

# Design and Optimization of Methanol Production using PyBOUND

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## ABSTRACT

In this paper, we study the design optimization of methanol production with the goal of minimizing methanol production cost. One challenge of methanol production via carbon dioxide (CO<sub>2</sub>) hydrogenation is the reduction of operating costs. The simulation of methanol production is implemented within the Aspen HYSYS simulator. The feeds are pure hydrogen and captured CO<sub>2</sub>. The process simulation involves a single reactor and incorporates recycling at a ratio of 0.995. The methanol production cost is determined using an economic analysis. The cost includes capital and operating costs, which are determined through the equations and data from the capital equipment-costing program. The decision variables are the pressure and temperature of the reactor contents. The optimization problem is solved using a derivative-free algorithm, pyBOUND, a Python-based black-box model optimization algorithm that uses random forests (RFs) and multivariate adaptive regression splines (MARS). The predicted minimum methanol production cost by pyBOUND is \$1396.56 per tonne of methanol, which corresponds to the pressure of 68.82 bar and temperature of 192.23°C while the actual cost is \$1393.95 per tonne of methanol at these conditions. The cost breakdown of methanol production is 75% hydrogen price, 11% utility cost, 8% capital cost, 5% carbon dioxide price, and 1% operating cost.

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**Keywords:** Methanol, Carbon Dioxide, Process Synthesis, Process Design, Simulation, Optimization, pyBOUND

## INTRODUCTION

Methanol is utilized as a feedstock for power generation, transportation fuel, and wastewater treatment, as well as for producing various value-added chemicals [1]. Methanol is environmentally friendly, and the use of methanol has lower risks, lower emissions, and higher performance than gasoline [2]. The data from the methanol market indicate that the methanol market is expected to be worth \$38.0 billion by 2028, growing at a compound annual growth rate of 4.2% during the forecast period [3]. Formaldehyde production from methanol is expected to be the largest demand in the forecasted period [3].

Methanol can be produced by two main processes: methanol from syngas and methanol from CO<sub>2</sub> hydrogenation. Traditionally, methanol is produced from syngas. The first commercial methanol plant was established in 1923 by BASF. Conventionally, methanol is produced

from petroleum products via hydrogenation of CO and CO<sub>2</sub> and reverse water gas shift reaction. In the commercial production of methanol from syngas, a catalyst known as CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> is widely employed [4-5]. The choice of copper-based catalysts for converting CO<sub>2</sub> to methanol is primarily driven by their affordability and high catalyst activity [6]. Nowadays, 80% of worldwide methanol is produced from natural gas [7].

Finding new and more sustainable energy sources is crucial to address the environmental crisis caused by the widespread use of fossil fuels. The largest source of CO<sub>2</sub> emissions among human activities that contribute to greenhouse gases (GHGs) is burning fuels for power and heat, accounting for more than 42% of the estimated anthropogenic CO<sub>2</sub> emissions [8]. Carbon capture utilization and storage is the most common technique to reduce anthropogenic CO<sub>2</sub> emissions. Methanol production from CO<sub>2</sub> hydrogenation (using CO<sub>2</sub> captured and pure hydrogen) is considered an important route to reduce CO<sub>2</sub>

emissions [9]. The impact of direct CO<sub>2</sub> hydrogenation to methanol on the environment is lower than production of methanol from syngas [10]. Many studies focus on the optimization of CO<sub>2</sub> hydrogenation process and present various heat integration within the methanol conversion unit [11-12]. Yousaf et al. summarized computational studies on techno-economic analysis of CO<sub>2</sub> hydrogenation [13]. Most studies on the methanol production design using capture CO<sub>2</sub> and pure hydrogen attempt to reduce the production cost due to the high hydrogen price.

We optimize methanol production via CO<sub>2</sub> hydrogenation in this work. The goal is to minimize the methanol production cost by adjusting the pressure and temperature of the reactor contents. The hydrogenation process is in Aspen HYSYS, and the optimization problem is solved using pyBOUND, a Python-based black-box optimization algorithm using random forests [14]. The paper is organized as follows: The next section provides an overview of the general pyBOUND framework. The Case study section provides information on the simulation and economic analysis of the CO<sub>2</sub> hydrogenation process. The optimization formulation section describes an objective function and constraints of the case study. The Results and Discussion section presents the optimum operating conditions and costs. Our concluding remarks and future directions are summarized in the last section.

## A PYTHON-BASED BLACK-BOX OPTIMIZATION USING RANDOM FORESTS, PYBOUND [14]

pyBOUND is a two-stage algorithm. The first stage employs random forests (RFs) and generates better decision variable bounds, shrinking the search space. The second stage refines the solution using multivariate adaptive regression splines (MARS). A general pyBOUND framework is depicted in Figure 1.

### pyBOUND Stage 1: Shrinking the Search space using RFs

For the first stage, the algorithm reduces the size of the original search space by solving a series of global deterministic subproblems using RF models. This stage consists of sampling, construction of an RF model, global optimization of the constrained approximation problem, and collection of new sampling points. The initial data set is generated using a Sobol sequence design. The overall constrained approximation model, which consists of the RFs model objective equation, the RF model constraints, and variable bounds, is solved to optimality using deterministic global optimization methods. The decision variable bounds are generated from the solution of the constrained approximation optimization problem. The constrained approximation models with the RF models are

MILPs, which are solved with CPLEX (version 22.1.1).

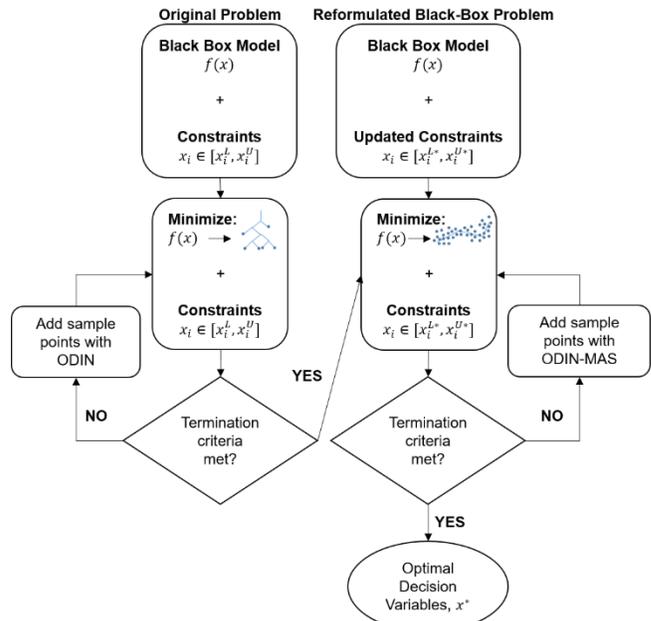


Figure 1. General pyBOUND framework [14].

The algorithm determines a single set of bounds based on the threshold bounds given by every RF tree. The three methods for reducing variable bounds called the cutting methods were studied for bounds reduction. The methods are selecting the widest set of bounds (Wide), selecting the bounds where at least two trees intersect each other (Intersection), and averaging the bounds given by each tree for a single set of bounds (Average). The “Intersection” cutting method is selected for optimization problems with less than ten decision variables, and the “Average” cutting method is selected and implemented for problems with ten or more decision variables.

The ODIN sampling method [15] is selected to update the RF model training set with a termination criterion that depends on the size of the decision variable vector and maximum reduction in the search space.

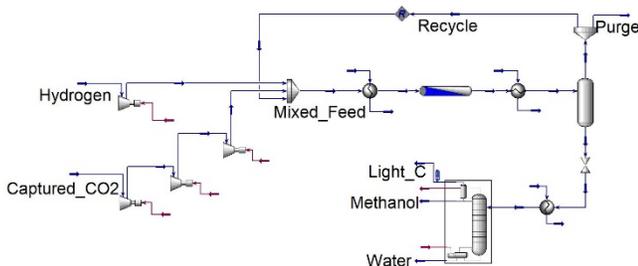
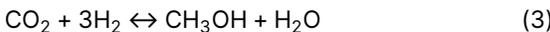
### pyBOUND Stage 2: Refinement of Solution using MARS Models

This stage refines the solution with a local search in the reduced search space, constructs the model, and improves the model with adaptive sampling. Based on the final form of the trained MARS surrogate model, a deterministic optimization problem is formulated and solved to refine the solution. MARS models result in MINLP optimization models, which are solved with ANTIGONE [16]. New sample points are added in the second stage using adaptive sampling on a hybrid of the ODIN sampling method and Mixed Adaptive Sampling (MAS) [17], referred to as ODIN-MAS [15].

## CASE STUDY: METHANOL PRODUCTION

### Process Simulation

The process flow diagram for methanol production implemented within the Aspen HYSYS simulator (version 14) is depicted in Figure 2. The feeds of the process are pure hydrogen and captured CO<sub>2</sub> with a molar flow rate of 3000 kmoles per hour and 1000 kmoles per hour, respectively. Pure hydrogen is fed at 30 bar and 25°C and then compressed to the desired pressure. Captured CO<sub>2</sub> is fed at 2 bar and 28°C through the three-stage compressors to increase pressure before being combined with pure hydrogen. The mixed feed is heated up and enters the reactor, which is modeled as a plug flow reactor and catalytic reaction. The reactions of methanol production via CO<sub>2</sub> hydrogenation follows Equations (1) – (3). The reactor is simulated using a kinetic model [18]. After that, the stream of produced methanol and unreacted feed enters the cooler before it is separated. The vapor stream is recycled and purged with a 0.995 recycle ratio. The liquid phase stream is sent to the distillation column after cooling. The specifications of the distillation column are a 1.52 reflux ratio and 40°C of distillate temperature. The methanol product purity is specified at 99.1% by weight.



**Figure 2.** Methanol production via CO<sub>2</sub> hydrogenation.

### Economic Evaluation

The methanol production cost is determined using an economic analysis. The cost includes both capital and operating costs. These costs are determined through the equations and data from the capital equipment-costing program [19]. The data was adjusted for inflation from the year 2001-2023 by using values of the Chemical Engineering Plant Cost Index, CEPCI. The value of CEPCI in 2001 and 2023 is 297 and 799.1, respectively [20]. The capital cost is calculated using the costing technique. This technique depends on the specific equipment type, the specific system pressure, and the specific material of

construction. In this work, the equipment costs are estimated based on gross root cost ( $C_{GR}$ ), which involves total module cost ( $C_{TM}$ ), Equations (4)-(5), where  $n$  represents the total number of equipment, and bare module cost ( $C_{BM}$ ), Equation (6).  $F_M$  and  $F_p$  are the material factor and pressure factor, respectively.

$$C_{GR} = C_{TM} + 0.50 \sum_{i=1}^n C_{BM,i}^0 \quad (4)$$

$$C_{TM} = \sum_{i=1}^n C_{TM,i} + 1.18 \sum_{i=1}^n C_{BM,i} \quad (5)$$

$$C_{BM} = C_p^0 F_{BM} = C_p^0 [B_1 + B_2 F_p F_M] \quad (6)$$

where  $C_p^0$  is the purchased cost for a base condition which can be calculated following Equation (7).

$$\log_{10} C_p^0 = K_1 + K_2 \log_{10}(A) + C_3 (\log_{10}(A))^2 \quad (7)$$

$A$  is the capacity or size parameter for the equipment. The overall assumptions used for the cost estimation are as follows:

- The plant operates for 8400 hours per year.
- The plant is expected to have 20 years of plant operation and a 10% interest rate.
- Direct supervisory and clerical labor are taken 18% of labor cost.
- Maintenance and repairs are taken 6% of the fixed capital investment.
- Operating supplies are taken 0.9% of the fixed capital investment.
- Laboratory charges are taken 15% of labor cost.
- Local taxes and insurance are taken at 3.2% of the fixed capital investment.
- Plant overhead cost is the summation of 70.8% of labor cost and 3.6% of the fixed capital investment.
- Administration cost is the summation of 17.7% of labor cost and 0.9% of the fixed capital cost.

### OPTIMIZATION FORMULATION

We consider the methanol production via CO<sub>2</sub> hydrogenation as a black-box optimization problem of the form given in Equations (8)-(9),

$$\min_x f(x) \quad (8)$$

$$\text{subject to } x_i \in [x_i^L, x_i^U] \quad \forall i \in \{1,2\} \quad (9)$$

The objective of the optimization problem is to minimize the methanol production cost where  $f(x)$  represents the methanol production cost with the decision

variables of the process with finite bounds  $[x_i^L, x_i^U]$ ,  $x_i$  represents the decision variables:  $x_1$  is the pressure and  $x_2$  is the temperature of the reactor contents. The range of each decision variable is given in Table 1.

**Table 1:** Initial range of decision variables.

Decision variables	Lower bound	Upper bound
Pressure (bar)	50	80
Temperature (°C)	190	210

## RESULTS AND DISCUSSION

The goal is to minimize methanol production cost by applying a derivative-free optimization algorithm, pyBOUND. From the results of the RF stage, the “Intersection” cutting method is used to shrink the search space of the optimization problem. The results at each iteration of the RF stage are shown in Table 2.

**Table 2:** The reduction of search space.

Iteration	1	2	3
Volume of reduction (%)	53.13	72.90	80.13
Number of sample points	20	15	15
Lower bound	50, 190	62.66, 190	62.66, 190
Upper bound	80, 199.38	80, 199.38	80, 196.88

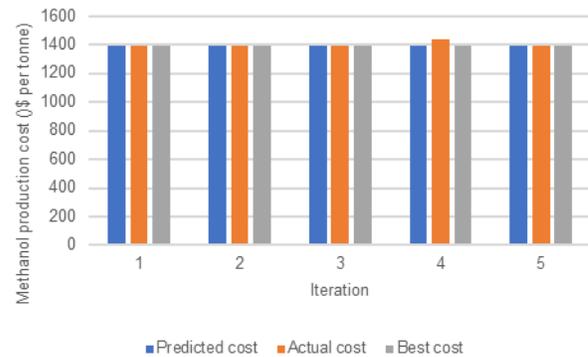
The criterion for the termination of the RF stage is specified as the maximum volume reduction of search space of 0.75. The bound of the pressure is reduced to the range 62.66 – 80 bar and the bound for temperature is reduced to the range 190 – 196.88°C. Eighty percent of the search space is reduced compared to the original search space. The third row of Table 2 shows the number of sample points. Originally, the number of sample points was generated with ten times the number of decision variables (20 sample points). After applying pyBOUND, the final number of sample points in the RF stage is 15, while the number of function evaluations is 30, which is due to some sample points being cut during the RF stage iterations. Fifteen sample points are then used as the initial sample set for the MARS stage.

The results of the MARS stage at each iteration are shown in Table 3. Figure 3 also shows the results of the predicted, actual, and best methanol production cost at each iteration. The best methanol production cost is the lowest cost in the training data set. In the MARS stage, the sample points are added at each iteration using ODIN-MAS algorithm. The pyBOUND algorithm stopped at 144 sample points while the R-squared value of the

model increased after increasing the number of sample points. For the first iteration, the model can not fit well with only twenty sample points. The value of R-squared at the first iteration shows a negative value. At the second iteration, the total number of sample points used to construct the MARS model increased to 37, and the value of R-squared is a positive value.

**Table 3:** MARS model and optimal results

Iteration	Function evaluation	R-squared	Predicted optimum location (bar, °C)
1	20	-0.05	68.84, 192.26
2	37	0.26	68.80, 192.34
3	58	0.50	68.68, 192.24
4	90	0.86	72.51, 192.32
5	144	0.88	68.82, 192.23

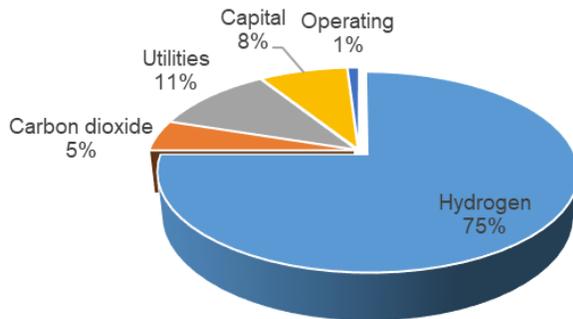


**Figure 3.** The values of minimum methanol production cost at each iteration.

The predicted methanol production costs at each iteration are close to the actual methanol production costs. Finally, the pyBOUND algorithm stopped with the criteria of R-squared value more than 0.6 and the Euclidean distance between the best objective values of the last three iterations less than 0.0004. The error between predicted and actual methanol production costs is 0.19%. The optimum methanol production cost is \$1396.56 per tonne of methanol, corresponding to a pressure of 68.82 bar and a temperature of 190.23°C, while the actual methanol production cost at these conditions is \$1393.95 per tonne of methanol. We found that the best objective value is \$1393.80 per tonne of methanol. This value is close to the actual objective value and the best location is similar to the predicted optimal location. The Euclidean distance between the best and actual objective values is 0.02 at the last iteration. The algorithm run time is 458.5 min, which is divided into 79.92 min for the RF stage and 378.58 min for the MARS stage. From the total run time, the time for pyBOUND is 17.32 min, with the remaining

time spent by Aspen HYSYS process simulation.

At the optimum, the contribution of various factors to the cost is illustrated in Figure 4. The contribution of raw materials, including CO<sub>2</sub> and H<sub>2</sub> prices, are 5% and 75%, respectively. The utilities make up 11% of the overall cost. The capital and other operating expenses are 7% and 1%, respectively. The H<sub>2</sub> price is identified to be the major cost of this process.



**Figure 4.** Cost breakdown.

## CONCLUSION AND FUTURE WORK

The pyBOUND algorithm has been successfully applied to the optimization of methanol production via CO<sub>2</sub> hydrogenation process. The minimum cost of methanol production is determined. The algorithm, pyBOUND, demonstrates that the algorithm can estimate the optimum value of the methanol production cost with a small number of sample points. Future work on pyBOUND will focus on applying the algorithm to problems with high number of decision variables and several chemical engineering problems. The optimum value obtained by pyBOUND is comparable to other optimization methods. pyBOUND might exhibit improvements when compared to existing algorithms for both high dimensionality problems and for locating the true optimal decision variable values. We will consider the hyperparameters of the RF stage for consistency of generating variable bounds and investigate the impact of the stopping criteria of the pyBOUND algorithm.

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