RSM approach for stochastic sensitivity analysis of the economic sustainability of a methanol production plant using renewable energy sources

D. Bellotti*, L. Cassettari, M. Mosca, L. Magistri*

(*) TPG, University of Genoa, Italy

ABSTRACT

This study aims at investigating the economic viability, at the pre-feasibility level, of a 5MW electrolyser base-methanol production plant, coupled with a PV power plant. The Authors investigated the impact of different parameters, such as the PV plant size, the electrical energy cost and the components capital costs on the methanol production cost and on the system economic viability. It was also analyzed the minimum recommended sale price of the methanol in order to assure an adequate time frame for the return of the investment, considering a different combination of the investigated parameters.

An economic sensitivity analysis, based on the RSM approach, was performed in order to define the most promising economic conditions under which the plant can be considered a profitable investment in terms of ARR. A guide for an economically viable plant design, allowing for the identification of the most suitable combination of the economic parameters, was proposed as a kind of "maps of existence". For the reference case, the Methanol Production Cost (MPC) resulted around 324 €/ton and the minimum methanol sale price to achieve a PBP of 10 years. The sensitivity analysis identified the cost of electricity and the capital cost of the electrolyser as the most affecting parameters for the system economic viability. In terms of ARR, the methanol price represents the most significant factor. Considering a methanol sale price ranging between 400 and 1200 €/ton, the ARR varied from 5% (20 year of PBP) to 20% (5years of PBP). From the environmental point of view, it is worth underling that the methanol production plant here proposed allows to recycle about 5800 tons of CO_2 per year and to avoid the consumption of about 5.2 MNm^3 of NG per year (compared to the traditional production).

Keywords: CO_2 utilization, renewable energy, power to methanol, economic sensitivity analysis, Response Surface Methodology

NOMENCLATURE

Abbreviation

ANOVA	*Analysis of Variance*
ARR	*Average Rate of Return*
CC	*Capital Cost*
CCD	Central Composite Design
CCS	*Carbon Capture Sequestration*
DoE	*Design of Experiment*
FCC	Face-Centered Central Composite
GHG	*Greenhouse gas*
ICE	*Internal Combustion Engine*
MPC	*Methanol Production Cost*
NOx	*Nitrogen Oxide*

NPV	*Net Present Value*
PBP	*Pay Back Period*
PEC	*Purchased Equipment Cost*
PEM	*Polymer electrolyte membrane*
PM	*Particulate Matter*
PV	*Photovoltaic*
RES	Renewable Energy Sources
RSM	*Response Surface Methodology*
TCI	*Total Capital Investment*
TPG	*Thermochemical Power Group*

1. Introduction

Until today, the scientific community agreed with the fact that the increase of Earth's temperature during the last century is due to an increase in the GHG emissions as consequence of human activities (Intergovernmental Panel On Climate Change IPCC, 2014). In particular, the CO_2 emissions represent about 65% of the total GHG emission. Some important actions need to be taken in order to face the problem of global climate change and, indeed, new technologies need to be developed in order to reduce the global GHG emission.

Beyond hypotheses as evocative as unrealistic about the total replacement of the fossil fuels with RES, still, for several decades to come, coal, oil, and natural gas will continue to play a primary role in both industrial and civil uses (U.S. Energy Information Administration, 2017). Therefore, the possibility of producing an innovative fuel with a low environmental impact, as the methanol, is an option that deserves to be investigated.

The methanol production by the CO_2 captured from the flue gases of the fossil-fueled power plant and by the H2 produced through the water electrolysis employing the renewable energy is expected to be one of the most promising technologies for the emission reduction in the next future (Blumberg et al., 2019) (Bozzano and Manenti, 2016).

In the last years, the methanol market is significantly grown considering that it is becoming more and more interesting as electrical energy storage medium, as hydrogen carrier or directly as fuel for transport and power production.

The methanol showed great potential as a substitute of the diesel and gasoline for automotive transportation and offers significant benefits from the environmental impact point of view thanks its "soot-free" combustion and the lower CO2 emissions compared to the fossil fuels (Zhen and Wang, 2015)

The maritime sector has shown in recent years an increasing interest in methanol in place of the traditional fuel to face the main issue related to the more and more strictly emission regulation. (Ellis et al., 2018; "Methanol Institute," 2018)

The methanol synthesis process through CO_2 hydrogenation is rather well known and studies on the reaction mechanism and catalyst have been carried out in order to investigate the possibility to improve the system conversion and efficiency (Leonzio, 2018). Up to now, the main challenge to the diffusion of this kind of technology is mainly related to its economic feasibility.

Several thermo-economic analyses have been proposed in literature considering different potential applications of the electrolyzer-based methanol synthesis process depending on the electrical energy and CO_2 sources.

The integration of the power to methanol plant with a fossil-fueled power plant for the valorization of the CO_2 captured from the flue gases and the improvement the system flexibility was investigated by Atsonios et al. (2016), and by Bellotti et al. (2019).

Szima and Cormos (2018) analyzed the methanol production from CO_2 provided by an industrial plant and H2 produced employing renewable energy, including a gas turbine and the integration of an ORC cycle to improve the system efficiency. Instead, the potentialities of the methanol as renewable energy storage were analyzed by Matzen et al. (2015) where the methanol was synthesis utilizing hydrogen produced by water electrolyzer power by wind energy and CO2 supplied by a bio-ethanol plant. The results were compared to the traditional fossil-based process by a multi-decision matrix on the base of economic and sustainability indicators; the renewable-integrated concept gained the highest overall weighted score.

Hank et al. (2018) evaluated the production cost of sustainable methanol employing wind energy compared to a grid connect option. All the cited works performed an economic analysis of the system comparing and evaluating the impact of different parameters (energy cost, hydrogen production cost, methanol price, etc..) on the methanol production cost and on the system economic viability. All of them agree that the most critical component is the electrolyzer due to its high capital cost and the significant energy consumption required. Some works report also a sensitivity analysis to evaluate the percentage variation of different economic parameters on the system profitability. Nevertheless, in all the cases, the analysis of effect was limited to qualitative analysis and to a superposition principle.

The present work aims to innovate by proposing a different methodology for the sensitivity analysis based on the use of the Response Surface Methodology-RSM approach that allows, for the quantification of the effects of the different parameters on the outputs and their interactions that, in some cases, can result even more effective than the single parameters.

The main advantage of such approach is that helps to achieve a more comprehensive description of the problem and a more effective analysis, as already put in evidence by other recent studies conducted by the authors (Bendato et al., 2016) (Bendato et al., 2015).

In this study the Authors intend to analyze the economic viability, at the pre-feasibility level, of a 5MW electrolyser based-methanol plant coupled with a PV power plant , by varying some parameters (such as the PV plant size, the electrical energy cost, and components capital costs). The scope is to evaluate their impact on the system feasibility and to identify the most promising conditions. Moreover, the minimum price at which the methanol should be sold in order to assure an adequate time of the return of the investment is investigated considering a different combination of the parameters above mentioned.

At first, the analysis has been carried out on a 10MW PV plant as reference case and considering the actual Italian economic scenario, hence the current capital cost of the components and the current market values for the electrical energy purchase and the methanol sale. Then, an economic sensitivity analysis has been performed in order to define the most promising economic conditions under which the plant can represent a profitable investment. Moreover, it was possible to sketch a kind of “maps of existence” that can represent a guide to the economically viable plant design allowing for the identification of the best combination of the economic parameters.

The main goal is to provide a comprehensive overview of the problem from the economic standpoint according to an exhaustive sensitivity analysis performed by using the RSM approach, that at the best knowledge of the authors was not already proposed.

2. Methodology

The aim of the Design of Experiments (DoE) techniques, is to determine, in stochastic systems, the influence on a selected objective function for one or more independent variables (named factors), varying among different levels or treatments. The significance of such factors is determined through a statistical comparison of the average of the observations under each treatment (Box and Draper, 1987,)(Montgomery, 2013). An important evolution of DoE is the so-called Response Surface

Methodology (RSM) that aims to define the optimal design (the grid of candidate points in the experimental region) in order to build regression models for the objective function.

To fit a first-order regression model, the RSM identifies as best experimental design the Two-Level Factorial Design. to fit second-order regression models, the Central Composite Design (CCD) or the Face-Centered Central Composite (FCC) design are adopted. D-optimal, I-Optimal or user-defined designs are suitable to fit higher order regression models. Figure 1 shows the grid of candidate points, the total numbers of candidate points and the fitted regression model for a two-level factorial design, a CCD and a FCC in a 2-dimensional experimental region (two factors) are respectively represented.

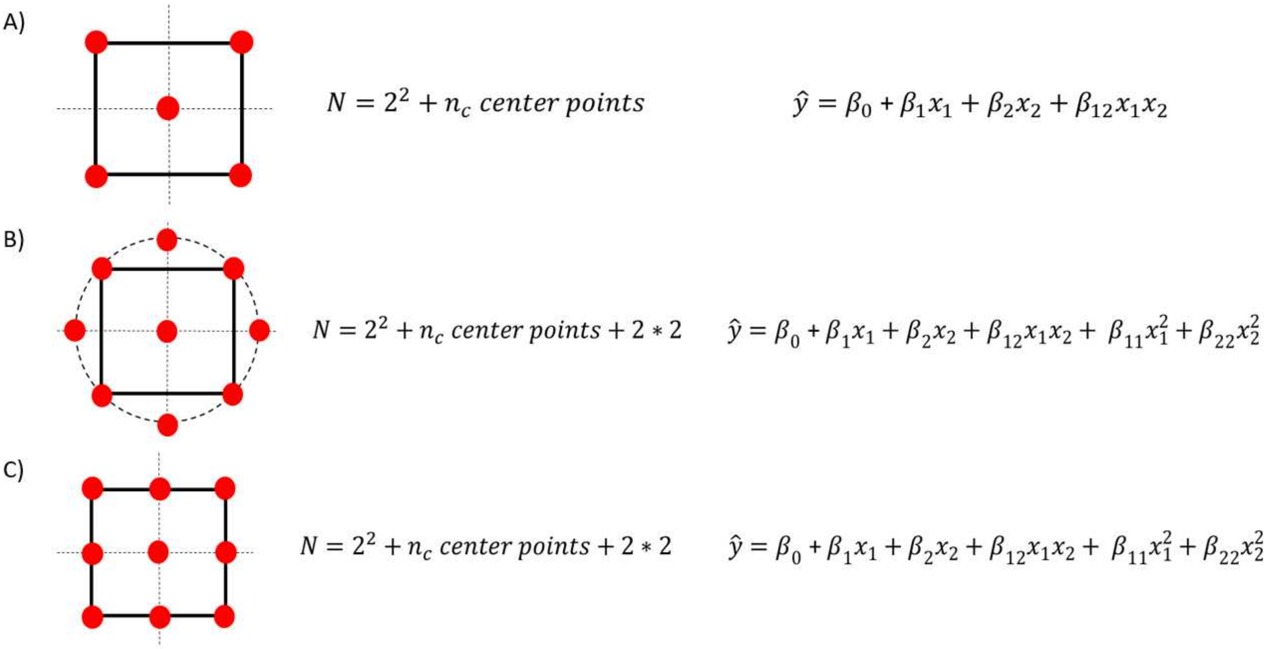


Figure 1 A) Two-level Factorial Design: grid of candidate points and first-order regression model for a 2-dimensional space; B) Central Composite Design: grid of candidate points and second-order regression model for a 2-dimensional space; C) Face-Centered Composite Design: grid of candidate points and second-order regression model for a 2-dimensional space

Response surface methodology proved to be an adequate modeling tool for the mathematical representation of several systems and also a useful tool for optimizing process conditions in the industrial behavior. Brown and Brown (2012) used the RSM approach to optimise the process parameter of an auger reactor fot the bio-oil production. Grahovac et al. (2012) performed the optimization of multiple responses in the context of the ethanol production from thick juice. Applications of the RSM approach correlated to an economic analysis of an industrial process are reported by Rodrigues et al. (2019), in which a statistical optimization of the supercritical CO_2 extraction of Eucalyptus bark at industrial scale was performed; the RSM optimization performed in this work intended to maximize the Total Yield and Productivity, and to minimize the cost of Manufacturing (COM) and Process Energy of the supercritical fluid extraction process. The analysis was carried out considering different process factors and three (of the four) responses modeled by RSM (i.e. COM, Productivity, and Process Energy), it required the knowledge of economic parameters such as capital investment, process costs, and human labor expenses. Ascough et al. (2013) used RSM to develop an integrated farm-level economic/environmental risk framework for trade-off analysis between farm profitability and environmental externalities (impacts). The RSM approach in this study uses a surface regression least squares method to fit linear, quadratic and cross product response combined surfaces. Ekren and Ekren (2008) used response surface methodology (RSM) in size optimization of an autonomous PV/wind integrated hybrid energy system with battery storage. In this study the response surface output performance measure is the hybrid system cost and the design parameters are the PV size, wind turbine rotor swept area and the battery capacity. The optimum result obtained by RSM was confirmed by using the loss of load probability (LLP) and autonomy analysis.

The main steps followed to build the regression model are outlined in the following diagram.

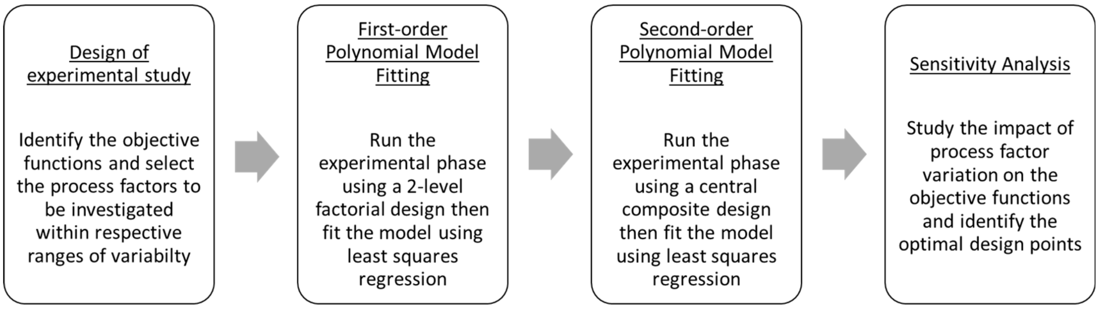


Figure 2 Steps for building response surface metamodels

3. Plant layout description

The conceptual block diagram of the system under investigation is reported in Figure 3.

The methanol is synthesized from the carbon dioxide captured from the exhaust gas of a coal-fired power plant and the hydrogen produced by a 5MW PEM water electrolyzer. A PV plant is installed for the methanol plant electrical energy supply. During the period in which the solar energy is not available, it is assumed to purchase the required electrical energy from the grid.

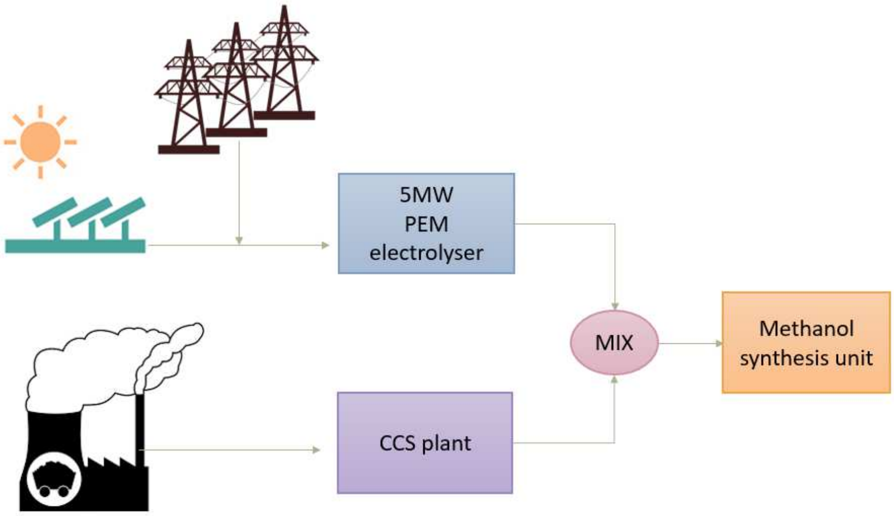


Figure 3 Simplified plant layout

Below, the main components of the system under investigation are described:

Photovoltaic power plant

The PV plant is installed for the methanol plant energy supply. The PV panels' average efficiency is assumed to be equal to 18% with a specific power of about 200 W/m^2. The PV panels production is calculated on the basis of the average monthly solar radiation related to the Northern Italy (ENA, 2013). Moreover, the plant equivalent operating hours are set equal to the Italian average for 2015 (GSE, 2016) of about 1200 hours. Figure 4 shows the average monthly solar radiation for Northern Italy.

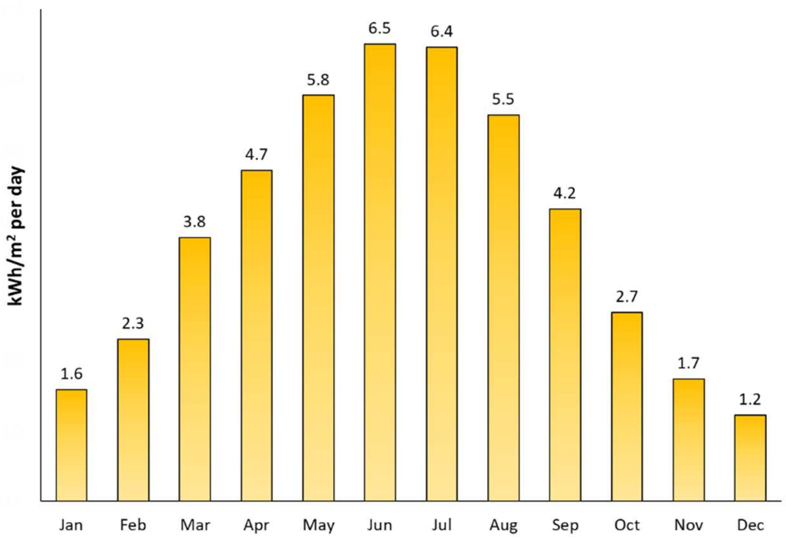


Figure 4 Average monthly insulation curve (ENA, 2013)(GSE, 2016)

According to the previous works from the authors and taking into account the low solar energy availability (about 1200 h_{eq}), the PV plant size needs to be, at least, twice the PEM size, so that the energy produced can be a relevant part of the plant energy balance (at least 25%). Therefore, assuming to install a 5MW PEM electrolyzer, a 10MW PV plant is the minimum size to consider(Rivarolo et al., 2014)(Bellotti et al., 2015)

PEM water electrolyzer

The PEM electrolyzer is a device that produces hydrogen and oxygen throughout the water electrolysis process. The energy consumption is assumed to be equal to about 4.7 kWh/Nm^3 of H_2, meaning that for each MWh consumed, about 19 kg/h of H2 and 152kg/h of oxygen are produced.

In the system under investigation, the considered PEM size is 5MW which enables a production of about 832 ton/yr of H_2, assuming system availability equal to 95%.

Carbon capture system

The amine-based CCS system is installed in order to sequestrate the necessary CO_2 for the methanol synthesis from the exhaust gas of a coal-fired power plant. The CO_2 content in the flue gas is assumed to be equal to 19% in mass. The capture efficiency is assumed to be equal to 90% and the thermal and electrical energy consumption of the CCS system is set equal to 3 GJ/tonCO_2 and 110kWh/tonCO_2, respectively. The CCS system is sized in order to be able to capture the required amount of CO_2, hence it is able to process about 3500kg/h of flue gases, sequestrating about 700kg/h of CO_2. The CO_2 that exits the CCS is pre-compressed up to 30bar before being mixed with the hydrogen and sent to the methanol synthesis unit.

Methanol synthesis unit

The methanol is synthesized from hydrogen and carbon dioxide, according to the following reaction:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_r = -49\ kJ/mol$$

The catalytic reaction is exothermic and takes place in a range of temperature and pressure of 250 – 300 °C and 50 -100 bar on $CuO/ZnO/Al_2O_3$ as catalyst. In the present work, the H_2 and CO_2 flows are mixed in stoichiometric ratio (1:3) and sent to the reactor for the methanol synthesis. Then, the gaseous products enter the distillation section in order to separate the water and obtain the methanol in liquid form. The reactor conversion efficiency (defined as the ratio between the mass of methanol actually produced and the mass of methanol that can be theoretically produced at the stoichiometric conditions) is assumed to be equal to 96%.

In Table 1, the main technical parameters of the plant component are reported.

Table 1 Main technical parameters (Rivera-Tinoco et al., 2016)(Van-Dal and Bouallou, 2013)(Jadhav et al., 2014)(Bellotti et al., 2017)(Mohammad R M Abu-Zahra et al., 2007)

Photovoltaic panels	
Panel average efficiency	18%
Panel specific power	196 W/m2
Equivalent operating hours	1200 h
PEM Electrolyser	
Electrical consumption	4.7 kWh/Nm^3 di H_2
Pressure	30 bar
Efficiency	75%
PEM availability	95%
Carbon Capture system	
Treatment kind	Amines (MEA) (30%)
Flue gases inlet T[°C] and p[bar]	40°C, 2bar
Thermal energy consumption per tonne of CO_2	3 GJ_{th}/kgCO2
CO_2 outlet temperature[°C] pressure[bar]	40°C, 2 bar
CO_2 capture rate	90%
Methanol Reactor	
Working Pressure	80 bar
Temperature	240 °C
Recirculation factor of unreacted syngas	0.85
Conversion efficiency	96%
Molar H_2 : CO_2 ratio	3:1

In Table 2, the energy and mass balance of the plant is reported, assuming a 10MW PV plant. The overall energy consumption includes both the PEM electrical energy demand and the auxiliaries (i.e. compressors, pumps).

Table 2 Main thermodynamic results

Annual 10MW PV plant production	12000 MWh
Annual electrical energy purchased from the grid	33771 MWh
Annual electrical energy consumption	45771 MWh/yr
Annual methanol production	4047 ton /yr
Annual Oxygen production	6324 ton/yr

4. Economic assumption

The Italian economic scenario is taken as reference for the thermo-economic analysis. The main economic assumptions referred to the base case are reported in the following.

Electrical energy cost

As demonstrated in previous works of the authors (Rivarolo et al., 2014), considering the low capacity factor of the PV plant, the sole use of the renewable energy is not sufficient to assure an adequate exploitation rate of the plant; it is, therefore, necessary to purchase energy from the grid when electricity from the PV plant is not available. Hence the cost of the electrical energy represents a term of primary importance for the economic feasibility of the plant under investigation. In Figure 5, the monthly average electrical energy market price between 2013 and 2017 is reported. The prices range between 30€/MWh and 70€/MWh and the average value is equal to about 50€/MWh ("GME - Gestore dei Mercati Energetici SpA," 2018). The same range of values is used in the sensitivity analysis in order to investigate the influence of the energy cost.

In the reference case analysis, the electrical energy for the electrolyzer supply is assumed to be purchased from the grid at 30 €/MWh.

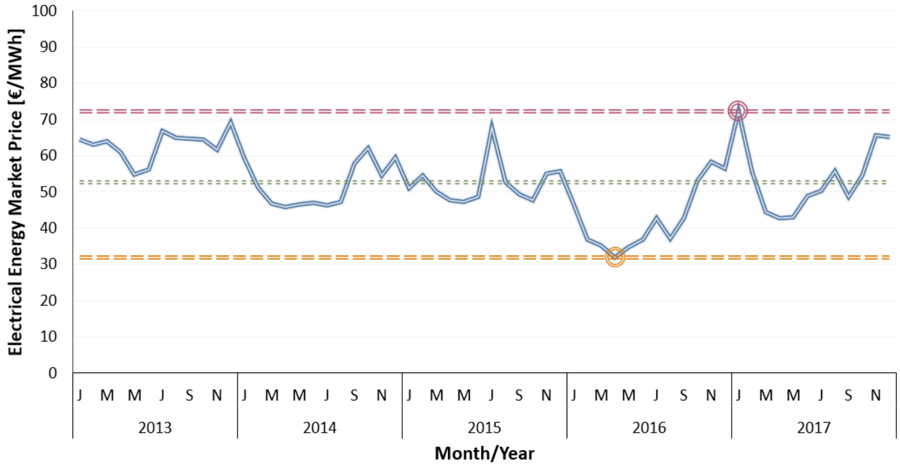


Figure 5 Italian monthly average electrical energy market price between 2013 and 2017 ("GME - Gestore dei Mercati Energetici SpA," 2018)

Methanol selling price

The methanol selling price depends on the economic scenario where the plant is going to operate; in this analysis, the European market is chosen as a target for the methanol sale. The average European Posted Contract Price of methanol between 2013 and 2018 is about 350 €/ton, fluctuating in the range of 225 and 450 €/ton and the mode is around the 370€/ton as reported in ("Methanex Corporation," 2018)("Methanol Market - Global Industry Analysis, Size, Share, Growth, Trends and Forecast 2017 - 2026," 2017). Moreover, the average Non-Discounted Reference price in the same period is about 415€/ton. For simplicity and in consideration of the previous works from the authors (Bellotti et al., 2019, 2017), the methanol price for the reference case is assumed equal to 400€/ton.

Oxygen selling price

As already discussed in previous works, the sale of oxygen co-produced by the electrolyzer is crucial for the methanol plant economic feasibility. The oxygen selling price is assumed 150 €/ton, which represents the minimum selling price for the medical use of oxygen (Intratec, 2018). It is worth noting that the oxygen purity produced by electrolyzer (>99.9%) is sufficient for medical and industrial applications, therefore no further purification treatments are needed. (EIGA and ASSOCIATION, 2015)

Purchased equipment cost estimation

The total Purchased Equipment Cost (PEC) is the sum of the capital cost of each plant component calculated in accordance to the cost functions reported in Table 3. The cost functions are extrapolated from literature data, applying the cost-capacity method or directly from private communication with the manufacturer (Mohammad R.M. Abu-Zahra et al., 2007; Asif et al., 2018; International Renewable Energy Agency (IRENA), 2018; Pérez-Fortes et al., 2016; "Private Communications by Hydrogenics," 2018).

Table 3 Main components cost functions

Photovoltaic plant	$C_{PV} = 1822.6 \cdot \left(P_{inst[\mathrm{k}W]}\right)^{0.85}$
PEM Electrolyser	$C_{PEM} = 1.3 \cdot 10^{6}\left(P_{inst[MW]}\right)^{0.815}$
CCS system	$C_{CCS} = 4855.2\ \left(M_{in\ [kg/\mathrm{h}]}\right)^{0.65}$
Methanol synthesis unit	$C_{MR} = 7106.85\ \left(M_{in\ [kg/\mathrm{h}]}\right)^{0.7}$

Total Capital Investment cost estimation

The Total Capital Investment (TCI) cost is calculated starting from the PEC of the plant: it is assumed that the PEC is about the 45% of the TCI (Mohammad R.M. Abu-Zahra et al., 2007). Moreover, it is assumed that the TCI corresponds to the Initial Investment.

Plant lifetime

The plant lifetime is assumed to be equal to 20 years, considering the lifetime of the electrolyzer ("Private Comunications by Hydrogenics," 2018) and PV plants, which represent the most expensive plant components.

In this analysis the economic parameters such as inflation, interest rate and taxation are not considered, for simplicity, because the main purpose of the work is to evaluate the relative effect of some parameters over the economic feasibility of the system under investigation.

The economic indicators considered are the following:

- The methanol production cost: it is useful to define the minimum methanol sale price that needs to be applied in order to guarantee a positive cash flow and it is calculated in accordance with the following equation:

$$\boldsymbol{MeOH_{cost}} = \frac{\boldsymbol{annual\,fixed\,cost + annual\,net\,variable\,cost}}{\boldsymbol{annual\,methanol\,production}} \qquad [€/\boldsymbol{ton_{MeOH\,prod}}] \tag{1}$$

  where the annual fixed cost is the annual rate of the TCI that is calculated over the 20years of the plant lifetime and the annual net variable costs are the electrical energy purchase cost, net of the income, coming from the sale of the oxygen at 150€/ton.

- The PayBack Period calculated in accordance with the following equation:

$$\boldsymbol{PBP} = \frac{\boldsymbol{Initial\ Investment}}{\boldsymbol{Annual\ Cash\ inflow}} \tag{2}$$

  where the annual cash inflow is assumed to be constant over the plant lifetime and it is calculated as follow:

$$\boldsymbol{Annual\ Cash\ inflow = Annual\ O_2\ income + Annual\ MeOH\ income - \ Annual\ varibale\ cost} \tag{3}$$

Since the plant lifetime is assumed to be equal to 20yr, 10yr of PBP is chosen as the threshold for the plant economic viability.

- The *Average Rate of Return* (ARR) can be used as an alternative to the PBP parameter to evaluate the plant feasibility. The ARR divides the average profit by the initial investment, to get the expected ratio of return.

In this case the ARR is a percentage value calculated as the reciprocal of the PBP and the threshold value is set equal to 10%.

$$\boldsymbol{ARR = \frac{1}{PBP} \times 100} \quad [\%] \tag{4}$$

5. Reference Case results

At first, the analysis is carried out considering a reference case represented by a 10MW PV plant and a 5MW PEM electrolyzer based methanol plant. The resulting TCI is equal to about 25 M€. The PEC percentage distribution between the main plant components is reported in Figure 6.

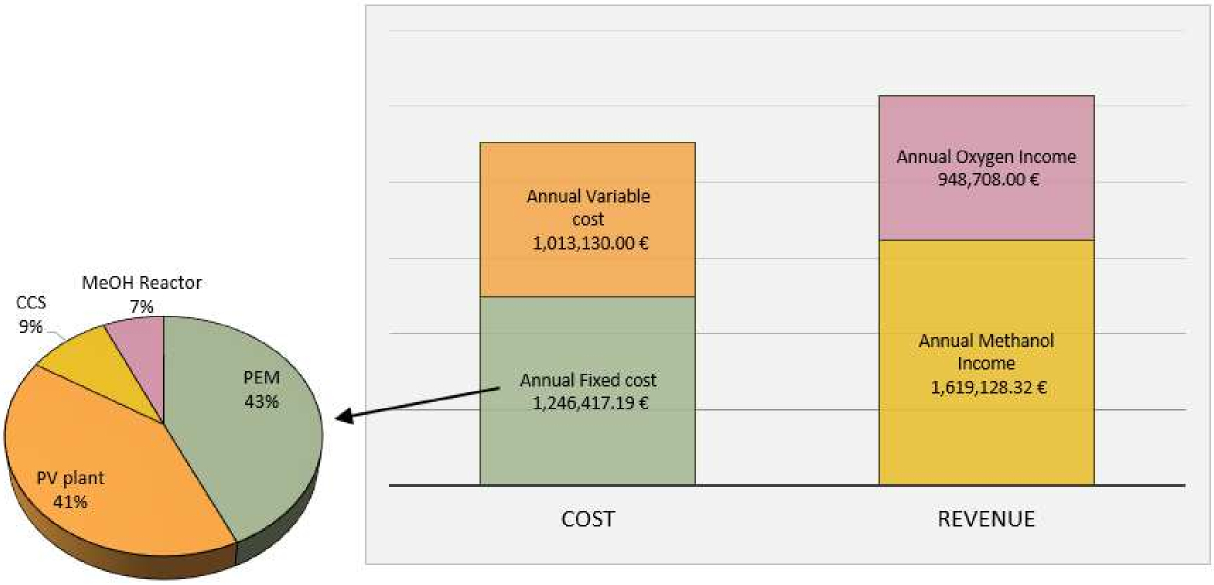


Figure 6 Reference case - Cost and revenues comparison and annual fixed cost percentage breakdown

The most expensive components are the PEM electrolyzer and the PV plant, that represent 43% and 41% of the PEC respectively. The CCS and Methanol unit costs are comparable and lower than 10% of the PEC.

Considering the strong impact of the PEM cost on the total capital cost and considering that the electrolyzer is the component with the lowest technology readiness level, it is reasonable to assume that its capital cost will decrease in the next future. For this reason, the percentage reduction in electrolyzer capital cost is taken into account as a parameter for the sensitivity analysis.

For the reference case, the MPC (Methanol Production Cost) results around 324 €/ton and the PBP and the ARR are equal to about 15.7% and 6.5% respectively. Therefore, on the base of the economic assumption presented above, the reference case presents a PBP higher than 10 years, meaning that the plant cannot be defined cost effective. However, considering the environmental constraints, it is possible to perform a sensitivity analysis in order to identify the parameters that mostly affect the plant economic feasibility and to define the minimum value of the methanol sale price, for achieving a PBP equal to 10 years at least.

6. Sensitivity Analysis Results And Discussion

In the present work, a sensitivity analysis is carried out in order to evaluate the influence of some parameters on the economic feasibility of the methanol production plant. In particular, the methanol production cost and the ARR are investigated in function of a number of parameters:

- PV plant size;
- Electrical energy purchasing cost;
- Percentage reduction of PEM electrolyzer capital cost;
- Methanol sale price.

The methanol sale price range is chosen taking into consideration the results coming from the methanol production cost analysis.

The RSM approach and the ANOVA technique have been used to perform a sensitivity analysis, aimed at the evaluation of the impact on the plant economic viability in consideration of different economic parameters. The statistical analysis and graphical analysis of the data were performed by using Design Expert software (Version 10.0, Stat-Ease, USA). The analysis of variance (ANOVA) was selected to assess the statistical significance of the effects, by using Fisher's test. The Lack of Fit F-test was used to evaluate the goodness of the fit of the regression models.

In the following, the results related to the methanol production cost and the ARR analyses are reported.

Methanol production cost

In Table 4 the range of the parameters considered for the Methanol Production Cost (MPC) analysis are reported.

Table 4 Methanol production cost analysis factors and respective ranges

Factor	Name	Unit	Low level	Midrange level	High level
A	PV plant size	MW	10	15	20
B	Percentage reduction of PEM capital cost	%	0	25	50
C	Electrical energy purchasing cost	€/MWh	30	50	70

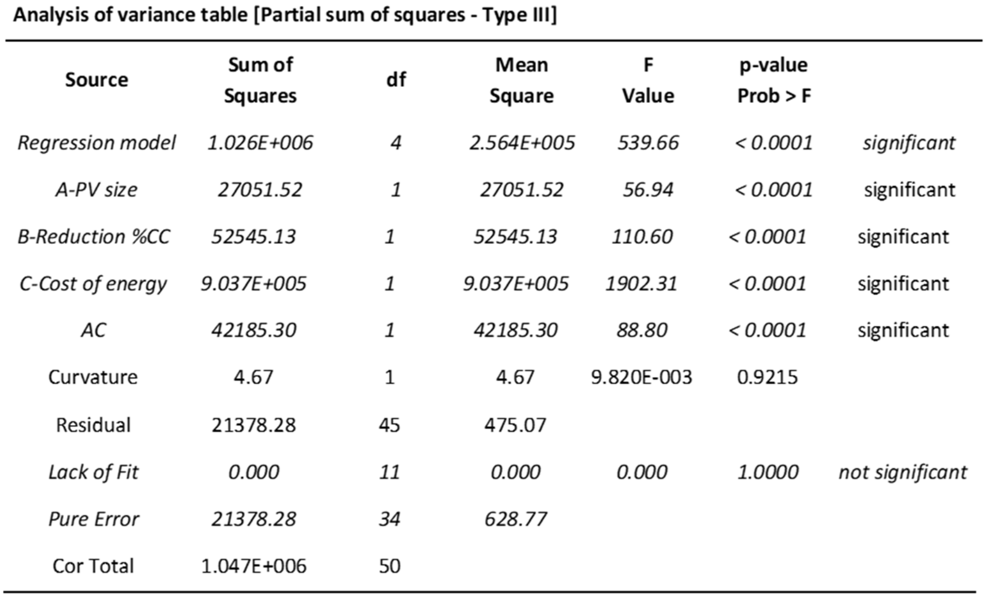
The resulting factorial design for the MPC sensitivity analysis is a 2^3 design with a center point, represented by a cube in the R^3 space. The vertices of the cube represent the experimental points that must be tested.

For each combination of the factors ($2^3 + 1$), three replications of the calculated MPC are taken into account, by considering the minimum, average and maximum annual solar radiation.

The ANOVA analysis showed that the MPC passed the F test on Regression and, therefore, the first-order model can be considered to be a satisfying approximation of the problem.

The test of the residual normality, throughout the "Residual vs predicted plot" (reported in **Error! Reference source not found.**), showed that no transformation of the response is needed: the points on the plot appeared to be randomly scattered around zero, so it was reasonable to assume that the error terms had a mean of zero. The vertical width of the scatter did not appear to increase or decrease across the fitted values, so the Authors could assume that the variance in the error terms was constant.

In Figure 7, the ANOVA results for the MPC are reported.



Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Regression model	*1.026E+006*	*4*	*2.564E+005*	*539.66*	*< 0.0001*	*significant*
A-PV size	*27051.52*	*1*	*27051.52*	*56.94*	*< 0.0001*	significant
B-Reduction %CC	*52545.13*	*1*	*52545.13*	*110.60*	*< 0.0001*	significant
C-Cost of energy	*9.037E+005*	*1*	*9.037E+005*	*1902.31*	*< 0.0001*	significant
AC	*42185.30*	*1*	*42185.30*	*88.80*	*< 0.0001*	significant
Curvature	4.67	1	4.67	9.820E-003	0.9215	
Residual	21378.28	45	475.07			
Lack of Fit	*0.000*	*11*	*0.000*	*0.000*	*1.0000*	*not significant*
Pure Error	*21378.28*	*34*	*628.77*			
Cor Total	1.047E+006	50				

Figure 7 MPC analysis – ANOVA results

The ANOVA table reports that the chosen regression model (the first-order model) is significant, meaning that the model is a good representation of the problem under investigation. Moreover, the ANOVA analysis shows that the most significant terms are A, B, C and the interaction term AC, while the other interactions can be neglected, as reported in Table 5.

Table 5 highlights that the factor that mainly affects the methanol production cost is the Cost of Energy (factor C) with a percentage contribution higher than the 86%.

Table 5 MPC analysis – "Effect results"

Term	Stdized Effect	Sum of Squares	% Contribution
A-PV size	-47.48	27051.52	2.58
B-Reduction %CC	-66.17	52545.13	5.02
C-Cost of energy	274.43	9.04E+05	86.33
AB	-3.30E-12	0	0
AC	-59.29	42185.3	4.03
BC	1.70E-12	0	0
ABC	-1.70E-12	0	0
Pure Error		21378.28	2.04

The MPC Objective function in terms of coded factors is reported below:

$$MPC_{coded} = 433.64 - 23.7397 * A - 33.0861 * B + 137.215 * C - 29.6456 * AC \qquad (5)$$

By default, the high levels of the factors are coded as *+1* and the low levels of the factors are coded as *-1*. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients and their own sign.

The equation presents a constant term, three terms related to the single factors and an interaction factor. The constant term represents the MPC value, corresponding to the center of the design space (all factor equal to 0). Looking at the coefficients in absolute value of the single factors, it is possible to note that the most influent factor is C (the electrical energy cost), with a coefficient equal to 137.215. In terms of percentage contribution on the response, the C-factor counts more than 86%. The positive sign indicates that increasing the C value the cost of methanol increases. The second factor in terms of magnitude is B, the percentage reduction of the PEM capital cost. In this case, the B-sign is negative, meaning that increasing the B value the MPC is reduced. Factor A has a negative coefficient (as C) but with a lower absolute value. Moreover, the influence of A is lower than the influence of its interaction with C. The coefficient of the AC term is 30.91 with negative sign, meaning that the higher is the product AC, the lower is the MPC value and vice versa. The interaction term makes the regression surface not flat but presents a slight twist, as shown in Figure 8.

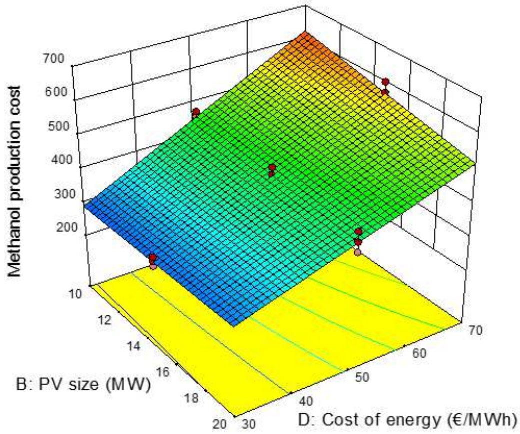


Figure 8 Methanol production cost as function of the factors B and D, for A and C equal to the midterm value

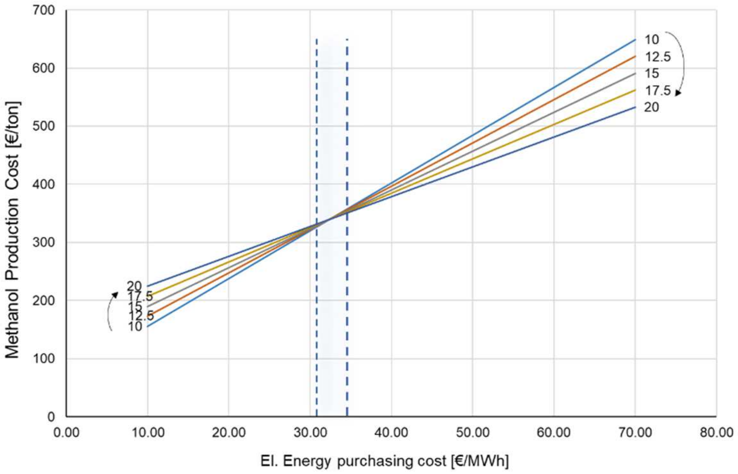


Figure 9 Methanol production cost as function of the electrical energy cost and for different value of the PV plant size [MW]

The effect of the interaction is shown in Figure 9. For low values of the electrical energy cost, the MPC increases with the PV size, therefore, the impact on the cost of the PV plant PEC is higher than the cost related to the electrical energy purchase. Vice versa, for high electrical energy cost, the MPC decreases with the PV size. It is interesting to note the presence of a break-even area where the methanol production cost results almost constant for each PV plant size. The electrical energy purchase cost at the intersection corresponds to the value for which the total cost (made of the TCI and the electrical purchase) is the same in the intersecting cases. In other words, the lower is the PV size, the lower is the TCI, and the lower gets the annual amount of produced energy, hence, the higher is the amount of the purchased electrical energy and vice versa. For example, considering 10MW and 20MW PV plant installed, the value of electrical energy cost for which the total costs are equivalent (and hence the MPC results constant) is equal about to 32.38€/MWh.

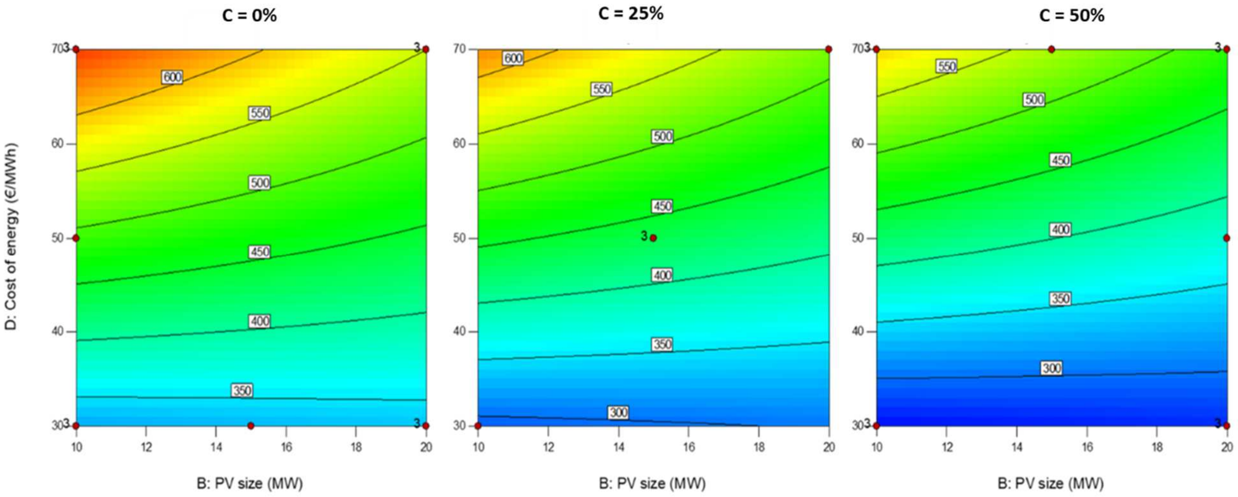


Figure 10 MPC as function of the PV size and the electrical energy cost for different values of the PEM capital cost reduction

The methanol production cost results in the range 200 ÷ 600 €/ton. Therefore, for the following analysis, the methanol sale price is assumed to be in the range 400 ÷ 1200 €/ton.

Pay Back Period

In order to evaluate the PBP, the methanol sale price shall be included as parameter in the analysis. Therefore, in this case, the sensitivity analysis was performed considering four variables. In Table 6, the variation range of the four considered parameters is reported.

Table 6 Methanol production cost analysis factors and respective ranges

Factor	Name	Unit	Low level	Midrange level	High level
A	Methanol selling price	€/ton	400	800	1200
B	PV plant size	MW	10	15	20
C	Percentage reduction of PEM capital cost	%	0	25	50
D	Electrical energy purchasing cost	€/MWh	30	50	70

The resulting factorial design for the PBP sensitivity analysis is a 2^4 design with a center point, represented by a hypercube in the R^4 space.

The PBP passes the F test on Regression and, therefore, the first-order model is capable of providing a satisfying approximation of the problem. However, the response-normality check and the constant error check show that a transformation of the response is needed: the “residual vs predict plot“ shows the existence of a specific values-pattern (Figure 11).

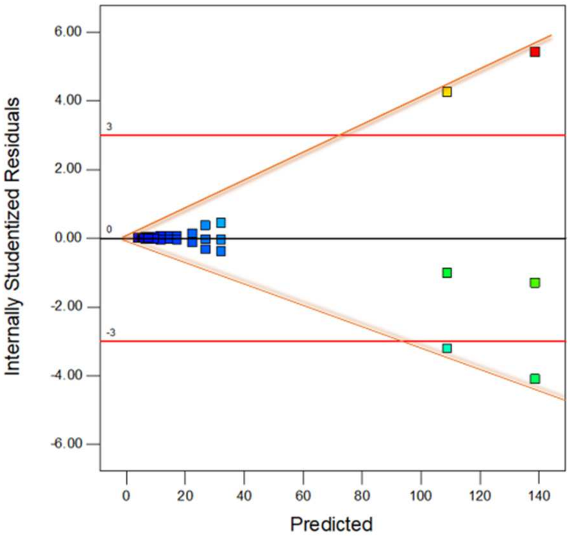


Figure 11 PBP analysis - Residual vs Predicted plot

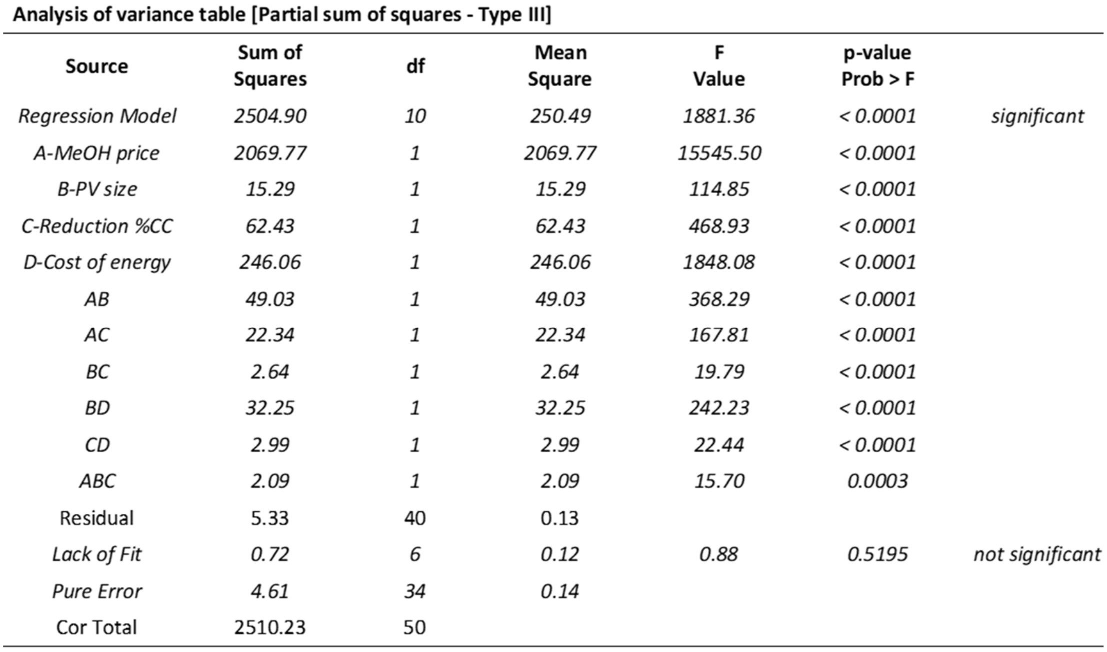
In particular, the mean residual does not change with the predicted values, but the spread of the residual increases proportionally to the predicted values. In accordance with the BOX-COX analysis, an inverse transformation of the response is applied as follows:

$$y' = \frac{1}{y} \tag{6}$$

Because the inverse of the PBP is indeed the ARR, in the following, the analysis will be performed in reference to the ARR.

<u>Average Rate of Return</u>

Similarly to the PBP, the ARR passes the F test on regression as shown in Figure 12.



Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Regression Model	*2504.90*	*10*	*250.49*	*1881.36*	*< 0.0001*	*significant*
A-MeOH price	*2069.77*	*1*	*2069.77*	*15545.50*	*< 0.0001*	
B-PV size	*15.29*	*1*	*15.29*	*114.85*	*< 0.0001*	
C-Reduction %CC	*62.43*	*1*	*62.43*	*468.93*	*< 0.0001*	
D-Cost of energy	*246.06*	*1*	*246.06*	*1848.08*	*< 0.0001*	
AB	*49.03*	*1*	*49.03*	*368.29*	*< 0.0001*	
AC	*22.34*	*1*	*22.34*	*167.81*	*< 0.0001*	
BC	*2.64*	*1*	*2.64*	*19.79*	*< 0.0001*	
BD	*32.25*	*1*	*32.25*	*242.23*	*< 0.0001*	
CD	*2.99*	*1*	*2.99*	*22.44*	*< 0.0001*	
ABC	*2.09*	*1*	*2.09*	*15.70*	*0.0003*	
Residual	5.33	40	0.13			
Lack of Fit	*0.72*	*6*	*0.12*	*0.88*	*0.5195*	*not significant*
Pure Error	*4.61*	*34*	*0.14*			
Cor Total	2510.23	50				

Figure 12 ARR analysis – ANOVA results

The “Lack of Fit F-value" of 0.88 implies that it is not significant, meaning that the regression model well-fits the problem. The model standard deviation and mean values are 0.36 and 10.47, respectively. The “residual vs predicted plot” shows that the constant error assumption can be confirmed.

The “effect analysis” based on the normal plot (Figure 13) shows that the significant model terms are A, B, C, D, AB, AC, BC, BD, CD, ABC. The only two-factor interaction resulting not significant is AD, which represents the interaction between the methanol sale price and the electrical energy cost. The most affecting term is A, with a contribution impact higher than 82%. The second most influent factor is D, with a percentage contribution of around 9.8%. Among the interaction terms, the most affecting are AB and BD with a percentage contribution of 1.95 % and 1.28 %, respectively. It is interesting to note that the factor B presents a percentage contribution value lower than both the interaction terms above mentioned.

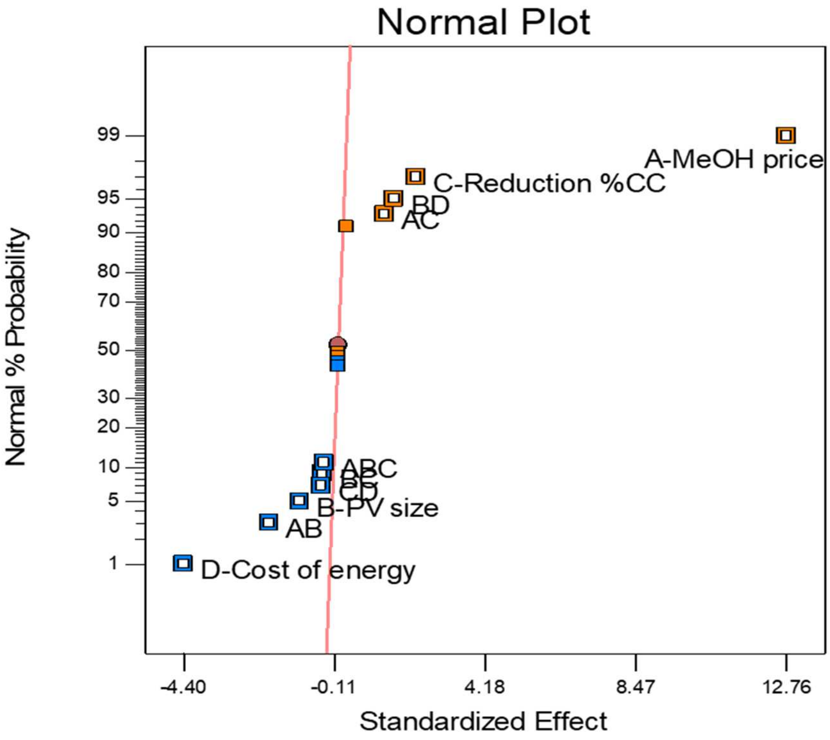


Figure 13 ARR – Normal Plot Effect analysis

The regression model for the ARR, in terms of coded factors, is reported below.

$$ARR_{coded} = 10.77 + 6.34 * A - 0.55 * B + 1.13 * C - 2.24 * D - 1.00 * AB + 0.67 * AC - 0.23 * BC + 0.82 * BD - 0.23 * CD - 0.21 * ABC \tag{7}$$

The regression model for ARR, in terms of actual factors, is as follow:

$$\begin{aligned} ARR = {} & 5.6664 + 0.0202635 * MeOH\ price - 0.155065 * PV\ size - 0.00598245 * Reduction\ \%CC \\ & - 0.223686 * Cost\ of\ energy - 0.000401009 * MeOH\ price * PV\ size + 0.000130836 \\ & * MeOH\ price * Reduction\ \%CC + 0.00146484 * PV\ size * Reduction\ \%CC \\ & + 0.00819699 * PV\ size * Cost\ of\ energy - 0.000499007 * Reduction\ \%CC \\ & * Cost\ of\ energy - 4.17407e - 006 * MeOH\ price * PV\ size * Reduction\ \%CC \end{aligned} \tag{8}$$

The equation, in terms of actual factors, can be used to make predictions about the response, for given levels of each factor.

In Figure 14 the perturbation plot is reported. It shows the effects of all factors at the midpoint of the design. It is possible to note that while increasing the value of the factors A and D, the ARR consequently increases; vice versa, the increasing value of the factors B and C have a negative impact on the ARR.

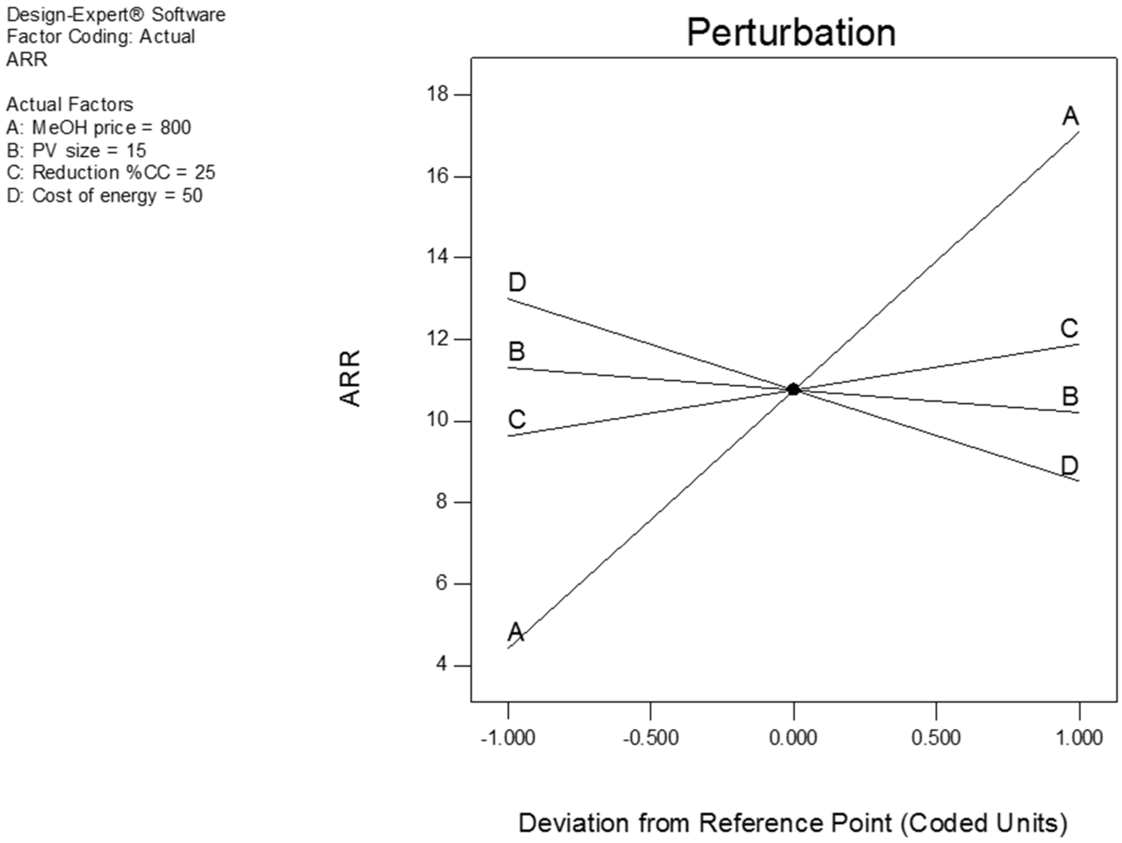


Figure 14 ARR – perturbation factors plot

In Figure 15, the response surfaces of the ARR, as function of factors A and B, A and C, B and C, C and D, are reported.

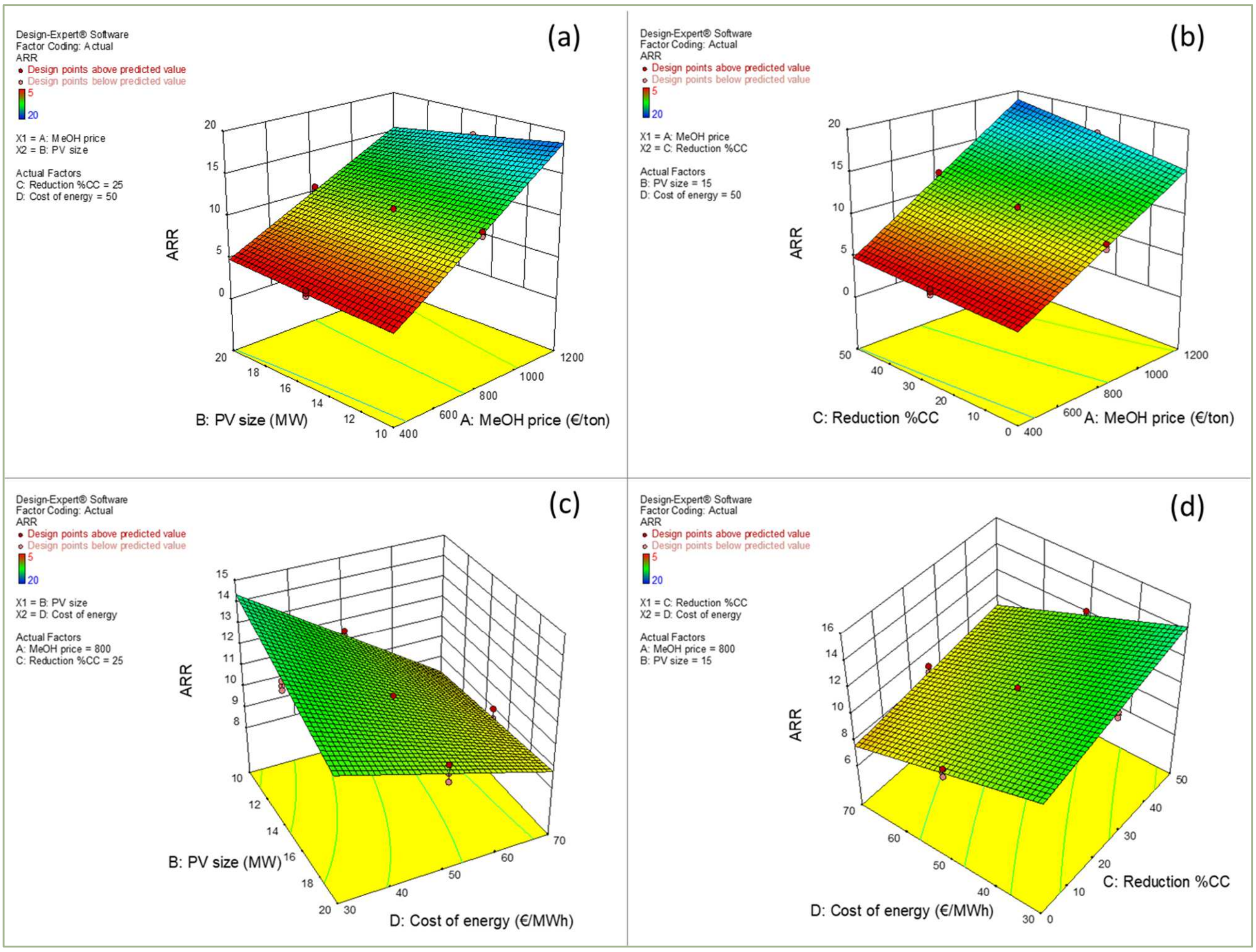


Figure 15 Response surfaces of ARR as function of the factors (a) A and B, (b) A and C, (c) B and D, (d) C and D.

One of the most interesting outputs of the RSM, for the economic analysis, is the possibility to draw a map of the ARR values as function of the different factors.

Figure 16 reports a matrix of contour graphs of the ARR as function of the PV size (B) and the Methanol sale price (A) in dependence of the low, middle and high level of the Electrical energy purchasing cost (D) and the percentage reduction of the capital cost of the PEM (C).

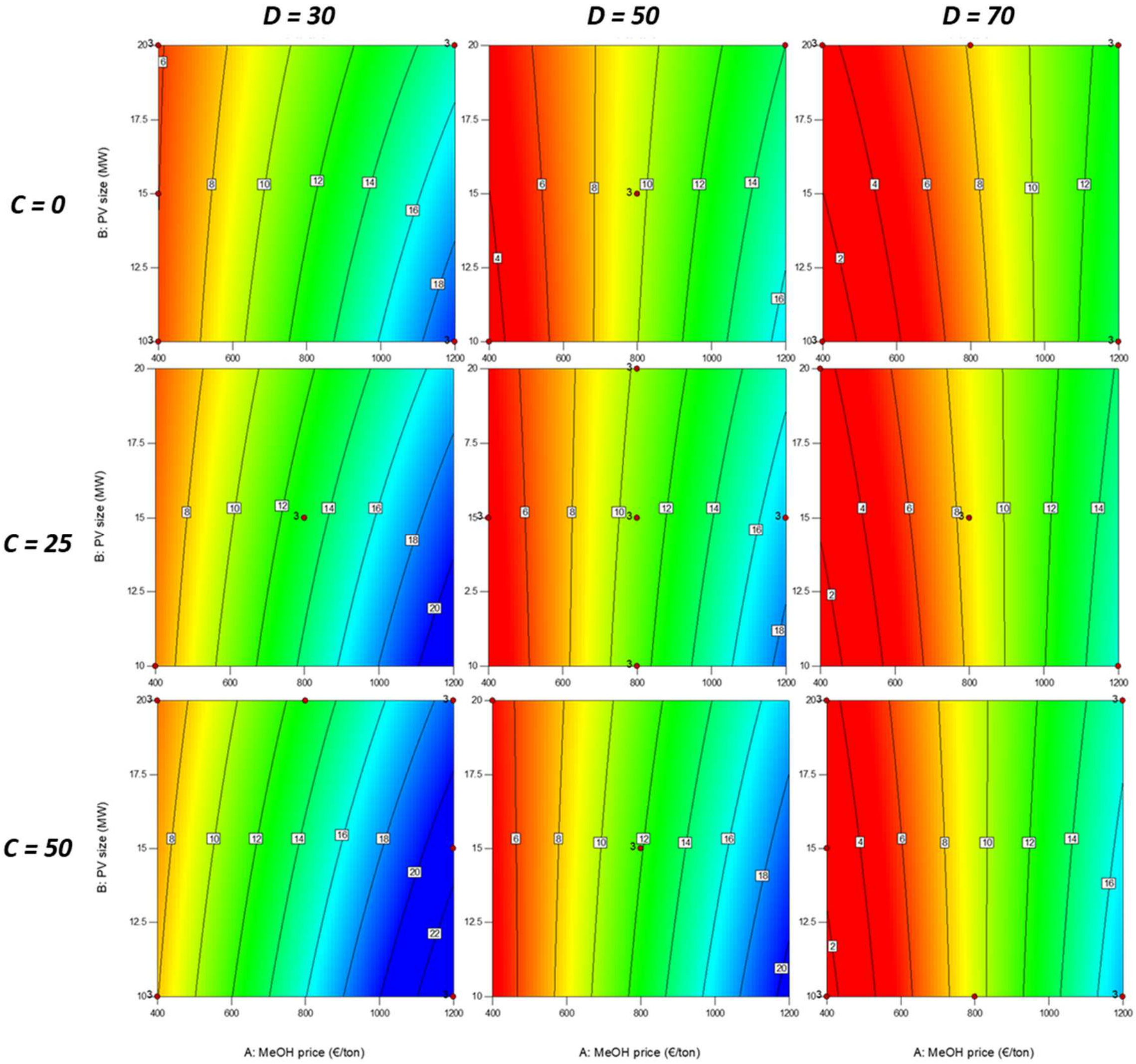


Figure 16 ARR contours matrix plots as function of the factors A (MeOH price) and B (PV size) for different values of factors C (PEM %CC reduction) and D (Energy cost)

It is possible to define the minimum price for methanol sale, that allows for an ARR equal to 10% (i.e. 10 yrs. of PBP, that is set as the lowest acceptable value) taking into account the scenario constraints such as the electrical energy purchase cost. For example, having fixed the PV size equal to 20MW and not considering the reduction in PEM cost,, the ARR results equal to 10% for C= 30 €/MWh and A around 750 €/ton, or for C = 70 €/MWh and A is around 950 €/ton. Furthermore, it is possible to define the optimal PV size as function of the electrical energy price: it is worth noting that for a fixed A, at low value of D, the ARR decreases (i.e. PBP increases); for increasing PV size, instead, the trend diverts for high value of D (see also Figure 17). On the other hand, having fixed the PV size, the minimum value of A increases while increasing the electrical energy cost. This trend is more visible for C equal to zero and tends to fade reducing the capital cost of the PEM. Finally, the increase of C allows for a reduction of the methanol-sale price for the same values of D and B.

For example, having fixed the PV size equal to 10 MW and the electrical energy cost to 30€/MWh (as in the reference case), the values of A that make the ARR equal to 10% are 625€/ton for C=0%, 580€/ton for C=25%, and 500€/ton for C=50%. Hence, a reduction in the capital cost of PEM of 50% allows for a reduction in methanol sale price of the 20%. Or, in other words, for a fixed value of the methanol sale price equal to 625€/ton, the reduction of the PEM capital cost of the 50% allows for an increase of 25% of the ARR, resulting equal to about 12.5% (i.e. 8 yrs. of PBP).

However, if the electrical energy cost increases up to 70 €/MWh, for the same PV size (10MW) and not considering the capital cost reduction, the minimum methanol sale price rises from 625 up to 975€/ton. Nevertheless, if the PV size increases up to 20MW, the methanol sale price decreases to 950€/ton. Moreover, if the option to reduce the PEM capital cost to 50 % is considered, the lower value of A results equal to 827 €/ton, with 10MW of PV plant, against the 835€/ton with 20MW of PV plant. It is worth noting that the values of the methanol sale price above mentioned are rather high compared to the actual market value. Nevertheless, it cannot be forgotten that the methanol produced in this kind of plant has a low environmental impact, being synthesized by using wasted CO_2 and renewable energy.

In Figure 17, the ARR map as function of the PV plant size (factor B) and the electrical energy cost (factor D) is reported for different values of the methanol sale price (factor A) and of the percentage reduction of the PEM capital cost (factor C).

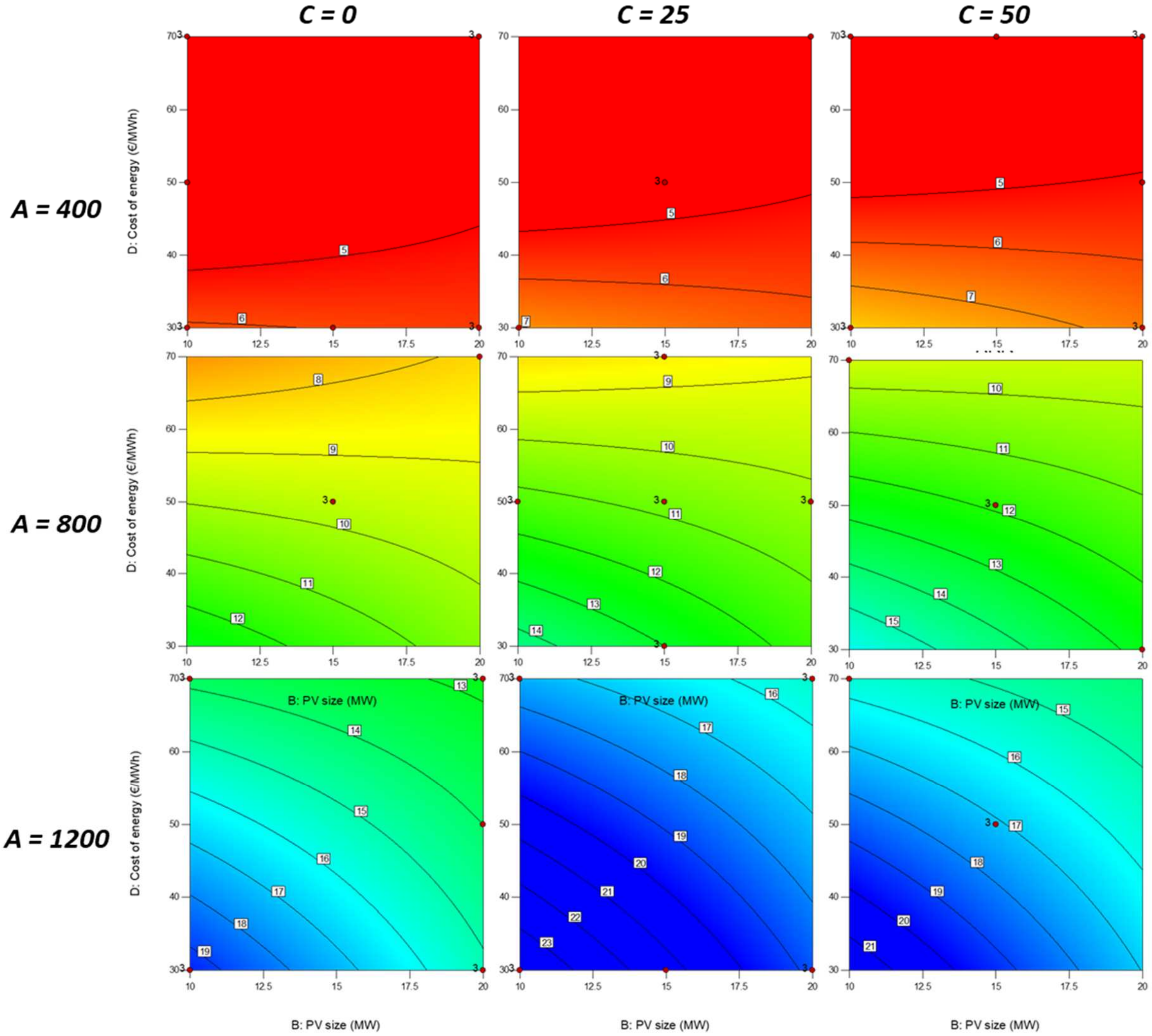


Figure 17 ARR contours matrix plots as function of the factors B (PV size) and D (energy cost) for different values of factors A (MeOH price) and C (PEM %CC reduction)

In Figure 18, the single plots of the ARR, as function of each factor used in the sensitivity analysis, are reported.

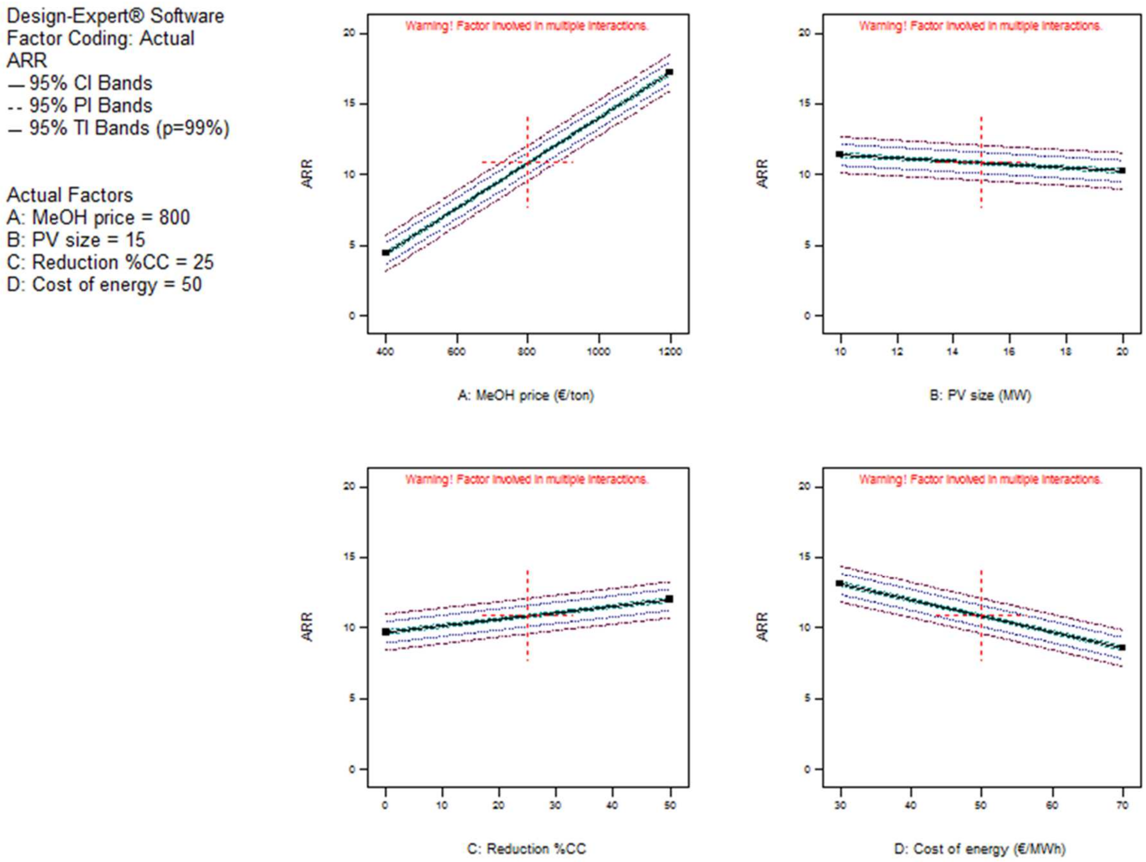


Figure 18 ARR as function of single factor

7. Conclusions

In the present work, the economic viability of a 5MW electrolyser base-methanol production plant, coupled with a PV power plant, was investigated by the use of the RSM approach. At first, a preliminary analysis on a reference case was performed, in order to identify the components' cost that most affect the economic viability of the plant under investigation. Afterwards, the RSM approach was used to perform a sensitivity analysis, that would lead to evaluate the capacity of the three main design variables (the PV plant size, the electrical energy purchasing cost, a percentage reduction in the PEM electrolyser capital cost) to affect the methanol production cost and, then, including the methanol sale price as variable, the ARR. The "maps of existence" created by using the RMS approach are one of the most important outcomes of the study as they may represent an useful baseline for an economically viable plant design.

The main results of the study are summarised below:

- From the capital cost point of view, the PEM electrolyser and the PV plant resulted to be the most influent elements (43% and 41% of the total investment cost, respectively); while the relevance of the CCS system and the methanol synthesis unit resulted marginal, representing an overall value lower than the 20% of the total cost;

- Considering the high electrical energy consumption of the electrolyser, the variable that most affects the methanol production cost is the electrical energy purchasing cost, accounting the 86% of the total;
- In the case with an installed PV plant of 10MW, assuming 30€/MWh as cost of energy purchased from the grid and considering the current cost of the electrolyser, the minimum methanol sale price able to ensure a 10 years PBP, resulted 625 €/ton;
- In case that the cost of the electrolyser was reduced by 25% and 50%, the minimum methanol sale price would have decreased to around 600 €/ton and 500€/ton, respectively.

The main implications of the study are the following:

- It is of utmost importance to continue the research for improving the electrolyser technology, in order to achieve a significant reduction in the capital cost or a relevant increase in efficiency;
- The amount of energy produced by the PV plant is strictly dependent on the panel's efficiency. Therefore, future studies on the materials designated to the solar radiation capture, can lead to an increase in energy efficiency and, hence, in energy production. For example, for the same m^2 of installed panels, an increase of the 20% in actual efficiency (18%) allows for an increase in energy production and the PBP can be reduced down to 25%;
- The same result can be obtained, for the same panel efficiency, in terms of an increase of the equivalent operating hours, by choosing an installation site with a higher daily solar irradiation (as it changes significantly with the latitude).

The methanol production cost resulted basically higher than the actual market value, but it could be justified considering that the methanol has proved to be a valuable low carbon alternative to the diesel fuel in the automotive transportation sector. Considering that, in the European scenario, the actual diesel fuel market average value is around 1.5€/l (about 1.8€/kg) ("Global Petrol Prices," 2018), assuming the energy equivalence, the resulting methanol sale price is about 860€/ton.

In the end, it is worth to underline that the methanol produced with this method allows to recycle more than 5800 ton/yr of CO_2, that can be recovered from the industrial plants. Nonetheless, compared to the traditional natural gas-based production chain, this concept allows for saving about 5.2 MNm^3 of NG and for avoiding the related emission of about 10000 ton/yr of CO_2

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the 'EU Framework Programme for Research and Innovation Horizon 2020' under the grant agreement No. 637016 (MefCO2).

REFERENCES

Abu-Zahra, M.R.M., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007. CO2capture from power plants. Part II. A parametric study of the economical performance based on mono-ethanolamine. Int. J. Greenh. Gas Control 1, 135–142. https://doi.org/10.1016/S1750-5836(07)00032-1

Abu-Zahra, M.R.M., Schneiders, L.H.J., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007. CO2capture from power plants. Part I. A parametric study of the technical performance based on monoethanolamine. Int. J. Greenh. Gas Control 1, 37–46. https://doi.org/10.1016/S1750-5836(06)00007-7

Ascough, J.C., Fathelrahman, E.M., Hoag, D.L., 2013. Using Response Surface Methodology for Economic and Environmental Trade-offs at the Farm Level. Air, Soil Water Res. 6, ASWR.S11697. https://doi.org/10.4137/ASWR.S11697

Asif, M., Gao, X., Lv, H., Xi, X., Dong, P., 2018. Catalytic hydrogenation of CO2from 600 MW supercritical coal power plant to produce methanol: A techno-economic analysis. Int. J. Hydrogen Energy 43, 2726–2741. https://doi.org/10.1016/j.ijhydene.2017.12.086

Atsonios, K., Panopoulos, K.D., Kakaras, E., 2016. Investigation of technical and economic aspects for methanol production through CO2hydrogenation. Int. J. Hydrogen Energy 41, 2202–2214. https://doi.org/10.1016/j.ijhydene.2015.12.074

Bellotti, D., Rivarolo, M., Magistri, L., Massardo, A.F., 2017. Feasibility study of methanol production plant from hydrogen and captured carbon dioxide. J. CO2 Util. 21. https://doi.org/10.1016/j.jcou.2017.07.001

Bellotti, D., Rivarolo, M., Magistri, L., Massardo, A.F., 2015. Thermo-economic comparison of hydrogen and hydro-methane produced from hydroelectric energy for land transportation. Int. J. Hydrogen Energy 40. https://doi.org/10.1016/j.ijhydene.2014.12.066

Bellotti, D., Sorce, A., Rivarolo, M., Magistri, L., 2019. Techno-economic analysis for the integration of a power to fuel system with a CCS coal power plant. J. CO2 Util. 33, 262–272. https://doi.org/10.1016/j.jcou.2019.05.019

Bendato, I., Cassettari, L., Mosca, M., Mosca, R., 2016. Stochastic techno-economic assessment based on Monte Carlo simulation and the Response Surface Methodology: The case of an innovative linear Fresnel CSP (concentrated solar power) system. Energy 101, 309–324. https://doi.org/10.1016/j.energy.2016.02.048

Bendato, I., Cassettari, L., Mosca, M., Mosca, R., 2015. A design of experiments/response surface methodology approach to study the economic sustainability of a 1 MWe photovoltaic plant. Renew. Sustain. Energy Rev. 51, 1664–1679. https://doi.org/10.1016/J.RSER.2015.07.074

Blumberg, T., Morosuk, T., Tsatsaronis, G., 2019. CO 2 -utilization in the synthesis of methanol: Potential analysis and exergetic assessment. Energy 175, 730–744. https://doi.org/10.1016/j.energy.2019.03.107

Bozzano, G., Manenti, F., 2016. Efficient methanol synthesis: Perspectives, technologies and optimization strategies. Prog. Energy Combust. Sci. 56, 71–105. https://doi.org/10.1016/j.pecs.2016.06.001

Brown, J.N., Brown, R.C., 2012. Process optimization of an auger pyrolyzer with heat carrier using response surface methodology. Bioresour. Technol. 103, 405–414.

EIGA, ASSOCIATION, E.I.G., 2015. SAFE DESIGN AND OPERATION OF ON SITE GENERATION OF OXYGEN 93% FOR MEDICAL USE.

Ekren, O., Ekren, B.Y., 2008. Size optimization of a PV/wind hybrid energy conversion system with battery storage using response surface methodology. Appl. Energy 85, 1086–1101. https://doi.org/10.1016/j.apenergy.2008.02.016

Ellis, J., Ramne, B., Bomanson, J., Molander, P., Tunér, M., Aakko-Saksa, P., Svanberg, M., Rydbergh, T., Berneblad, B., 2018. Final Report – Summary of the SUMMETH Project Activities and Results.

ENA, 2013. Atlante italiano della radiazione solare [WWW Document]. URL http://www.solaritaly.enea.it/CalcComune/Calcola.php (accessed 4.16.18).

Global Petrol Prices [WWW Document], 2018. URL https://www.globalpetrolprices.com (accessed 5.22.18).

GME - Gestore dei Mercati Energetici SpA [WWW Document], 2018. URL http://www.mercatoelettrico.org/it/ (accessed 5.15.18).

Grahovac, J., Dodić, J., Jokić, A., Dodić, S., Popov, S., 2012. Optimization of ethanol production from thick juice: A response surface methodology approach. Fuel 93, 221–228. https://doi.org/10.1016/j.fuel.2011.10.019

GSE, 2016. Solare Fotovoltaico - Rapporto Statistico 2016.

Hank, C., Gelpke, S., Schnabl, A., White, R.J., Full, J., Wiebe, N., Smolinka, T., Schaadt, A., 2018. Sustainable Energy & Fuels Economics & carbon dioxide avoidance cost of hydrogen and recycled carbon dioxide – power-to- methanol 1244–1261. https://doi.org/10.1039/c8se00032h

Intergovernmental Panel On Climate Change IPCC, 2014. Climate Change 2014: Synthesis Report., Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. https://doi.org/10.1017/CBO9781107415324

International Renewable Energy Agency (IRENA), 2018. Renewable Energy Prospects for the European Union, Remap 2030.

Intratec, 2018. Production Cost Reports [WWW Document]. URL https://www.intratec.us/ (accessed 5.15.18).

Jadhav, S.G., Vaidya, P.D., Bhanage, B.M., Joshi, J.B., 2014. Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies. Chem. Eng. Res. Des. 92, 2557–2567. https://doi.org/10.1016/j.cherd.2014.03.005

Leonzio, G., 2018. State of art and perspectives about the production of methanol, dimethyl ether and syngas by carbon dioxide hydrogenation. J. CO2 Util. 27, 326–354. https://doi.org/10.1016/J.JCOU.2018.08.005

Matzen, M., Alhajji, M., Demirel, Y., 2015. Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix. Energy 93, 343–353. https://doi.org/10.1016/j.energy.2015.09.043

Methanex Corporation [WWW Document], 2018. URL https://www.methanex.com/ (accessed 5.15.18).

Methanol Institute [WWW Document], 2018. URL https://www.methanol.org/uses/ (accessed 6.15.18).

Methanol Market - Global Industry Analysis, Size, Share, Growth, Trends and Forecast 2017 - 2026 [WWW Document], 2017. URL https://www.prnewswire.com/news-releases/methanol-market (accessed 5.15.18).

Moellenbruck, F., Kempken, T., Dierks, M., Oeljeklaus, G., Goerner, K., 2018. Cogeneration of power and methanol based on a conventional power plant in Germany. J. Energy Storage 19, 393–401. https://doi.org/10.1016/j.est.2018.08.018

Montgomery, D., 2013. Design and Analysis of Experiments, 8th ed.

Pérez-Fortes, M., Schöneberger, J.C., Boulamanti, A., Tzimas, E., 2016. Methanol synthesis using captured CO2as raw material: Techno-economic and environmental assessment. Appl. Energy 161, 718–732. https://doi.org/10.1016/j.apenergy.2015.07.067

Private Comunications by Hydrogenics, 2018.

Rivarolo, M., Bellotti, D., Magistri, L., Massardo, A.F., n.d. Feasibility study of methanol production from different renewable sources and thermo-economic analysis. Int. J. Hydrogen Energy 41. https://doi.org/10.1016/j.ijhydene.2015.12.128

Rivarolo, M., Bellotti, D., Mendieta, A., Massardo, A.F., 2014. Hydro-methane and methanol combined production from hydroelectricity and biomass: Thermo-economic analysis in Paraguay. Energy Convers. Manag. 79. https://doi.org/10.1016/j.enconman.2013.11.044

Rivera-Tinoco, R., Farran, M., Bouallou, C., Auprêtre, F., Valentin, S., Millet, P., Ngameni, J.R., 2016. Investigation of power-to-methanol processes coupling electrolytic hydrogen production and catalytic CO2reduction. Int. J. Hydrogen Energy 41, 4546–4559. https://doi.org/10.1016/j.ijhydene.2016.01.059

Rodrigues, V.H., de Melo, M.M.R., Portugal, I., Silva, C.M., 2019. Simulation and techno-economic optimization of the supercritical CO2 extraction of Eucalyptus globulus bark at industrial scale. J. Supercrit. Fluids 145, 169–180. https://doi.org/10.1016/j.supflu.2018.11.025

Szima, S., Cormos, C.C., 2018. Improving methanol synthesis from carbon-free H2and captured CO2: A techno-economic and environmental evaluation. J. CO2 Util. 24, 555–563. https://doi.org/10.1016/j.jcou.2018.02.007

U.S. Energy Information Administration, 2017. International Energy Outlook 2017. Int. Energy Outlook IEO2017, 143. https://doi.org/www.eia.gov/forecasts/ieo/pdf/0484(2016).pdf

Van-Dal, É.S., Bouallou, C., 2013. Design and simulation of a methanol production plant from CO2hydrogenation. J. Clean. Prod. 57, 38–45. https://doi.org/10.1016/j.jclepro.2013.06.008

Vanderghem, C., Brostaux, Y., Jacquet, N., Blecker, C., Paquot, M., 2012. Optimization of formic/acetic acid delignification of Miscanthus×giganteus for enzymatic hydrolysis using response surface methodology. Ind. Crops Prod. 35, 280–286. https://doi.org/10.1016/j.indcrop.2011.07.014

Zhen, X., Wang, Y., 2015. An overview of methanol as an internal combustion engine fuel. Renew. Sustain. Energy Rev. 52, 477–493. https://doi.org/10.1016/j.rser.2015.07.083