

# Process Optimization under Parameter Uncertainty Conditions in CCU Process

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**Abstract:** In order to produce methanol using CO<sub>2</sub> and H<sub>2</sub>, several processes about the related catalytic reaction has been suggested and simulated. There may be systematic uncertainties like parameters of reaction kinetics, so a modelling method considering the parametric uncertainty is proposed and can give more informative data compared to the conventional modelling methods. However, the resulting distributional model requires large computational burdens due to the iterative calculations for convergence. To solve the problem, generalized extreme value distribution (GEVD) and neural network (NN) modellings are utilized. The formation parameters of GEVD are fitted by NN and as a result distributional reactor model in an explicit formulation is proposed. Compared to the shallow structured neural network for learning the formulation parameters, the deep neural network shows improved performance especially adjacent to the boundary layers of process inputs. As its explicit and distributional formulation, the proposed model is expected to be utilized for real-time stochastic model based approaches in optimization and control with reduced computational load.

*Keywords:* Process optimization, Methanol production, Carbon capture and utilization, Parametric uncertainty, Neural network, Generalized extreme value distribution

## 1. INTRODUCTION

CO<sub>2</sub> capture and utilization (CCU) is a technique utilizing the capture CO<sub>2</sub> as a raw material to produce high value added product and expected to reduce the global warming problem related to the green house gas emissions Al-Mamoori et al. (2017); Baena-Moreno et al. (2019). One of the key technologies in CCU is the synthesis of base materials like methanol (Van-Dal and Bouallou (2013)), ethanol (Atsonios et al. (2016)), formic acid (Ahn et al. (2019)) or dimethyl ether (Michailos et al. (2019)).

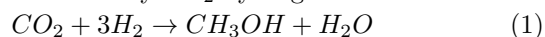
Producing methanol technology by CO<sub>2</sub> hydrogenation, which is also known as power-to-fuel concept, is one of the key CCU technologies (Al Shakhshir et al. (2017); Boretti (2013)). For now, most methanol is produced by the reforming natural gas due to the low economic feasibility (Ali et al. (2015); Manenti et al. (2011)). However, various attempts have been made globally to commercialize the methanol production process by CCU technology (Al-Kalbani et al. (2016); Pérez-Fortes et al. (2016)). Commercial reactors for producing methanol from CO<sub>2</sub> and H<sub>2</sub> have been developed and the several issues like the removal of the reaction heat, pressure drop, cost, and scalability have been dealt with (Lange (2001); Bozzano and Manenti (2016)). In addition, simulation based approaches have been studied in various levels of the modelling such as one dimensional reactor (Leonzio et al. (2019)), process (Milani et al. (2015); Asif et al. (2018)) and computational fluid dynamics modelling (Cui and Kær (2020)).

In the aspect of modelling, the conventional approaches used only a single set of kinetic parameters in general. However, not only in the reaction kinetics but also in the

process itself, parametric uncertainties on the methanol production process model can exist. From the best of the author's knowledge, the effect of parametric uncertainty on the methanol production process using CO<sub>2</sub> hydrogenation have not been studied. So, this study focused on the parametric uncertainty in the reaction kinetics and proposed an explicit and distributional methanol production reactor model using several machine learning techniques.

## 2. METHANOL PRODUCTION REACTOR MODEL UNDER KINETIC PARAMETER UNCERTAINTY

To simulate the methanol production reactor (MPR) and process, it is assumed that multiple tubular packed bed reactor with commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is used. The packed bed reactor and related assumptions are depicted in Figure 1 (a). Also, a recycle process is added as described in Figure 1 (b) in order to increase the conversion and selectivity by reusing the not-converted reactants. Well-known reaction kinetics about the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst by Van den Bussche and Froment are used (Bussche and Froment (1996)). Reaction 1 ( $r_1$ ) is about methanol production by CO<sub>2</sub> hydrogenation:



For  $r_1$ , the heat of reaction is  $\Delta H_{298,r_1}^0 = -49.5$  [kJ/CO<sub>2</sub>mole]. The kinetic equation of  $r_1$  is

$$r_1 = \frac{k_1 p_{\text{CO}_2} p_{\text{H}_2} \left(1 - \frac{p_{\text{me}} p_{\text{H}_2\text{O}}}{K_{eq,1} p_{\text{H}_2}^3 p_{\text{CO}_2}}\right)}{\left(1 + k_c \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} + k_a p_{\text{H}_2}^{0.5} + k_b p_{\text{H}_2\text{O}}\right)^3} \quad (2)$$

$$\log_{10} K_{eq,1} = \frac{3066}{T} - 10.592 \quad (3)$$

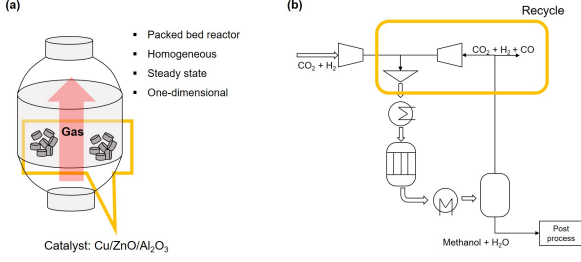


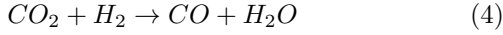
Fig. 1. (a) Methanol production reactor and assumptions for simulation, (b) Simplified methanol production process with separation and recycle

Table 1. Nominal parameters for methanol producing reactor

Parameter	[Unit]	Value
$T_{ref}$	[K]	501.75
$\rho_p$	[kgcat/m <sup>3</sup> ]	1175
$d_p$	[m]	0.006
$\phi$	[.]	0.04
$D_t$	[m]	0.058
$U$	[J/s/m <sup>2</sup> /K]	1000
$N_t$	[.]	150
$F_{tot,0}$	[mole/s]	100
$F_{me,0}$	[mole/s]	0
$F_{H_2O,0}$	[mole/s]	0
$F_{CO,0}$	[mole/s]	0
Pressure	[Pa]	$55 \times 10^5$

where  $p_i$ ,  $k_j$ ,  $T$  and  $K_{eq,1}$  are the partial pressure [bar], kinetic parameters, temperature [K] and equilibrium constant, respectively.

Reaction 2 ( $r_2$ ) is known as the reverse water gas shift (rWGS) and its formulation is:



For  $r_2$ , the heat of reaction is  $\Delta H_{298,r_2}^0 = 41.2$  [kJ/CO<sub>2</sub>mole] and kinetic equation is

$$r_2 = \frac{k_2 p_{CO_2} \left(1 - \frac{p_{CO} p_{H_2O}}{K_{eq,2} p_{H_2} p_{CO_2}}\right)}{\left(1 + k_c \frac{p_{H_2O}}{p_{H_2}} + k_a p_{H_2}^{0.5} + k_b p_{H_2O}\right)} \quad (5)$$

$$\log_{10} K_{eq,2} = -\frac{2073}{T} + 2.029 \quad (6)$$

Although there exist other kinetic models such as by Graaf et al. (Graaf et al. (1986)), the simulation result becomes the same as the equilibrium conversion is approached or towards the exit of the reaction (Leonzio et al. (2019)). Other side reactions except for rWGS are negligible due to the high selectivity of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, so these are omitted in this study.

The kinetic parameters in equation (2) and (4) are defined as:

$$k_j = k_j^* \exp\left(-\frac{E_j}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right), j \in (1, 2, a, b, c) \quad (7)$$

where  $E_j$ ,  $R_g$  and  $T_{ref}$  are the activation energy, gas constant and reference temperature, and their values are given in Table 1.

For the base simulation, the balance equations by Leonzio et al. are used in this study (Leonzio et al. (2019)). The resulting ordinary differential equations (ODEs) are solved using *ode45* function in MATLAB. A portion of the vapor stream with a specific recycle ratio ( $R$ ) fuses with the original feed stream, then the mixed stream enters the reactor again. Due to the recycle process, iterative simulation needs until the simulations are converged. As the recycle process is progressed, the outlet flow rates increase and converged to the certain values. After several simulations by changing the recycle ratio, it is concluded that the recycling can increase the conversion and methanol production. This result shows the similarity with the work by Leonzio et al. which verified its feasibility using literature and experimental data (Leonzio et al. (2019)).

The existing kinetic parameters are obtained from the lab-scale experiments (Bussche and Froment (1996)). These have the distributional information such as the mean and standard deviation values and the normal Gaussian distribution is assumed. However, the conventional simulation studies have used the mean values of the kinetic parameters only (Leonzio et al. (2019)). So, the results have a limitation that only limited information about the process may be obtained.

In other words, a simulation result considering uncertainty can be achieved by using the mean and standard deviation values of the kinetic parameters. Compared to the simulation result using fixed value of kinetic parameters, it can give information about the probability density functions (PDFs) of the important process outputs. These PDFs can be utilized to develop stochastic optimization or control schemes of MPR processes. In this study, we also assumed the normal distribution for the kinetic parameters from the given data by Bussche et al. (Bussche and Froment (1996)). Furthermore, this study assumes the standard deviation values which are five times larger than the existing values to reflect a real process with conservativeness. Under an uncertainty condition, Monte Carlo simulation is used to iteratively sample and simulate the cases and generate a distribution of the process output (Mooney (1997)).

Four process input variables are considered:

- (1) Inlet temperature of mixed stream to reactor ( $T_i$ )
- (2) Jacket temperature ( $T_j$ )
- (3) Recycle ratio ( $R$ )
- (4) H<sub>2</sub>/CO<sub>2</sub> ratio in the inlet stream except recycle ( $P_{H_2/CO_2}$ )

As a result of changing the process input variables, three key output variables are reflected:

- (1) Selectivity of  $r_1$  ( $S_1 = \frac{X_1}{X_1 + X_2}$ )
- (2) Process conversion ( $X_p = \frac{CO_2(\text{outlet}) - CO_2(\text{inlet})}{CO_2(\text{inlet})}|_{process}$ )
- (3) Reactor conversion ( $X_1 = \frac{CO_2(\text{consumed in r1})}{CO_2(\text{inlet})}|_{reactor}$ )

As results of the Monte Carlo simulation under parametric uncertainty, distributional process output data are obtained. Figure 2 (a) shows a case that median values of input variables are used, and Figure 2 (b) shows a case using the process input variables adjacent to the boundary layers. Although the parametric uncertainty is

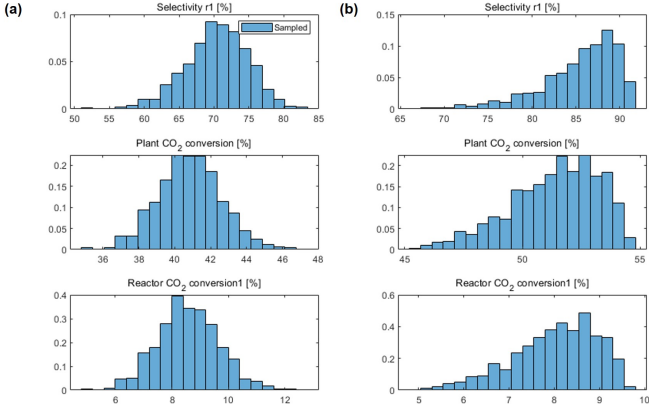


Fig. 2. Vanilla distributional MPR simulation result: (a) At the median process inputs, (b) With the process inputs adjacent to the boundary layers

assumed to be a normal distribution, the key output's probability distribution function is skewed in a certain range as especially presented in Figures 2 (b). This result is because the model has a severe nonlinearity in the mass and energy balance and reaction equations. Thus, the skewed PDF needs to be fitted by a specific distributional function such as generalized extreme value distribution (GEVD) which has additional degree of freedom for the model parameter, rather than just the normal Gaussian distribution which only considers the mean or standard deviation. Furthermore, the distributional MPR model needs to have less computational burden for a single execution because model based optimization or control problem is time-consuming applications. Thus, a new distributional MPR model which has an explicit formulation and considers the skewness is proposed by using sampled data and machine learning technique.

### 3. DISTRIBUTIONAL MPR MODEL COMBINED WITH MACHINE LEARNING TECHNIQUES

In order to find the formation parameters of the skewed probability density functions of outputs, generalized extreme value distribution (GEVD) modelling is utilized (Hosking (1985)). GEVD modelling technique is generally used to model the smallest or largest value among a large set of measurement data which are randomly sampled in the independently and identically distributed (i.i.d.) manner. There exist three formation parameters for GEVD: the location parameter  $\mu_{GEVD}$ , scale parameter  $\sigma_{GEVD} (> 0)$  and shape parameter  $k_{GEVD}$ . The advantages of GEVD to fit the skewed PDF of outputs are the small number of formation parameters and the predicting performance. Compared to the other methods such as kernel distribution which needs the whole historical data to predict a new output distribution, GEVD uses only three formation parameters ( $\mu_{GEVD}$ ,  $\sigma_{GEVD}$  and  $k_{GEVD}$ ). In addition, its predicting performance outperforms other methods such as Weibull distribution method especially adjacent to the boundaries of process inputs.

In order to solve the problem of the heavy computational loads for a single execution and make the model applicable for real-time approaches, an explicit formulation of the distributional MPR model is proposed using sampled

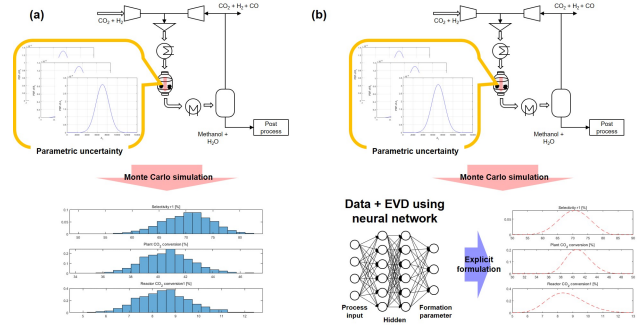


Fig. 3. (a) Vanilla distributional MPR modelling method, (b) Proposed explicit and distributional MPR modelling method

data and machine learning techniques. Neural network (NN) technique has been generally used for supervised or unsupervised learning in several applications (Jeong and Lee (2018)), so is applied in this study. The input variables for neural network learning are the same as the process inputs ( $T_i$ ,  $T_j$ ,  $R$  and  $P_{H_2/CO_2}$ ) and the output variables for neural network learning are the formation parameters ( $\mu_{GEVD}$ ,  $\sigma_{GEVD}$  and  $k_{GEVD}$ ) of each process outputs ( $X_{1,r}$ ,  $X_{1,p}$  and  $S_1$ ).

Compared to the vanilla distributional MPR modelling method which is defined to have no machine learning applications as in Figure 3 (a), the proposed method has additional steps for learning the relationship between the process inputs and distributional output. First, 1000 process input data points are selected randomly by Latin hypercube sampling technique in the given ranges (Stein (1987)) in order to generate the simulation data for fitting GEVD (Stein (1987)). Second, 1000 iterative Monte Carlo simulations are executed and distributional results of process output ( $S_1$ ,  $X_p$  and  $X_1$ ) and their PDF are given for each selected input data point. Third, the GEVD formulation parameters of each process output are estimated by MLE (Kotz and Nadarajah (2000); Embrechts et al. (2013)). Fourth, the weights of neural network are estimated using the data set. Finally, the results of neural network and GEVD are combined to make an explicit formation of distributional MPR model. The procedure for constructing an explicit distributional MPR model is illustrated in Figure 3 (b).

Sampled data and the distributional MPR model in an explicit formulation are compared to prove the validity of the proposed method. First, simulation results which express the GEVD formulation parameters using shallow neural network are shown in Figures 4. Under median process input conditions, both distributions of the process outputs by sampled data and the predictive model show less skewness and high similarity. However, the proposed model cannot predict the distribution of process output adjacent to the boundary layers of process input. Especially, predictions of  $X_p$  and  $X_1$  by the proposed method with shallow structured neural network show poor performances compared to  $S_1$ . It is because  $X_p$  and  $X_1$  have more narrow distribution than  $S_1$  while having the skewness.

Also, simulation results which express the GEVD formulation parameters using deep neural network are shown in Figures 5. As the shallow structured case, both distri-

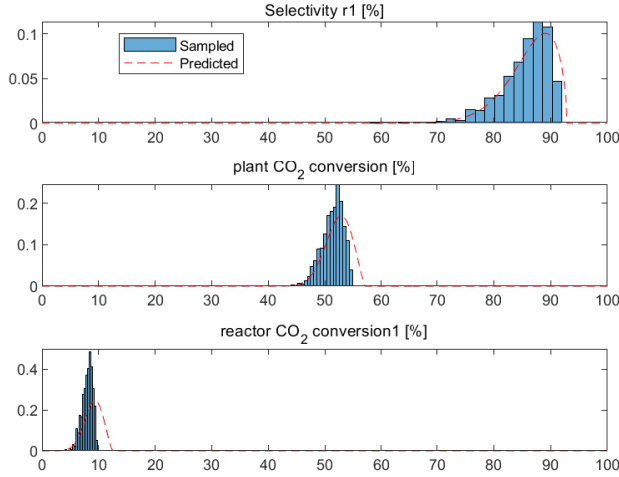


Fig. 4. Probability density function of the process output variables nearby the boundary layer. GEVD formulation parameters are learned using shallow neural network.

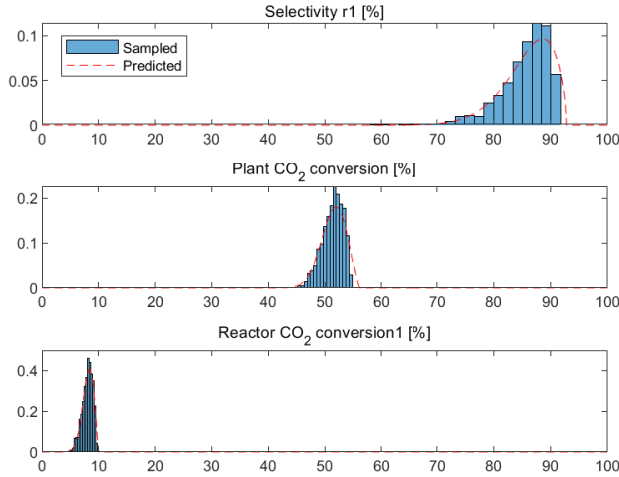


Fig. 5. Probability density function of the process output variables nearby the boundary layer. GEVD formulation parameters are learned using deep neural network.

butions of the process outputs by sampled data and the predictive model show less skewness and high similarity under the median process input conditions. When the deep structured neural network is used, the proposed model can predict the distribution of process output well even adjacent to the boundary layers where the sampled data show a severe skewness. This result is because the deep structured neural network can fit the complex correlations between the process input and output.

#### 4. OPTIMIZATION USING EXPLICIT PDF OF CCU PROCESS

The distributional result of the MPR model can be more informative than that of the conventional single parameter set because it gives a probability density function of each

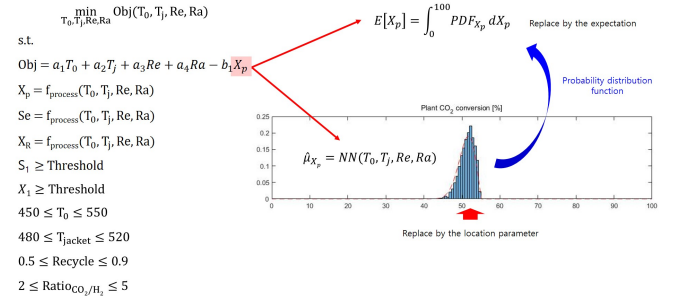


Fig. 6. Objective function expression in the optimization problem using explicit PDF

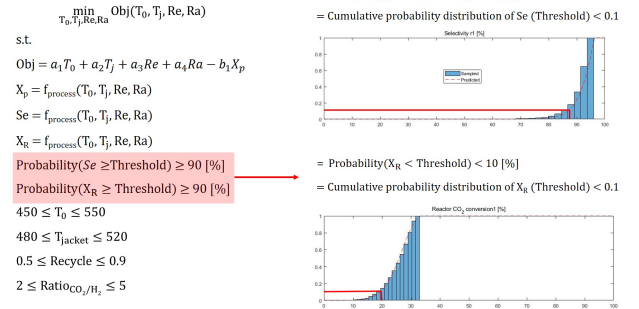
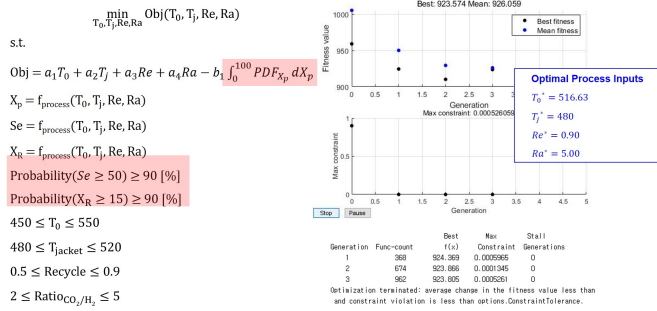


Fig. 7. Probability constraint expression in the optimization problem using explicit PDF

process output. The probability density functions of each process output can be used to solve a stochastic optimization problem or develop a robust control scheme of a MPR process. Also, the proposed method shows reduced computational time compared to the vanilla distributional simulation because of its explicit formulation using GEVD and neural network. This will make it possible to use the proposed model for the real-time applications of control and optimization in faster and easier ways.

Optimization problem using the explicit PFD of key output variables are given in Figures 6-7. In Figure 6, the objective function containing distributional function of  $X_p$  is changed using the explicit PFD: (1) Using expectation value, (2) Using the parameter  $\mu_{GEVD}$  of  $X_p$ . In Figure 7, the constraints containing probability of  $S_1$  and  $X_1$  are transformed using the explicit cumulative probability distribution function. As the case that the probability of  $S_1 \geq \text{Threshold}$  has greater than or equal to 90 percent is equivalent to the case that the probability of  $S_1 < \text{Threshold}$  has less than 10 percent, the constraint formation is simply changed by using CFD function of the  $S_1$ . With the same logic, the probability constraint expression about  $X_1$  can be obtained and the CFD functions are calculated using the explicit PDFs of each key process variables.

The optimization result is given in Figure 8. The expectation value of  $X_p$  is used to calculate the objective function and the threshold values are given in the Figure 8. Genetic algorithm is used for searching the optimal solution because it has a severe nonlinearity. Because the probability distributions are expressed as explicit formulations using GEVD and DNN, the computational loads are reduced compared to the vanilla distributional model applications.



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Fig. 8. Optimization result having probability objective and constraints by explicit PDF

## 5. CONCLUSION

Based on the conventional MPR modelling results, the parametric uncertainty on the kinetics is studied and several machine learning techniques are combined to make the model applicable for real-time optimization and control. By iterative Monte Carlo simulation, distributional process outputs are obtained and gives more informative data than the conventional method which uses only a single fixed parameter set. Furthermore, this study proposes an explicit formulation of distributional MPR model. First, the process outputs are fitted using GEVD to reflect the skewness especially adjacent to the boundary layers of process inputs. Second, the formation parameters of GEVD are learned using shallow and deep neural network. From the simulation results, it is concluded that the predictive performance of the method using deep structured neural network outperforms that of shallow one especially adjacent to the boundary layers of process inputs. Also, the proposed method has an explicit formulation and less computational load compared to the conventional method without post-process of data.

Using the proposed explicit and distributional MPR model which has a less computational burden and stochastic information, it is expected that several model based applications can be done. For example, a Pareto optimum of the operating condition which minimizes the energy consumption while maximizing the production yield can be found using the stochastic model. Also, a robust model predictive controller can be designed and applied in the real time applications because of its explicit formulation and less computational loads. Finally, the proposed methodology can be generally utilized in other reaction models with kinetic parameter uncertainty. Depending on the degree of skewness and characteristics the output distribution has, different machine learning techniques can be used such as Gaussian, Weibull or kernel distribution.

## ACKNOWLEDGEMENTS

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