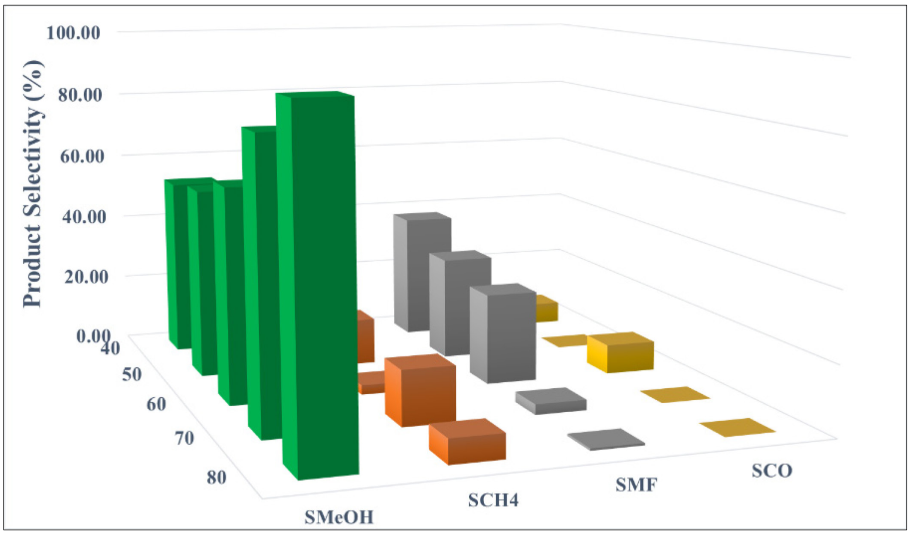


Figure 6. Effect of high reaction pressure of CZ(M)A catalyst on product selectivity

CONCLUSION

The main objective of this research was to identify an alternative method that is both efficient in terms of time and cost, in order to enhance the production of methanol. RSM has become a crucial tool in scientific-analytical research. RSM and OFAT, when used together, showed to be a valuable combo for providing reliable outcomes.

The optimized process operating conditions at low pressure range testing for the synthesized CZ(M)A catalyst for methanol synthesis via CO_2 hydrogenation has been investigated using RSM. Reduced quadratic model was proposed to correlate the experimental variables for all three responses (X_{CO2}, S_{MeOH}, and Y_{MeOH}). Empirical model equations are developed for CO_2 conversion (X_{CO2}), MeOH selectivity (S_{MeOH}) and MeOH yield (Y_{MeOH}). The optimized conditions were at H_2/CO_2 ratio of 10, temperature 300 °C, pressure 31 bar and GHSV 2160 mL/g h. The catalyst was then subjected to high pressure range testing (40 – 80 bar) using OFAT with the optimum H_2/CO_2, temperature, and GHSV from low pressure range testing using. CO_2 conversion and MeOH selectivity increased when reaction pressure increased. No CO or methyl formate formed at reaction pressure of 80 bar with CO_2 conversion of 68.35%, MeOH selectivity of 93%, and MeOH yield of 63.57%.

The combination of RSM and OFAT methods allows for a comprehensive understanding of the factors influencing process performance, optimization of process conditions, validation of optimization results, and insights for further improvement. This integrated approach helps us make informed decisions and achieve desired outcomes in process optimization and improvement efforts.

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NOMENCLATURE

Abbreviations

CZ(M)A	$Cu/ZnO/GVII/GV/GIV/Al_2O_3$
GHSV	Gas hourly space velocity
GVII	Group VII
GV	Group V
GIV	Group IV
MeOH	Methanol
RWGS	Reverse Water Gas Shift

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