Article

Methanol Synthesis: Optimal Solution for a Better Efficiency of the Process

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Abstract: In this research, an ANOVA analysis and a response surface methodology are applied to analyze the equilibrium of methanol reaction from pure carbon dioxide and hydrogen. In the ANOVA analysis, carbon monoxide composition in the feed, reaction temperature, recycle and water removal through a zeolite membrane are the analyzed factors. Carbon conversion, methanol yield, methanol productivity and methanol selectivity are the analyzed responses. Results show that main factors have the same effect on responses and a common significant interaction is not present. Carbon monoxide composition and water removal have a positive effect, while temperature and recycle have a negative effect on the system. From central composite design, an optimal solution is found in order to overcome thermodynamic limit: the reactor works with a membrane at lower temperature with carbon monoxide composition in the feed equal to 10 mol % and without recycle. In these conditions, carbon conversion, methanol yield, methanol selectivity, and methanol production are, respectively, higher than 60%, higher than 60%, between 90% and 95% and higher than 0.15 mol/h when considering a feed flow rate of 1 mol/h. A comparison with a traditional reactor is also developed: the membrane reactor ensures to have a carbon conversion higher of the 29% and a methanol yield higher of the 34%. Future researches should evaluate an economic analysis about the optimal solution.

Keywords: methanol reaction; equilibrium reactions; ANOVA analysis; response surface methodology; optimization

1. Introduction

Methanol production via CO_2 hydrogenation is an important representative among the chemical conversions of CO_2 and offers challenging opportunities for sustainable development.

As a raw material, methanol constitutes the basis for the production of hundreds of chemicals, such as formaldehyde, methyl tertbutyl ether (MTBE), acetic acid, methyl methacrylate, dimethyl terephthalate, and olefins (ethylene and propylene), all basic chemical building blocks for a number of common products [1]. Methanol can also be used as transportation fuel, as a fuel cell hydrogen carrier, as well as in wastewater treatment or in electricity production. It is then an excellent fuel and a key starting material of important industrial reactions [2]. In the recent years, also, methanol is suggested as alternative for chemical energy carrier [3,4].

Generally, in industrial applications, methanol can be produced from syngas, a mixture of CO, CO_2 and H_2 at 50–100 bar and 250 °C–300 °C, using copper and zinc-based catalyst [5,6]. These catalysts are already active at 200 °C and selective towards the formation of H_2 and CO_2. Alternative routes and its use as fuel and chemical are the core of methanol economy [4,7]. Pontzen et al. [8] experimentally show that methanol can be produced from CO_2 and H_2 using conventional catalysts as $CuO/Al_2O_3/ZnO$. However, studies show that the equilibrium yield of methanol from CO_2 at 200 °C and 50 bar is slightly less than 40%, whereas the yield from a mixture of CO_2 and CO at the same conditions is greater than 80% [9].

The production of methanol from pure CO_2 and H_2 has also some thermodynamic limits, as shown by Zachopoulos and Heracleous [10], suggesting the removal of water through sorbents. In fact, water inhibits the reaction rate of methanol formation via CO_2 hydrogenation [11]. In particular, water produced from reverse water gas shift greatly reduces the methanol synthesis rate by suppressing the reaction of methanol production.

Works related to these considerations are few in literature. In fact, works about the production of methanol by syngas are mainly present and different strategies are proposed to improve the efficiency of the process. Mainly, studies involve the in situ methanol removal. Examples are methanol adsorption on fine alumina powder or the use of a solvent, such as tetraethylene glycol, n-butanol, or n-hexane [12]. Westerterp et al. [13] suggest the selective adsorption of water and methanol on a solid, in a trickle bed reactor. An alternative method is based on the in situ separation of reaction products by condensing them on the surface of a condenser inside the reactor, close to the catalyst bed [14]. These solutions have some disadvantages due to the introduction of other chemicals, complicated operations and low space time yields. An alternative to overcome chemical equilibrium is the in-situ condensation of methanol without additional adsorbents or coolers. Van Bennekom et al. [15] suggest the condensation of methanol in situ at high pressure (200 bar) and low temperature (200 °C). It is evident that thermodynamic barrier can be eliminated by removal of reaction products based on the principle of Le Chatelier. Gallucci and Basile [16] suggest the recycle of unconverted synthesis gas after product separation by condensation or the water removal using selective, permeable membranes. The first membrane reactor for methanol production is used by Struis et al. [17] using lithiated Nafion membrane at 200 °C and 4.3 bar. In another work of Struis and Stucki [18] a modeling of membrane reactor for methanol reaction is developed, using a Nafion membrane: a single pass yield is improved by 40%. However, this application is limited because the operative temperature of Nafion membrane is lower than 200 °C. Chen and Yuan [19] analyze a one-dimensional isothermal pseudo-homogeneous model for membrane reactor producing methanol. A silicone rubber/ceramic composite membrane is used. Results show that conversion in membrane reactor is increased by 22% when compared to traditional fixed bed reactor. Also, Barbieri et al. [20] use a ceramic membrane for a reactor producing methanol. Gallucci et al. [21] analyze a zeolite membrane reactor: at the same conditions, conversions are higher in membrane reactor respect to traditional reactor. In other words, the same conversions can be obtained in membrane reactor with lower temperature and pressure compared to the traditional reactor. This aspect should notably reduce the energy demand. A mathematical model for zeolite membrane reactor permeable to water is developed by Gallucci and Basile [16]. Results shows that it is possible to have s higher conversion and methanol selectivity with respect to a traditional reactor at the same operating experimental conditions.

When considering the analyzed works reported in literature where syngas is used in the feed, the feasibility of methanol synthesis from CO_2 can be achieved by circumventing the thermodynamic limits through innovative solutions: the presence of CO, the operation at lower temperature, the recycle of unconverted gas, the presence of membrane permeable to water inside the reactor. In fact, a mixture of CO–CO_2 allows for having a higher conversion and yield, as shown by Kunkes and Behrens [22]. Several studies show that a maximum in methanol production from a mixture of CO–CO_2 occurs at CO_2 concentration of 2–5 mol % of total carbon [23–25]. Lower temperatures are preferred by thermodynamic even if kinetic is not favored and a more active catalyst should be developed. The recycle of unconverted gas to ensure a higher conversion is also suggested by Montebelli et al. [26]. However, this results in high investment and operating costs and large pressure drops. The extraction of water, an inhibitor for reaction, through membrane shifts the equilibrium toward to product, but requires higher capital investment [27].

In this research, an analysis of chemical equilibrium for methanol production by pure CO_2 and H_2 is carried out: the above proposed solutions, as the presence of CO in the feed considering that the maximum methanol production is obtained with 5 mol % of CO_2, lower operating temperature, the recycle of unconverted gas, and the presence of zeolite membrane permeable only to water,

are analyzed. An ANOVA analysis and a response surface methodology (RSM) through a central composite design (CCD) are developed to find the optimal solution that overcome thermodynamic limits ensuring a higher carbon conversion, methanol yield, methanol production and methanol selectivity. Data for these analyses are obtained by simulations of methanol reactor in Aspen Plus.

2. Materials and Method

2.1. ANOVA Modeling

For the methanol reactor, the estimation of main and interaction effects is developed by ANOVA analysis (analysis of variance); in this analysis, it is determined if effects and interactions among investigated factors are significant respect to experimental error (σ_ε). Main factors are evaluated by Yates's algorithm through Excel 2016 software. Statistical significance is checked by F-value (Fischer variation ratio) and *p*-value (significant probability value). Model terms are selected or rejected based on probability value within 95% of confidence interval (or 5% significance level). In this research, σ_ε is evaluated by means of the mean square (MS) of interactions that are not significant. A 2^4 full factorial design with 16 simulation tests is performed for this research [28]. A mathematical model could be obtained with significant factors and the quality of the model is assessed by the coefficient of determination, R^2. R^2 represents a pure correlation between measured and predicted values, and it is indicative of response variation explained by model. Then, in this statistic method all factor levels are fully changed so that it is possible to measure any variation in response. One of the most important advantages of this method is the limited number of experiments necessary to identify the best solution. CO composition in the feed, reaction temperature, the recycle of unconverted gases, and the removal of water through a zeolite membrane are considered as factors in this research. Carbon conversion, methanol yield, methanol production and methanol selectivity are considered as responses, for which mathematical models are developed.

2.2. Response Surface Methodology

The aim of RSM is to find the optimal operating conditions of the process or to determine a region that satisfies the operating specifications, maintaining a reduced number of experiments [29]. RMS is then used in process design and optimization.

The RSM methodology is developed using a central composite design for fitting a second order model. Generally, the CCD consists of 2^k factorial tests, 2k stars tests and n_c center point tests, where k is the number of studied factors in the experiment. Values at center points are used to estimate the curvature of surface plot. Star points are located at distance α from center point and are used to estimate the coefficient of quadratic terms. Factorial points are used to estimate the coefficient of linear terms and two-way interactions.

Experimental or simulation data are used to develop a second-order polynomial model as in the following correlation (see Equation (1)) [30]:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i \cdot A_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} \cdot A_i \cdot A_j + \sum_{i=1}^{k} \beta_{ii} \cdot A_i^2 + \varepsilon \tag{1}$$

where β_o is intercept, β_i, β_{ij}, β_{ii} are first-order, interactive, and second-order effects, respectively, i and j represent the number of k factors, while ε is residual error. This method is then able to evaluate interaction effects, pure quadratic effects, or third- and fourth-order effects and so on; it is the most efficient evaluation method, and it improves the quality of data. To determine the significance of each term in the equation and to estimate the goodness or fitting quality, the polynomial equation is validated by analysis of variance. A response surface plot is constructed by using the fitted model. In this research, with four factors, star points are set on the centers of each face of factorial face: the value of α is equal to 1 and the design is denominated as face-centered central composite design.

It requires only three levels of each factor, and in practice it is frequently difficult to change factor levels. 31 simulations in Aspen Plus are developed: 16 factorial tests, eight star tests, and six central tests, and one replication test. Software Minitab 18 is used to carry out the CCD analysis for response surface methodology.

2.3. Reactor Modeling

In order to carry out ANOVA and RSM analysis a modeling of methanol reactor is developed in Aspen Plus software, as shown in Figure 1. It is an equilibrium reactor where reactions and equilibrium constants are defined and it is fed with CO_2 and H_2, at flow rate equal to 1 mol/h, as shown in Table 1. Carbon dioxide and hydrogen are in stochiometric conditions.
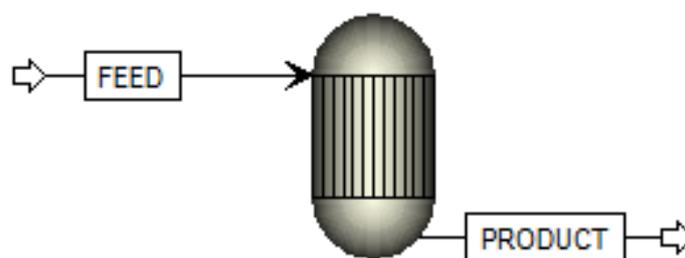
Figure 1. Equilibrium reactor for methanol production in Aspen Plus environmental.

Table 1. Material and energy balances of methanol reactor obtained in Aspen Plus environmental.

Factor	Feed	Product
Temperature (K)	493	493
Pressure (bar)	55	55
Vapor fraction	1	1
Total flow rate (mol/h)	1	0.766
CO_2 flow rate (mol/h)	0.25	0.165
H_2 flow rate (mol/h)	0.75	0.51
H_2O flow rate (mol/h)	0	0.084
CO flow rate (mol/h)	0	0.0069

The reactor is characterized according the following reactions (see Equations (2) and (3)):

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \, \Delta H_{298K} = -49.43 \text{ kJ/mol} \tag{2}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \ \Delta H_{298K} = +41.12 \text{ kJ/mol} \tag{3}$$
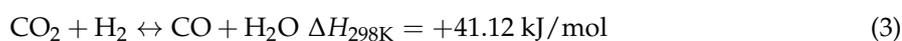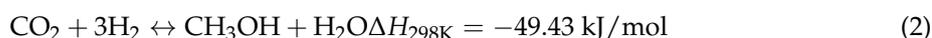
The equilibrium constants of two reactions are respectively the following (see Equations (4) and (5)) [24]:

$$\ln(Keq_1) = \frac{7060}{T} - 24.389 \tag{4}$$

$$\ln(1/Keq_2) = -\frac{4773}{T} + 4.672 \tag{5}$$

First reaction is exothermic so equilibrium constant decreases with temperature; second reaction is endothermic so equilibrium constant increases with temperature. As shown in [24], initially CO_2 reacts to give CO as well as methanol. Since the reverse water gas shift is endothermic, and because of decreasing CO_2 concentration, this slows down the hydrogenation of CO_2 at the reactor inlet. The reverse water gas shift reaches its equilibrium value and switches direction. This results in an inflection point in temperature profile and a concentration evolution of water and methanol. From this point onward, reactions are strictly in series.

A membrane reactor is modelled using six stages in series of reactors and water separators, because the aim of this research is to analyze the equilibrium of methanol reaction by removing water. In fact, membrane is considered to be both not permeable and poorly permeable to other compounds, due to the condensation of water in membrane pores. With these considerations, the presence of membrane inside the reactor is evaluated as percentage of water removal by reaction site to permeation site, as is also suggested by Gallucci and Basile [16].

SRK thermodynamic model is used to carry out simulations in Aspen Plus, because it is the better thermodynamic model for methanol system as found by Cheng et al. [31].

3. Results and Discussion

3.1. Results of ANOVA Analysis

Table 2 shows factors (CO concentration in the feed, reaction temperature, the recycle of unconverted gas, water removal through membrane) and the values of their levels chosen for the factorial plant.

Table 2. Factors and values of their levels chosen in the factorial design of ANOVA analysis.

Code	Factor	Level	
		(−)	(+)
A	CO concentration in the feed (mol %)	0	20
B	Temperature (°C)	200	280
C	Recycle (%)	0	90
D	Water removal (%)	0	80

Carbon conversion to methanol, methanol yield, methanol production, and methanol selectivity are the analyzed responses. Carbon conversion, methanol yield and methanol selectivity are defined, respectively, as in the following relations (see Equations (6)–(8))

$$\text{Conversion (\%)} = \frac{(CO_{2,in} + CO_{in}) - (CO_{2,out} + CO_{out})}{(CO_{2,in} + CO_{in})} \tag{6}$$

$$\text{MeOH yield (\%)} = \frac{MeOH_{out}}{CO_{2,in} + CO_{in}} \tag{7}$$

$$\text{MeOH selectivity (\%)} = \frac{MeOH_{out}}{(CO_{2,in} + CO_{in}) - (CO_{2,out} + CO_{out})} \tag{8}$$

Figure 2 shows the results of ANOVA analysis with significant factors and interactions, while Table 3 reports the general result of ANOVA analysis. As shown in Figure 2 carbon conversion in %, methanol production in mol/h, methanol yield in %, methanol selectivity in % are the chosen responses.
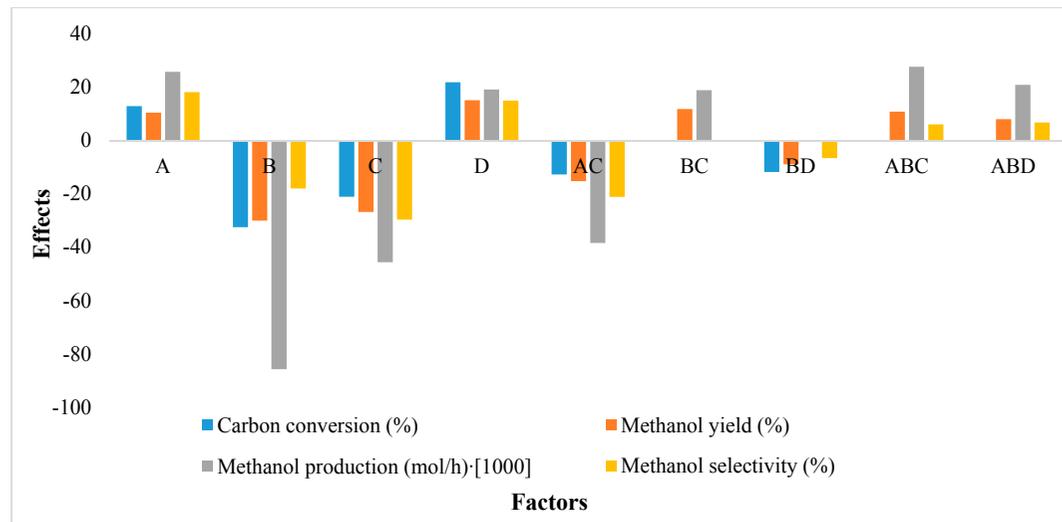
Figure 2. Results of ANOVA analysis considering only significant factors and interactions (A = CO concentration in the feed in mol %, B = Temperature in °C, C = Recycle in %, D = Water removal in %) with values of their effects.

Table 3. Results of ANOVA analysis (A = CO concentration in the feed in mol %, B = Temperature in °C, C = Recycle in %, D = Water removal in %).

Factors	Carbon Conversion (%)				Methanol Yield (%)				Methanol Production (mol/h)				Methanol Selectivity (%)			
	Effects	F-Ratio	*p*-Value	Remarks	Effects	F-Ratio	*p*-Value	Remarks	Effects	F-Ratio	*p*-Value	Remarks	Effects	F-Ratio	*p*-Value	Remarks
A	12.84	10.02	0.051	95%	10.40	15.92	0.016	98%	1.99	17.12	0.014	99%	18.12	71.14	0.001	100%
B	−32.54	64.32	0.001	100%	−30.07	133.03	0.000	100%	16.63	190.85	0.000	100%	−18.01	70.33	0.001	100%
AB	−4.71	1.35	0.310	69%	1.14	0.19	0.684	32%	0.02	0.32	0.603	40%	3.56	2.74	0.173	83%
C	−21.13	27.12	0.006	99%	−26.85	106.08	0.001	100%	13.26	54.08	0.002	100%	−29.71	191.31	0.000	100%
AC	−12.80	9.95	0.034	97%	−15.25	34.22	0.004	100%	4.28	38.28	0.003	100%	−21.17	97.12	0.001	100%
BC	9.34	5.30	0.083	92%	11.78	20.44	0.011	99%	2.55	9.19	0.039	96%	5.74	7.14	0.056	94%
ABC	4.77	1.38	0.305	69%	10.79	17.14	0.014	99%	2.14	19.78	0.011	99%	6.03	7.88	0.048	95%
D	21.83	28.96	0.006	99%	15.10	33.55	0.004	100%	4.19	9.43	0.037	96%	14.89	48.06	0.002	100%
AD	−3.93	0.94	0.387	61%	−6.32	5.87	0.072	93%	0.73	6.37	0.065	93%	−3.90	3.30	0.144	86%
BD	−11.87	8.56	0.043	96%	−8.99	11.89	0.026	97%	1.49	4.30	0.107	89%	−6.62	9.51	0.037	96%
ABD	1.89	0.22	0.665	33%	7.94	9.28	0.038	96%	1.16	11.24	0.028	97%	6.70	9.73	0.036	96%
CD	10.67	6.92	0.058	94%	3.95	2.30	0.204	80%	0.29	2.01	0.229	77%	1.15	0.29	0.621	38%
ACD	3.75	0.85	0.408	59%	1.53	0.35	0.588	41%	0.04	0.40	0.559	44%	0.90	0.17	0.698	30%
BCD	−6.19	2.33	0.202	80%	−3.44	1.74	0.258	74%	0.22	0.03	0.880	12%	−2.75	1.64	0.269	73%
ABCD	−1.91	0.22	0.663	34%	4.09	2.46	0.192	81%	0.31	3.25	0.146	85%	2.96	1.90	0.241	76%

Results show that significant factors and interactions have the same effect on the analyzed responses.

The effect indicates how the analyzed responses vary by changing the level of factor. In other words, the effect is the effect of an independent variable on a dependent variable averaging across the levels of any other independent variables. If by increasing the level of factor, the analyzed response increases the effect is positive; if by increasing the level of factor the analyzed response decreases the effect is negative.

In this study, all the main factors are significant. CO concentration and water removal through a membrane have a positive effect on all responses, while temperature and the recycle of unconverted gases have a negative effect on the studied responses. In order to improve the efficiency of the process with a higher methanol production, it is better to operate in presence of CO or with a membrane permeable to water or with a lower temperature or without the recycle of unconverted gas, allowing to have a reactor with lower sizes and more compact.

The positive effect of CO in the feed is reported by Van den Bussche and Froment [24], funding an optimal CO_2 composition in the feed. The positive effect of water removal is also found by Zachopoulos and Heracleous [10], using water sorption system. The negative effect of temperature is also reported by Skrzypek et al. [32]. The negative effect of recycle is due to the decreasing of kinetic. At fixed number of tubes, recycle has a negative effect: with a higher flow rate, superficial velocity increases and kinetic decreases producing a lower methanol [33]. Manenti et al. [34] suggest that conversion increases when the inlet flowrate is lowered, thanks to the increase in residence time. In fact, a lower volume of gas causes high residence times in the reactor and reaction is near to chemical equilibrium. For these reasons, stages of adiabatic reactors with intermedia refrigeration are also used.

Reaction temperature has a higher effect on carbon conversion, methanol yield and methanol production as compared to other significant factors and interactions. Recycling, instead, has a higher effect on methanol selectivity respect to other significant factors and interactions. These results suggest that temperature has an important role on equilibrium reaction. A higher efficiency of reaction is obtained operating at lower temperature, so new kind of catalysts need to be developed to operate at lower temperature.

Interaction AC has a negative effect: the effect of factor C is lower negative with factor A. The presence of CO and the recycle of produced gas determines a lower efficiency. Interaction BC has a positive effect on methanol production and methanol yield. It is possible to operate at a higher temperature using the recycle of produced gas in order to have a good efficiency of the process. However, the effect of this interaction is lower compared to the effect of main factors. Also, this interaction is not significant for carbon conversion and methanol selectivity.

Interaction BD has a negative effect on carbon conversion, methanol yield and methanol selectivity: the positive effect of membrane, factor D, becomes negative at a higher temperature, factor B. Also, in the presence of membrane, temperature must to be lower. Interactions of third order ABC and ABD have a positive effect on methanol yield, production and selectivity.

Generally, these results suggest that the use of membrane permeable to water or the presence of CO in the feed could improve the efficiency of the process with a higher carbon conversion, methanol yield, selectivity and production avoiding the use of recycle that increases the reactor volume and costs or avoiding the operation at a lower temperature that decreases kinetic.

In particular, membrane has a higher effect on carbon conversion and methanol yield while the presence of CO has a higher effect on methanol production and selectivity.

A mathematical model is developed for the analyzed responses as function of significant factors and interactions, as the following relations (see Equations (9)–(12)):

$$\text{Conversion } (\%) = 31.09 + 6.42 \cdot A - 16.26 \cdot B - 10.56 \cdot C - 6.39 \cdot AC + 10.91 \cdot D \\ -5.93 \cdot BD \ (R^2 = 0.9) \tag{9}$$

$$MeOH\ yield\ (\%)$$
$$= 27.9 + 5.2 \cdot A - 7.62 \cdot AC + 5.89 \cdot BC + 5.39 \cdot ABC + 7.5 \cdot 4D \tag{10}$$
$$- 4.49 \cdot BD + 3.97 \cdot ABD - 15.03 \cdot B - 13.42 \cdot C\ \left(R^2 = 0.96\right)$$

$$MeOH\ production\ \left(\tfrac{mol}{h}\right)$$
$$= 0.08 + 0.012 \cdot A - 0.042 \cdot B - 0.022 \cdot C - 0.019 \cdot AC + 0.009 \cdot BC \tag{11}$$
$$+ 0.013 \cdot ABC + 0.009 \cdot D + 0.010 \cdot ABD\ \left(R^2 = 0.95\right)$$

$$MeOH\ selectivity\ (\%)$$
$$= 25.61 + 9.05 \cdot A - 9.00 \cdot B - 14.85 \cdot C - 10.58 \cdot AC + 3.01 \cdot ABC \tag{12}$$
$$+ 7.44 \cdot D - 3.31 \cdot BD + 3.34 \cdot ABD + 7.44 \cdot D\ \left(R^2 = 0.9\right)$$

where A, B, C, D are main factors respectively CO composition in the feed, temperature, recycle of unconverted gases, and water removal, while BD, AC, BC are the interactions of second order and ABD and ABC are the interactions of third order.

The trend of residues in Figure 3 shows that the obtained mathematical models are correct: a good agreement between calculated and simulation data is present. This is also confirmed by the values of R^2: it is closer to unit for all mathematical models.
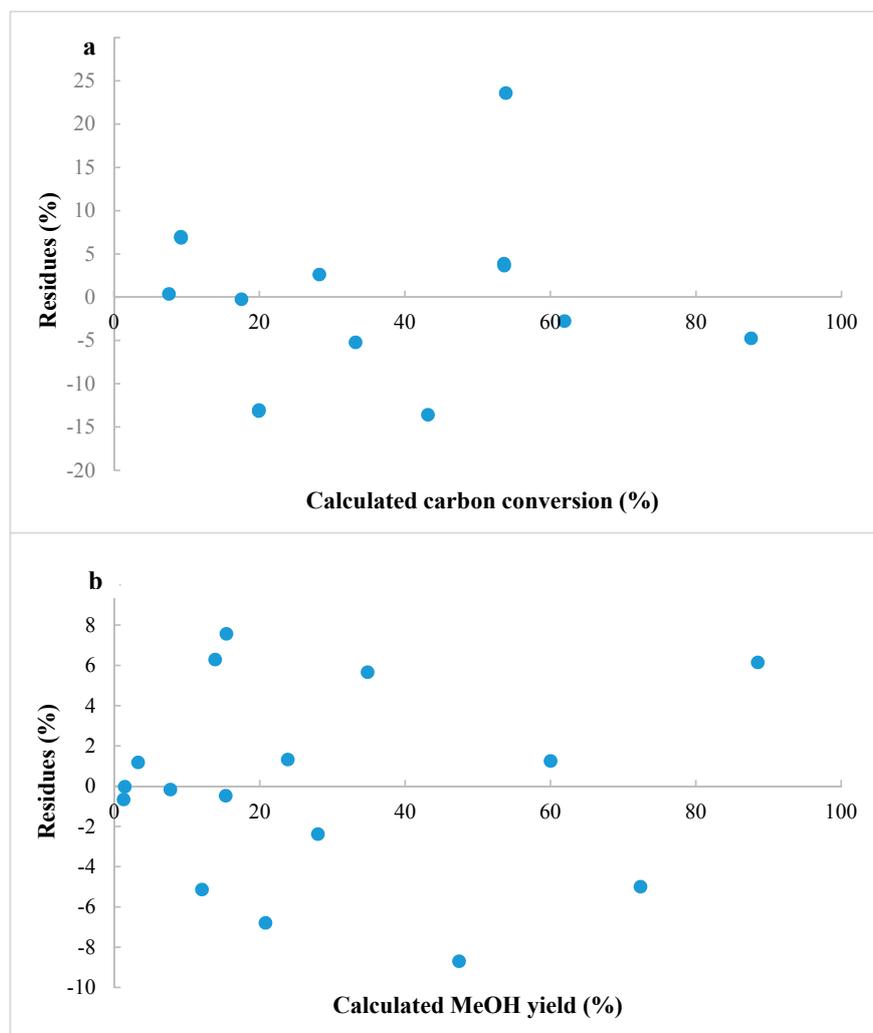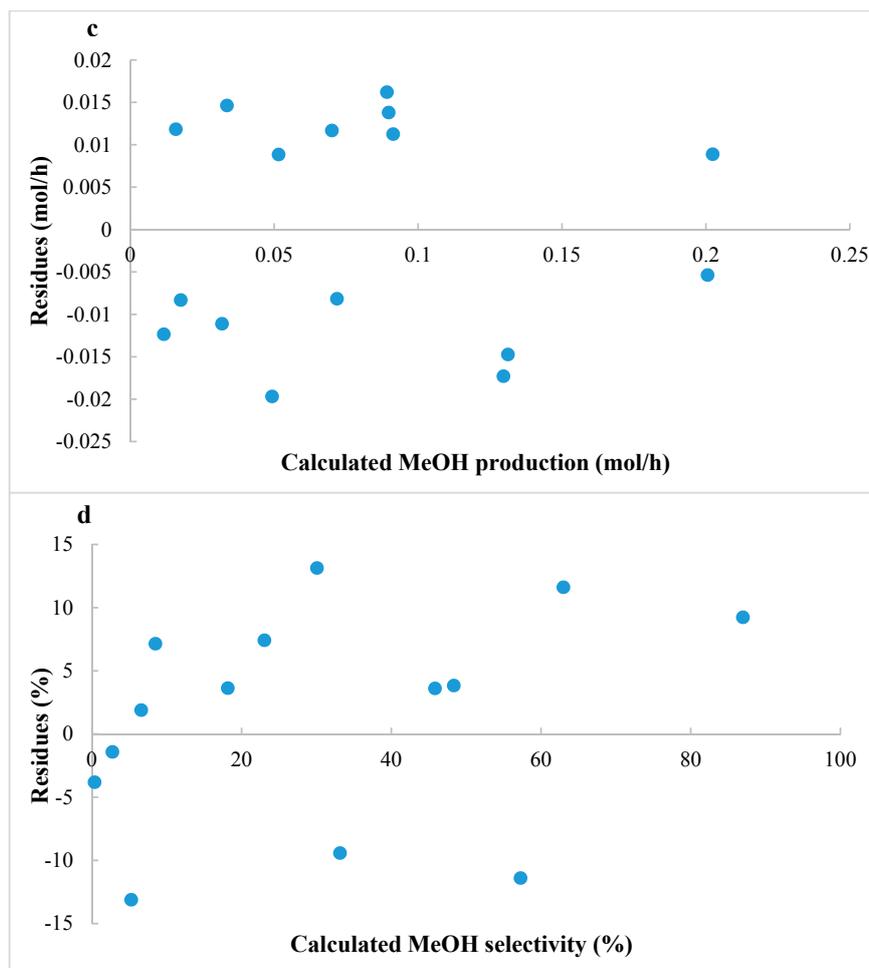

Figure 3. *Cont.*

Figure 3. Trend of residues for (**a**) carbon conversion, (**b**) methanol yield, (**c**) methanol production, and (**d**) methanol selectivity.

An accurate analysis is also developed for interaction factors with the test of two levels. Figure 4 shows the analysis of interaction AC and BD for carbon conversion. Results show that at a higher level of factor A, it is possible to improve carbon conversion to methanol by operating with factor C at a lower level, then without recycle. A higher value of conversion can be obtained with factor D at a higher level and factor B at a lower level.
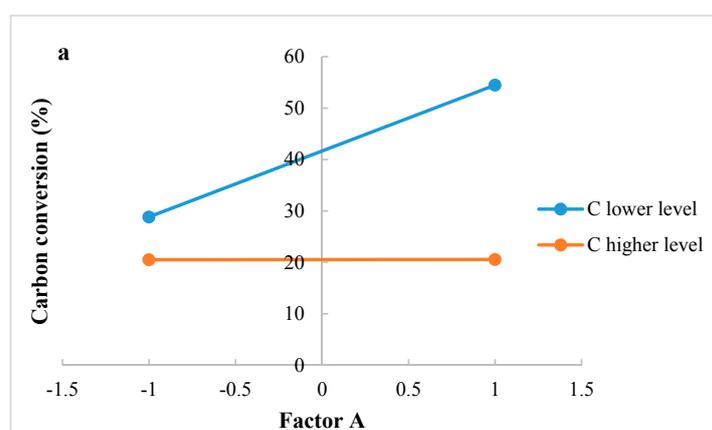
Figure 4. *Cont.*
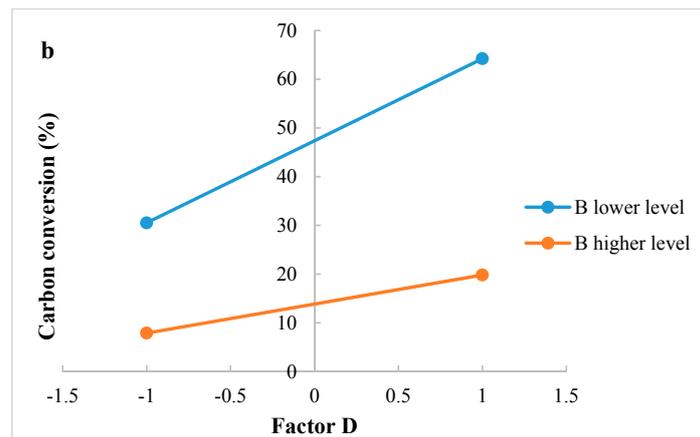
Figure 4. (**a**) Test of two levels for the analysis of interaction AC in carbon conversion; (**b**) Test of two levels for the analysis of interaction BD in carbon conversion. (A = CO composition in mol%, B = temperature in °C, C = recycle in %, D = water removal in %).

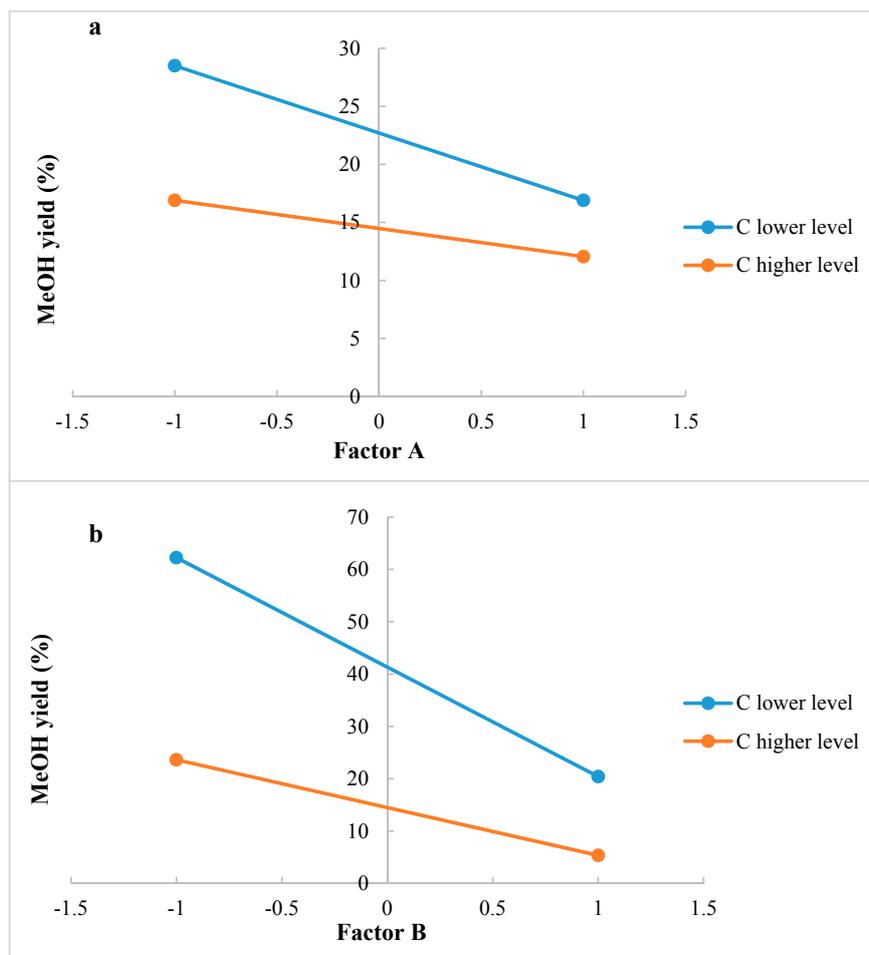Figure 5 shows the test of two levels for interactions AC, BC, BD, that are significant for methanol yield.
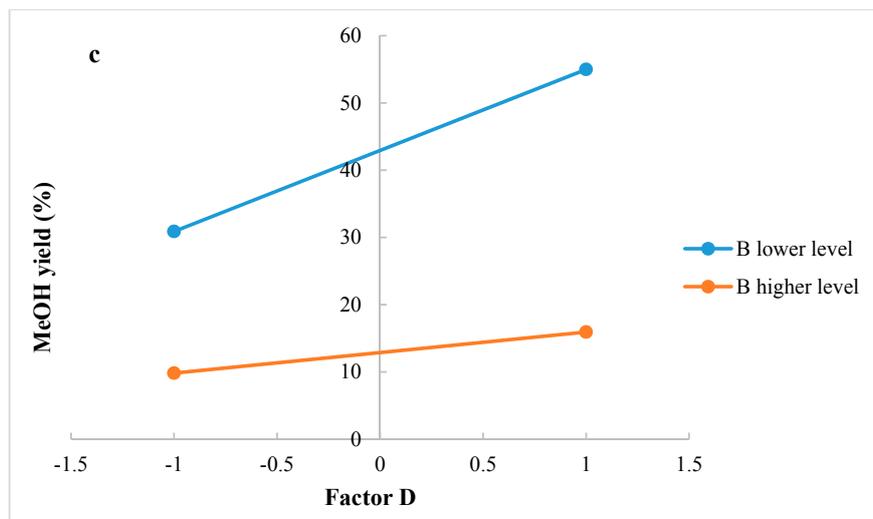

Figure 5. *Cont.*

Figure 5. (**a**) Test of two levels for the analysis of interaction AC in methanol yield; (**b**) Test of two levels for the analysis of interaction BC in methanol yield (**c**) Test of two levels for the analysis of interaction BD in methanol yield. (A = CO composition in mol%, B = temperature in °C, C = recycle in %, D = water removal in %).

With factor A at a lower level, a higher methanol yield is obtained with factor C at a lower level. However, in these conditions, a lower carbon conversion is obtained. Factor B and C at a lower level in interaction BC allows to have a higher methanol yield. In interaction BD, factor B and D must to be at a lower and higher level, respectively, to have a higher methanol yield: carbon conversion is also higher.

Figure 6 shows the test of two levels for interactions AC and BC in methanol production. Methanol production is higher at lower level of factor A and C in interaction AC. Factor B and C at a lower level ensure to have a higher methanol production. These conditions in interaction BC allow for also to have a higher methanol yield.
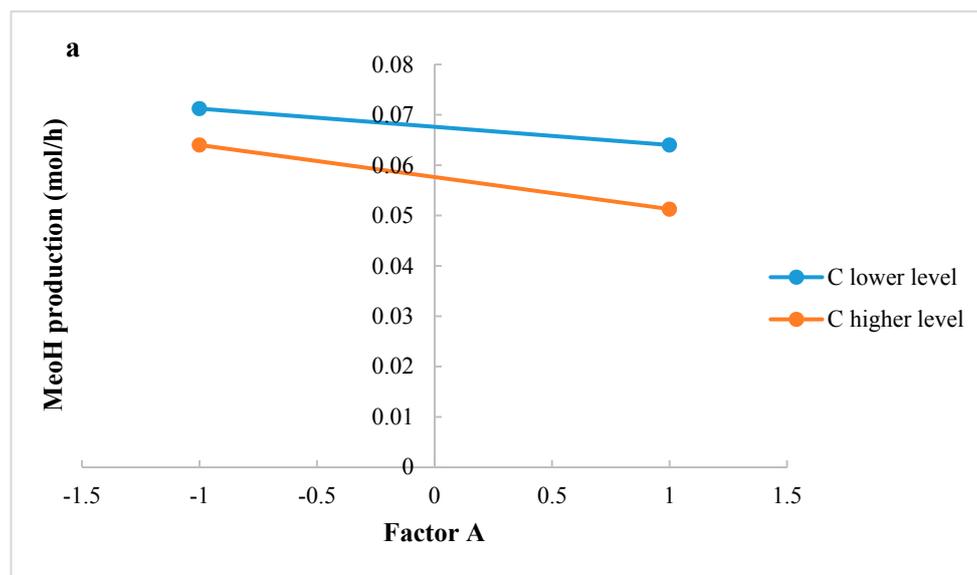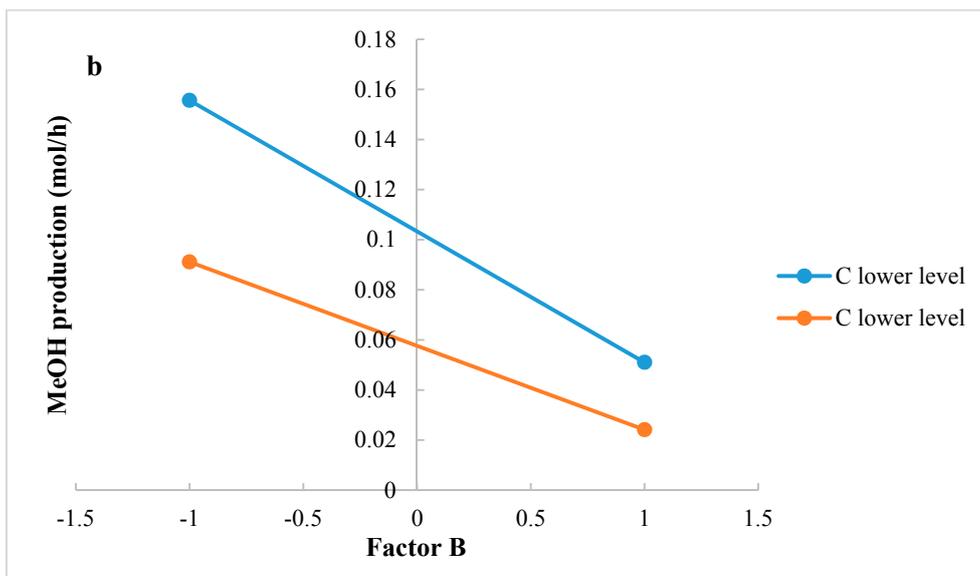

Figure 6. *Cont.*

Figure 6. (**a**) Test of two levels for the analysis of interaction AC in methanol production; (**b**) Test of two levels for the analysis of interaction BC in methanol production (A = CO composition in mol%, B = temperature in °C, C = recycle in %, D = water removal in %).

Figure 7 shows an analysis of significant interaction AC and BD for methanol selectivity. As for carbon conversion, for interaction AC a higher selectivity is obtained with factor A at a higher level and factor C at a lower level. In interaction DB, factor D and B at a lower level ensures a higher methanol selectivity.

The analysis of two levels suggests that a common interaction that ensures a higher efficiency for all analyzed responses is not present. In order to optimize the process, it is preferable to consider the main factors, in particular the addition of CO to pure CO_2 in the feed or the use of membrane permeable to water.
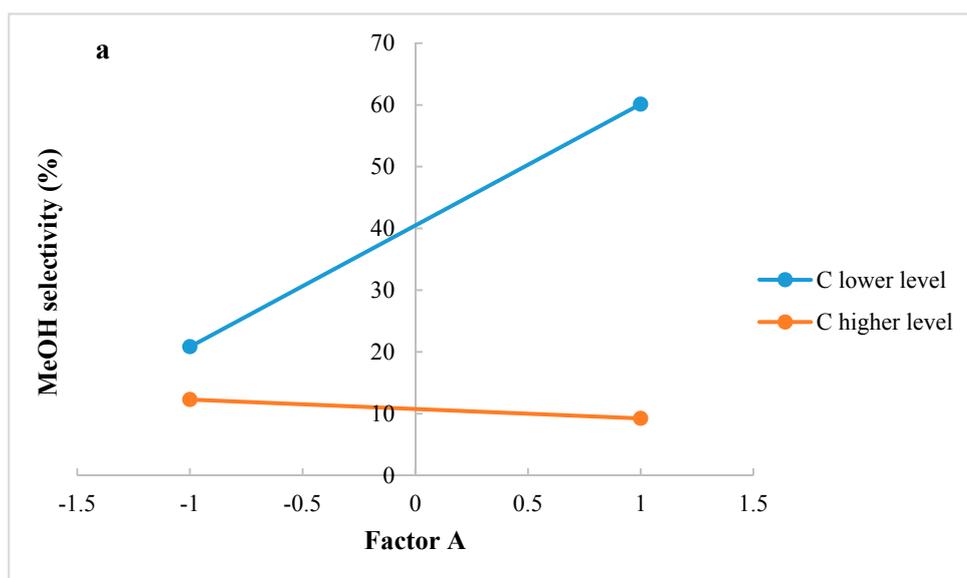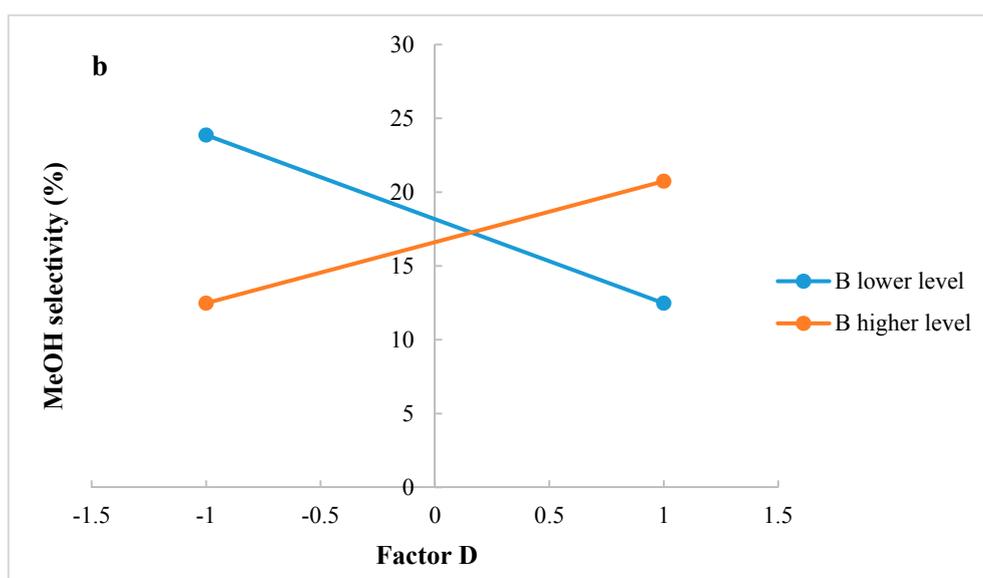

Figure 7. *Cont.*

Figure 7. (**a**) Test of two levels for the analysis of interaction AC in methanol selectivity; (**b**) Test of two levels for the analysis of interaction BD in methanol selectivity (A = CO composition in mol %, B = temperature in °C, C = recycle in %, D = water removal in %).

3.2. Results of Response Surface Methodology

Table 4 shows the chosen factors and the values of their levels set in a face centered composite central design, used to find the response surface plot of the responses analyzed in ANOVA analysis. Factors are the same used in previous ANOVA analysis: CO concentration in the feed, temperature, the recycle of unconverted gas and the removal of water through a membrane. An analysis of three levels is developed for each factors.

Table 4. Factors and values of their levels chosen in CCD analysis.

Code	Factor	Level		
		(−)	(0)	(+)
A	CO concentration in the feed (mol %)	0	10	20
B	Temperature (°C)	200	240	280
C	Recycle (%)	0	45	90
D	Water removal (%)	0	40	80

Figure 8 shows the response surface plot of carbon conversion: it is possible to have a conversion higher than 60% using a membrane reactor at single pass with a removal of water equal to 40% and a CO composition in the feed equal to 10% (Figure 8D). In this case, temperature can be lower, improving kinetic. The same conversion can be obtained also in other cases with membrane reactor and recycle of gases. However, this determines a reactor with greater sizes, increasing its costs, so they are not the better solutions. Then, among all better solutions a membrane reactor at single pass is chosen because it allows to decrease the costs. A carbon conversion higher than 60% can be obtained also at lower temperature, with CO composition in the feed equal to 20%, with recycle and water removal equal to 40% in the first case (Figure 8A). In the second case, carbon conversion higher than 60% can be obtained also in membrane reactor (water removal equal to 80%), with recycle, at lower temperature and with CO composition in the feed equal to 10% (Figure 8E). Figure 8 shows also that in many cases a temperature higher than 240 °C decreases carbon conversion because kinetic is not favored. In particular, carbon conversions are between 10% and 30%.
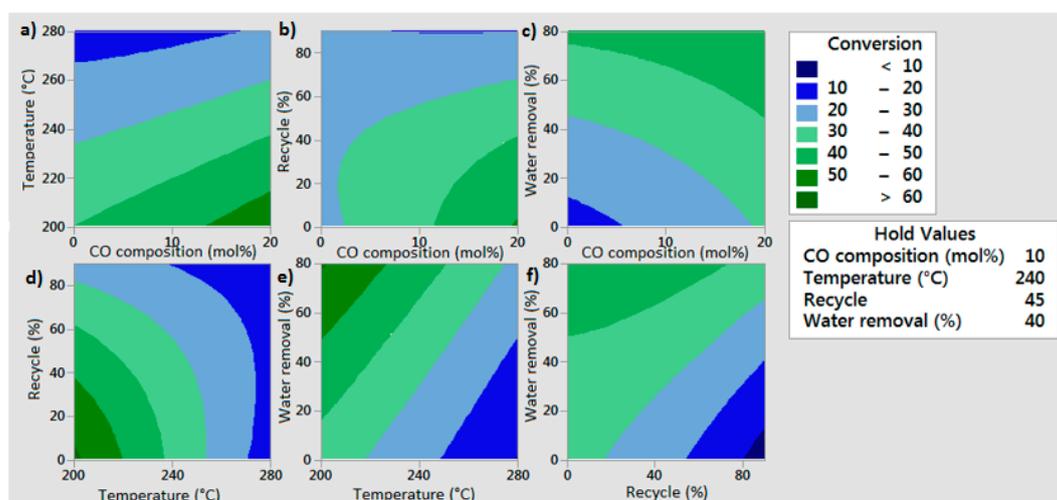
Figure 8. Surface plots of carbon conversion obtained by CCD analysis: (**a**) carbon conversion as function of temperature and CO composition in the feed; (**b**) carbon conversion as function of recycle and CO composition in the feed; (**c**) carbon conversion as function of water removal and CO composition in the feed; (**d**) carbon conversion as function of recycle and temperature; (**e**) carbon conversion as function of water removal and temperature; (**f**) carbon conversion as function of water removal and recycle.

Using a membrane reactor at single pass as in Figure 8D, methanol yield, production, and selectivity are also higher, as shown in Figures 9–11, respectively. A methanol yield higher than 60%, a methanol production higher than 0.15 mol/h and a methanol selectivity between 90% and 95% can be obtained.

Figure 9 shows that a quite high methanol yield between 50% and 60% can be obtained also in membrane reactor with recycle (but increasing costs) in two cases. In the first case, temperature is equal to 200 °C, CO composition in the feed is equal to 20 mol %, recycle is equal to 45%, and water removal is equal to 40% (Figure 9A). In the second case, temperature is 200 °C, water removal is 80%, CO composition in the feed is equal to 10 mol % and recycle is equal to 45% (Figure 9E).
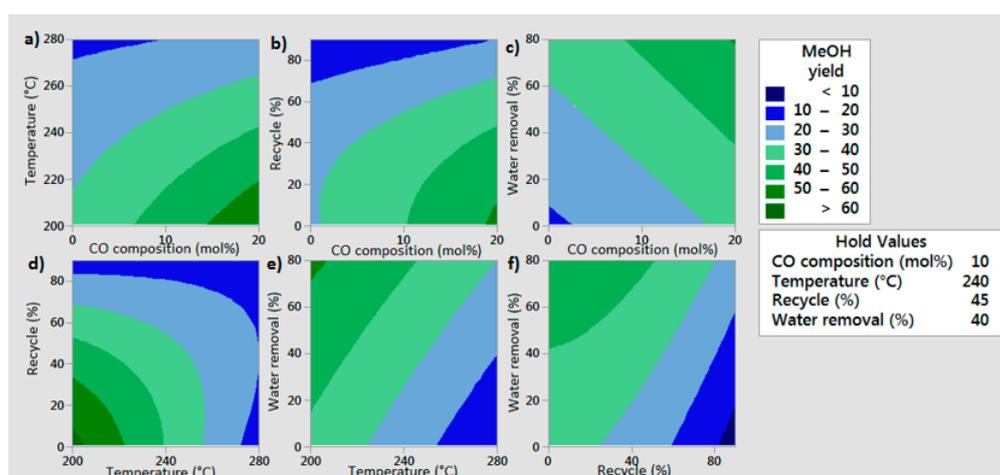

Figure 9. Surface plots of methanol yield obtained by CCD analysis: (**a**) methanol yield as function of temperature and CO composition in the feed; (**b**) methanol yield as function of recycle and CO composition in the feed; (**c**) methanol yield as function of water removal and CO composition in the feed; (**d**) methanol yield as function of recycle and temperature; (**e**) methanol yield as function of water removal and temperature; (**f**) methanol yield as function of water removal and recycle.

It is possible to have a methanol yield between 50% and 60% also in membrane reactor at single pass with CO composition in the feed equal to 20 mol %, temperature equal to 240 °C and water removal equal to 40% (Figure 9B). However, carbon conversion is between 40% and 50%. Generally, lower methanol yields are present at lower carbon conversions where higher temperatures are present.

Figure 10 shows that methanol production higher than 0.15 mol/h can also be obtained in other conditions that however do not ensure a higher carbon conversion and methanol yield (Figure 10A,E,F) or utilize a reactor with higher costs (Figure 10B,F). Results show that lower methanol productions are clearly and rightly present at lower carbon conversions.
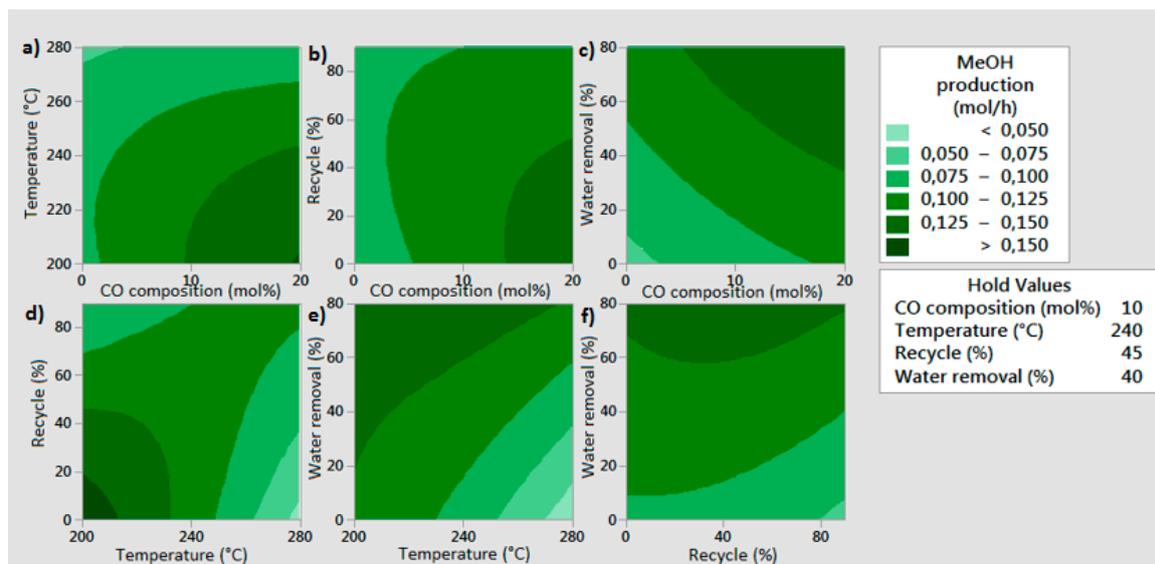

Figure 10. Surface plots of methanol production obtained by CCD analysis: (**a**) methanol production as function of temperature and CO composition in the feed; (**b**) methanol production as function of recycle and CO composition in the feed; (**c**) methanol production as function of water removal and CO composition in the feed; (**d**) methanol production as function of recycle and temperature; (**e**) methanol production as function of water removal and temperature; (**f**) methanol production as function of water removal and recycle.

Figure 11 shows that a methanol selectivity higher than 95% can be also obtained in two cases (Figure 11 C,E), but carbon conversion varies between 10% and 50%. The first case, Figure 11C, is when CO composition in the feed is 20 mol %, water removal is 80%, recycle is 45% and temperature is 240 °C. In this condition, carbon conversion is between 40% and 50%. The second case, Figure 11E, is when, temperature is 280 °C, recycle 45%, water removal 80%, and CO composition in the feed is 10 mol %: carbon conversion is lower and between 10% and 40%.
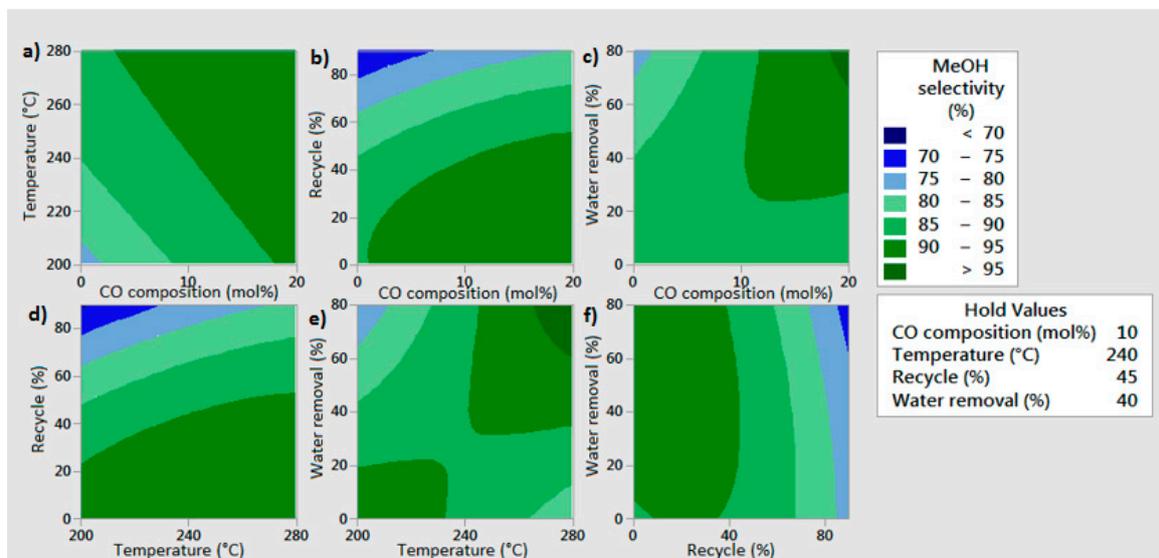
Figure 11. Surface plots of methanol selectivity obtained by CCD analysis: (**a**) methanol selectivity as function of temperature and CO composition in the feed; (**b**) methanol selectivity as function of recycle and CO composition in the feed; (**c**) methanol selectivity as function of water removal and CO composition in the feed; (**d**) methanol selectivity as function of recycle and temperature; (**e**) methanol selectivity as function of water removal and temperature; (**f**) methanol selectivity as function of water removal and recycle.

Optimal conditions and reactor configurations are then found to produce methanol by CO_2 and H_2. These results are in agreement with results found in ANOVA analysis where main factors can ensure a higher efficiency of the process.

Figures 12–15 show the trend of surface plot of carbon conversion, methanol yield, methanol production and methanol selectivity in the space as function of the analyzed factors.
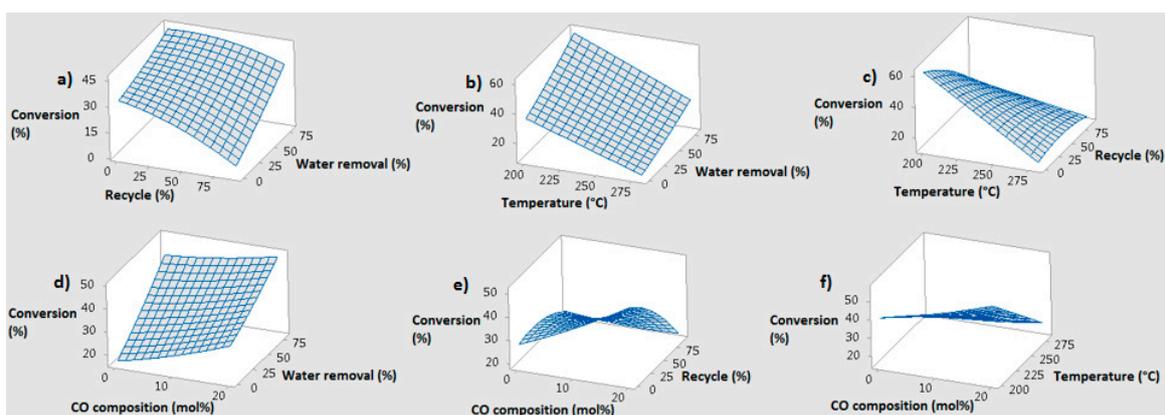

Figure 12. Carbon conversion plots as function of analyzed factors (hold values: recycle 45%, temperature 240 °C, water removal 40%, CO composition in the feed 10 mol%): (**a**) carbon conversion as function of recycle and water removal; (**b**) carbon conversion as function of temperature and water removal; (**c**) carbon conversion as function of temperature and recycle; (**d**) carbon conversion as function of CO composition in the feed and water removal; (**e**) carbon conversion as function of CO composition in the feed and recycle; (**f**) carbon conversion as function of CO composition in the feed and temperature.
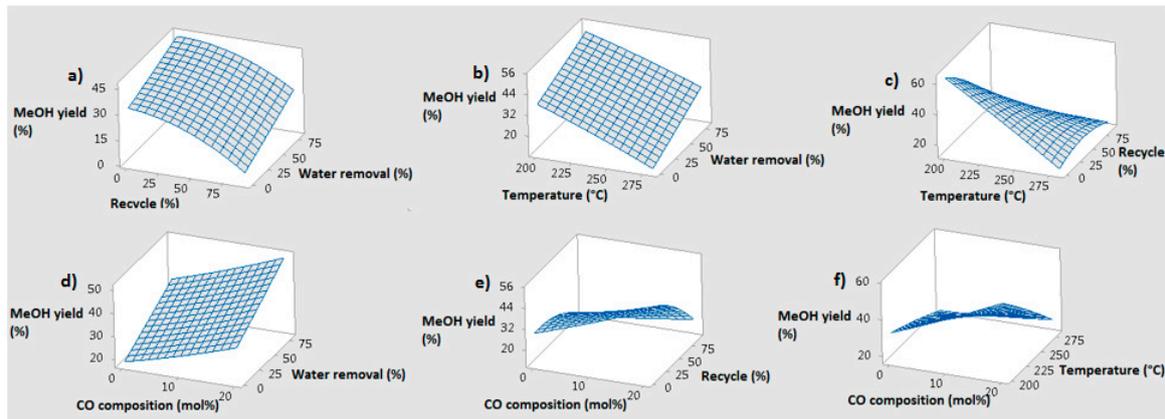
Figure 13. Methanol yield plots as function of analyzed factors (hold values: recycle 45%, temperature 240 °C, water removal 40%, CO composition in the feed 10 mol %): (**a**) methanol yield as function of recycle and water removal; (**b**) methanol yield as function of temperature and water removal; (**c**) methanol yield as function of temperature and recycle; (**d**) methanol yield as function of CO composition in the feed and water removal; (**e**) methanol yield as function of CO composition in the feed and recycle; (**f**) methanol yield as function of temperature and CO composition in the feed.
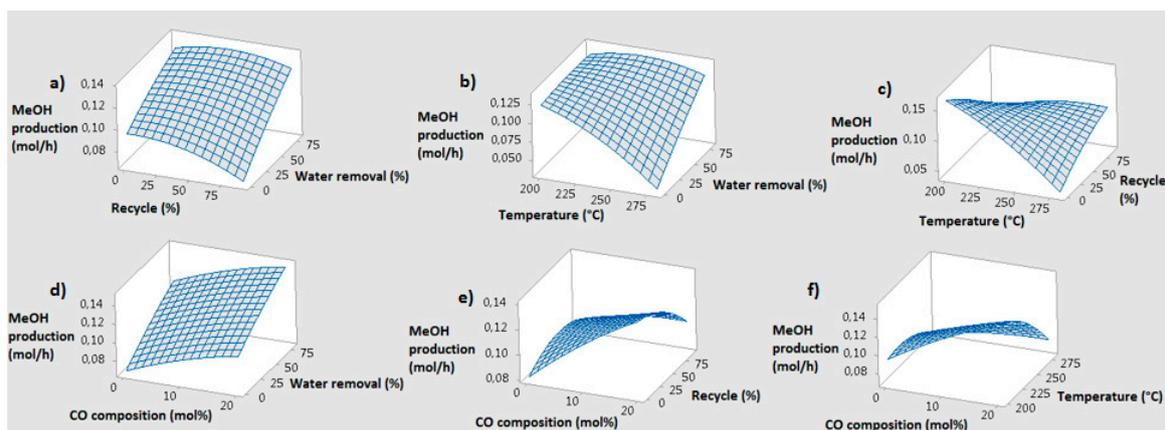

Figure 14. Methanol production surface plots as function of analyzed factors (hold values: recycle 45%, temperature 240 °C, water removal 40%, CO composition in the feed 10 mol%): (**a**) methanol production as function of recycle and water removal; (**b**) methanol production as function of temperature and water removal; (**c**) methanol production as function of temperature and recycle; (**d**) methanol production as function of CO composition and water removal; (**e**) methanol production as function of CO composition in the feed and recycle; (**f**) methanol production as function of CO composition in the feed and temperature.
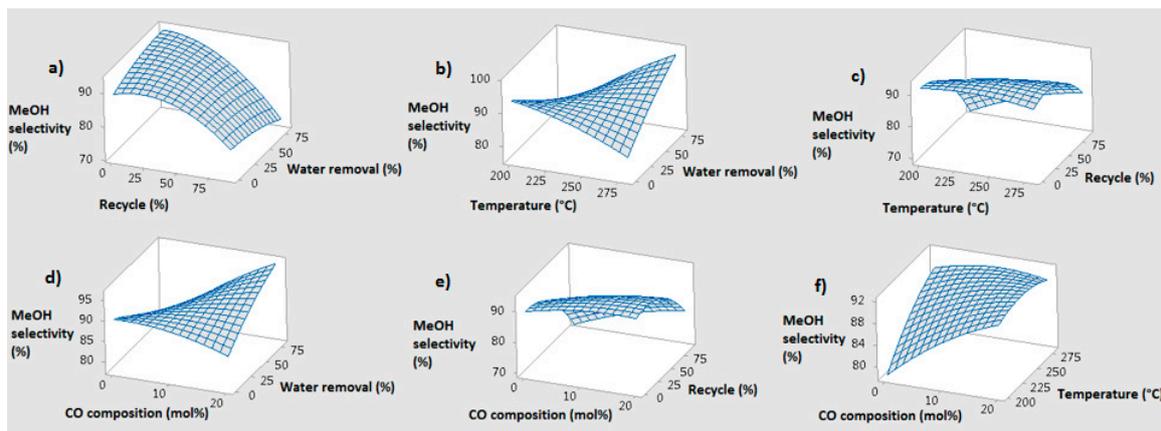
Figure 15. Methanol selectivity surface plots as function of analyzed factors (hold values: recycle 45%, temperature 240 °C, water removal 40%, CO composition in the feed 10 mol%): (**a**) methanol selectivity as function of recycle and water removal; (**b**) methanol selectivity as function of temperature and water removal; (**c**) methanol selectivity as function of temperature and recycle; (**d**) methanol selectivity as function of CO composition in the feed and water removal; (**e**) methanol selectivity as function of CO composition in the feed and recycle; (**f**) methanol selectivity as function of temperature and CO composition in the feed.

The quadratic expressions of these plots are the following (see Equations (13)–(16)):

$$\text{Conversion } (\%) = 32.55 + 5.37 \cdot A - 14.82 \cdot B - 9.26 \cdot C - 6.22 \cdot AC + 10.86 \cdot D \\ + 8.65 \cdot BC + 4.36 \cdot CD \tag{13}$$

$$\text{MeOH yield } (\%) = 32.97 + 7.63 \cdot A - 3.7 \cdot AC + 11.71 \cdot BC + 8.36 \cdot D - 3.7 \cdot AC \\ - 5.2 \cdot AB - 12.12 \cdot B - 11.98 \cdot C \tag{14}$$

$$\text{MeOH production } \left(\frac{\text{mol}}{\text{h}}\right) \\ = 0.114 + 0.017 \cdot A - 0.023 \cdot B - 0.019 \cdot AC + 0.022 \cdot D \\ + 0.021 \cdot BD + 0.038 \cdot BC \tag{15}$$

$$\text{MeOH selectivity } (\%) = 77 - 0.8 \cdot C + 8.42 \cdot BD \tag{16}$$

where A, B, C, D are main factors respectively CO composition in the feed, temperature, recycle and water removal, while BD, AC, BC are the interactions of second order.

A comparison between a membrane reactor with the optimal operating conditions found through the previous response surface methodology and a traditional reactor is developed. The traditional reactor is at 200 °C, 40 bar and the feed in amount of 1 mol/h contains CO_2 and H_2 in stochiometric conditions. Results are reported in Table 5. The advantages of membrane reactor are evident, allowing for a higher conversion, methanol production, and yield. In particular, carbon conversion and methanol yield are respectively increased by 29% and 34%. In addition, methanol production and hydrogen conversion are higher in membrane reactor, respectively, equal to 0.15 mol/h and 49%.

Table 5. Comparison between membrane reactor and traditional reactor for methanol production.

Factor	Membrane Reactor	Traditional Reactor
Carbon conversion (%)	62	33
Hydrogen conversion (%)	49	32
Methanol yield (%)	61	27
Methanol production (mol/h)	0.15	0.076

4. Conclusions

The main obstacle to methanol synthesis from CO_2 rich streams is thermodynamic. For pure CO, a one pass methanol yield of nearly 55% can be obtained at 252 °C, while pure CO_2 would only yield 18%.

In this research, different strategies to overcome thermodynamic limits in methanol production from pure CO_2 and H_2 are suggested and analyzed. The addition of CO to the feed, the operating at lower temperature, the recycle of unconverted gas, and the use of membrane removing water inside the reactor can be applied to have higher efficiencies in methanol production. An ANOVA analysis and a response surface methodology are carried out with the aim to find the best solution. In these analyses, chosen factors are: CO composition in the feed, operating temperature, the recycle of unconverted gases, and the presence of zeolite membrane permeable to water. The analyzed responses are: carbon conversion, methanol production, methanol yield and methanol selectivity. Results suggest that a higher carbon conversion, methanol yield, selectivity and production are obtained from a mixture of CO_2 and H_2, adding 10 mol % of CO in the feed, operating at 200 °C, and using a membrane reactor without recycle. In these conditions, when considering a feed flow rate of 1 mol/h carbon conversion, methanol yield, selectivity, and production are respectively higher than 60%, higher than 60%, 0.15 mol/h, and between 90% and 95%. A tradition reactor, operating at 200 °C, with hydrogen and carbon dioxide in stochiometric conditions allows for having a conversion only equal to 33% and a methanol yield of 27%: the advantages of optimized systems are evident. In addition, the traditional system produces only 0.076 mol/h of methanol, while membrane reactor can produce 0.15 mol/h of methanol with a feed flow rate of 1 mol/h. The feasibility of methanol synthesis from carbon dioxide can be achieved by circumventing the thermodynamic limitations, through innovative reactor design. Future research should evaluate economic considerations about the optimal solution.

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