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Robust design of experiments using constrained stochastic optimization

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Abstract: Process models that are affected by uncertainties need a robust mechanism to account for them in the model based design of experiments (DOE). The aim of this study is to design a set of experiments to estimate the parameters of multiscale kinetic models for the catalytic decomposition of ammonia. Along with uncertainties in the model, the problem is challenging due to constraints on experimental conditions. A stochastic D-optimal design is used to find the optimal experimental conditions using maximization of the expectation of properties of the Fisher information matrix (FIM). The expectation of FIM is calculated by sample average approximation (SAA) based on Monte Carlo simulations. Particle swarm optimization (PSO) is used to perform stochastic optimization to find the optimal set of experimental conditions. A novel method based on the rescaling of velocities is proposed for handling of equality and inequality constraints in particle swarm optimization.

Keywords: Optimal experimental design, constrained optimization, stochastic modeling and optimization, sensitivity analysis

1. INTRODUCTION

Dynamic mathematical models for chemical processes have been commonly applied in the area of control, optimization and monitoring of the processes. Additionally, for complex processes, these also aid in understanding the physics of the process. Experiments are performed for model validation and parameter estimation. However, with wide ranges of experimental conditions possible for chemical processes, and dependence of the model response on various parameters, optimal designs should be employed to reduce experimental effort. The design of experiments (DOE) is a technique used to design the experiments in a systematic manner. In general, DOE is applied to assess the factors that affect the response variables of the system (Telford, 2007). This organized way of designing experiments is helpful in achieving various experimental objectives such as hypothesis testing, model validation and parameter estimation with precise results (Jacquez, 1998). Many conventional design methods such as factorial designs with different levels, fractional factorial designs, response surface designs and methodology, and optimal designs have been used for experimental design (Ryan, 2007; Sarabia, 2009). Bayesian experimental design techniques have also been employed for linear and nonlinear systems (Chaloner & Verdinelli, 1995; Laínez-Aguirre, et al., 2015). However, unless carefully designed, they fail to account for uncertainties in model parameters.

The model based DOE as suggested by Beltrán-Oviedo, et al., 2009 uses statistical criteria to provide kinetically relevant experimental conditions and estimate parameters.

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The variation in estimated parameter influences the predicted output of the model, which is measured by the sensitivity matrix ($\boldsymbol{S}$):

$$\boldsymbol{S} = \left(\frac{\partial \boldsymbol{y}}{\partial \boldsymbol{\theta}^{\boldsymbol{T}}}\right) \quad (1)$$

where $\boldsymbol{y}$ is the output of the system and $\boldsymbol{\theta}$ is the parameter set for the problem. The output is affected by measurement noise that is often assumed to be normally distributed with zero mean and covariance $\sum$. The Fisher information matrix (FIM) given in eqn. (2), which is related to the inverse of the covariance matrix, is commonly used in model-based experimental design as it provides the information on the effect of the parameters without performing any experiment or simulation (Ludwig, 2011; Myung & Navarro, 2005)

$$\boldsymbol{F}(\boldsymbol{\theta}) = \left(\frac{\partial \boldsymbol{y}}{\partial \boldsymbol{\theta}^{\boldsymbol{T}}}\right)^{T} \boldsymbol{\Sigma}^{-1} \left(\frac{\partial \boldsymbol{y}}{\partial \boldsymbol{\theta}^{\boldsymbol{T}}}\right) \quad (2)$$

It provides a (probabilistic) measure of the identifiability of the parameters. If the measurement noise is uncorrelated and constant with time, the covariance matrix $\sum = \mathrm{I}$, which leads to the following simplification:

$$\boldsymbol{F}(\boldsymbol{\theta}) = \left(\frac{\partial \boldsymbol{y}}{\partial \boldsymbol{\theta}^{\boldsymbol{T}}}\right)^{T} \left(\frac{\partial \boldsymbol{y}}{\partial \boldsymbol{\theta}^{\boldsymbol{T}}}\right) \quad (3)$$

Various alphabetical optical designs (A, D, E, G and V) based on the FIM have been employed for selecting optimal experimental conditions (Ogunnaike, 2010). The presence of constraints on experimental conditions requires the development of constrained optimization techniques based on maximization of the properties of the FIM.

An important and widely studied system consisting of the catalytic decomposition of ammonia on ruthenium catalyst is designed to illustrate the procedure for optimal experiment design and parameter estimation on a multi-scale kinetic model of the process. This work uses stochastic optimization

techniques to maximize the value of the D-optimal statistical metric averaged over a number of samples. It is assumed that probability distributions governing the uncertainty in the parameters are known. Sampling average approximation, based on the Monte Carlo method, is used to evaluate the expectation of the objective function to be maximized. In the optimization step, particle swarm optimization (PSO) is performed with a heuristic procedure developed for constrained nonlinear optimization.

2. KINETICS AND REACTOR MODEL

The catalytic decomposition of ammonia is chosen as the system to design and implement a robust scheme for DOE using constrained optimization. The overall reaction is

$$2NH_3 \leftrightarrow N_2 + 3H_2 \qquad (4)$$

Various studies have been performed on modeling this catalytic system on ruthenium catalyst (Deshmukh, et al., 2004; Lee, et al., 2011; Prasad, et al., 2009). Based on these studies, this system can be divided into 3 sub-processes: *adsorption*, *desorption*, and *surface reaction* to produce N_2 and H_2. The rate constants for these 3 types of reaction are given in Table 1. Microkinetic models based on a detailed reaction mechanism including all relevant elementary reactions are used to model the ammonia decomposition as shown in Table 2.

Table 1. Rate constants of elementary reactions (Lee et al., 2011, Prasad et al., 2009). k: rate constant, s: sticking factor, θ: fractional surface coverage, E_a: activation energy, σ: site density

Reaction Type	Rate Constant
Adsorption	$k = \frac{s}{\sigma^n}\sqrt{\frac{RT}{2\pi M}}\left(\frac{T}{T_0}\right)^{\beta} e^{-\frac{E_a(\theta,T)}{RT}}$
Desorption	$k = \frac{A}{\sigma^{n-1}}\left(\frac{T}{T_0}\right)^{\beta} e^{-\frac{E_a(\theta,T)}{RT}}$
Surface Reaction	$k = \frac{A}{\sigma^{n-1}}\left(\frac{T}{T_0}\right)^{\beta} e^{-\frac{E_a(\theta,T)}{RT}}$

Table 2: Elementary reactions representing the decomposition of ammonia on a Ru surface (Lee et al., 2011)

No.	Reaction
1	$H_2 + 2* \rightleftharpoons 2H*$
2	$N_2 + 2* \rightleftharpoons 2N*$
3	$NH* + * \rightleftharpoons N* + H*$
4	$NH_2* + * \rightleftharpoons NH* + H*$
5	$NH_3* + * \rightleftharpoons NH_2* + H*$
6	$NH_3 + * \rightleftharpoons NH_3*$

The model was developed considering the reversible elementary reactions shown in Table 2 (* indicates a vacant site or, in conjunction with a chemical species, an adsorbate). The nominal values for the sticking coefficients and pre-exponentials to be used for the D-optimal design, and the coverage and temperature dependencies of the activation energies are taken from the work of Lee et al., 2011. A plug flow reactor (PFR) is used to model the reactor packed with catalyst with reactor specifications mentioned in Table 3.

Table 3: Reactor specifications

Characteristic	Value
Length(L, cm)	1.7
Diameter(D,cm)	0.41
Site density (s_a,mol/cm^2)	1.66 X 10^{-9}

The reactor model is represented as (Kumar, 2011):

$$\frac{dy_{k,gas}}{dx} = \frac{a_v M_w \sigma_{gas}}{\rho u} \qquad (5)$$

where y is the mass fraction of the species in the gas phase, a_v is the surface area to volume ratio of the catalyst, M_w the molecular weight of the species, u is the superficial gas-phase velocity, σ_k is the surface reaction rate, and ρ is the fluid density. The microkinetic model of Prasad et al. (2008) has two sets of parameters for each elementary reaction, the activation energy and the pre-exponential factor.

In this study, it is assumed that the activation energies calculated using the unity bond index quadratic exponential potential method (UBIQEP) are accurate and do not need to be estimated and the only parameters to be estimated are the pre-exponentials (Prasad and Vlachos, 2008).

Thermodynamic consistency at both enthalpic and entropic levels is often neglected in mechanism development and parameter estimation for these models (Mhadeshwar *et al.* 2003). Enthalpic inconsistency gives incorrect predictions of conversion/selectivity, and entropic inconsistency translates to incorrect predictions in the pre-exponential factors. Hence, both these inconsistencies distort the underlying equilibrium constant, which affects the prediction of equilibrium states. In the mechanism outlined in Table 2, there are 6 reversible reactions. In general, for the ith reversible reaction in the mechanism, the following equations form the basis of the enthalpic and entropic constraints:

$$E_i^f - E_i^b = \Delta H_i\,, \quad i = 1, \ldots, 6 \qquad (6)$$

$$\frac{A_i^f}{A_i^b} = e^{\Delta S_i/R}\,, \quad i = 1, \ldots, 6 \qquad (7)$$

where f and b stand for the forward and backward steps, A is the pre-exponential factor, E is the activation energy, R is the universal gas constant and ΔH and ΔS are the enthalpy change and entropy change of the reversible reaction respectively. However, only the constraint on the pre-exponentials should be implemented as the UBIQEP method ensures that the activation energies are in agreement with their constraints. These thermodynamic constraints leave just 6 parameters for consideration in the uncertainty analysis.

3. EXPERIMENTAL DESIGN AND OPTIMIZATION METHODOLOGY

A reasonable estimate of the nominal values of model parameters is required for D-optimal design. The need for stochastic modeling arises because the actual value of the parameters might be different from this nominal value, and

hence the D-optimal design and parameters estimated by the actual experiment data may end up being far from optimal. Thus, the design method should incorporate the uncertainty in the nominal values of the parameters and the solution proposed in the literature is to solve a stochastic optimization problem for the system (Lee et al., 2011).

3.1. Optimization Problem

The decision variables for the optimization problem (i.e., the design variables to be optimized) are temperature (T), pressure (P), ratio of catalyst surface area to the volume (a_v), residence time (τ) and inlet mole fractions of hydrogen (x_1), nitrogen (x_2), ammonia (x_3) and argon (x_4). Additionally, the sum of mole fractions is constrained to equal one. Each of the variables is restricted between an upper (UB) and lower bound (LB) in the form of inequality constraints. The optimization problem is formulated as:

$$X = [\,T \quad P \quad a_v \quad \tau \quad x_1 \quad x_2 \quad x_3 \quad x_4\,] \tag{8}$$

$$J = \log(\det(FIM)) \tag{9}$$

$$\max_X \quad \mathbb{E}_\varepsilon[J] - \beta(\,\mathbb{E}_\varepsilon[J^2] \;\; (\mathbb{E}_\varepsilon[J])^2) \tag{10}$$

$$subject\ to \quad \begin{matrix} LB \le X \le UB \\ A_{eq}X = B_{eq} \end{matrix} \tag{11}$$

where FIM is the Fisher information matrix, $\mathbb{E}_\varepsilon$ is the expectation operator and β is a weight applied to the variance of the expectation operator (Kall and Wallace, 1994), and A_{eq} and B_{eq} are matrices required to formulate the constraint equation for the set of decision variables such that sum of the mole fractions of gaseous species is equal to one.

Table 4: Bounds of decision variables for the optimization

Decision Variable	Symbol	Lower Bound (LB)	Upper Bound (UB)	Scaling
Temperature	$T(K)$	500	1000	Linear
Pressure	$P(atm)$	0.1	10	Logarithmic
Residence Time	$\tau(s)$	0.05	5.0	Logarithmic
Ratio of catalyst surface area to volume	$a_v(1/cm)$	150	15000	Logarithmic
Mole fraction of (NH_3)	x_1	0	1	Linear
Mole fraction of (H_2)	x_2	0	1	Linear
Mole fraction of (N_2)	x_3	0	1	Linear
Mole fraction of Ar	x_4	0	1	Linear

Since the optimization problem is stochastic, the expectation of the logarithm of the determinant of the FIM has to be evaluated and the logarithm of the FIM is used for scaling to cover a large range of values of the determinant of the FIM. However, for the case of deterministic optimization, the logarithm of the determinant of the Fisher information matrix calculated by using nominal values of the parameters is used as the objective function. Upper bounds (UB) and lower bounds (LB) along with scaling used for each variable are shown in Table 4.

Parametric sensitivity is calculated by perturbing each parameter one at a time, followed by numerical integration of the reactor model that includes individual rate expressions for each species for the given values of decision variables and uncertain parameters.

Along with the highly nonlinear nature of the objective function and difficulties in calculation of sensitivities for FIM, the equality constraint of the sum of mole fraction is difficult to incorporate because it leads to a constrained nonlinear optimization problem.

3.2. Uncertainties and sampling

The uncertainties associated with parameters are modeled as exogenous random inputs following uniform distributions added to the corresponding nominal values (Lee et al., 2011).

$$\log_{10} A_i = \log_{10} A_{i_0} + \varepsilon_{A_i} \tag{12}$$

where ε_{A_i} follows $U(-1,1)$ and A_i is the pre-exponential of the ith reaction and the A_{i+1} pre-exponential is calculated using equation 6. This is followed by picking a small number of random values (2 in this case, chosen to reduce the computational burden) from this distribution. This procedure is repeated for all the 6 pre-exponentials to be modeled stochastically and all possible combinations of these 6 vectors containing two values each were generated.

The ratio of catalyst surface area to reactor volume is one of the decision variables for the optimization problem. It is not possible experimentally to synthesize a catalyst with exactly this specification, and the uncertainty in this variable must be taken into account. This shows that in addition to the parameters, decision variables may also have uncertainties. The uncertainties associated with calculation of the random variables in this case are modeled as exogenous random inputs following a Gaussian distribution added to the nominal value of the decision variable.

$$a_v = a_{v_0} + \varepsilon_{a_v} \tag{13}$$

where ε_{a_v} follows $\mathcal{N}(0, (0.15a_{v_0})^2)$, a_v is the ratio of catalyst surface area to reactor volume and a_{v_0} is its nominal value, given by the optimization algorithm as a decision variable. The six parameters and one decision variable result in 7 random variables and 2^7 (128) possible combinations. In order to reduce the possible combinations, only the reactions 1, 2, 3 (Table 2) are considered to have uncertainty in their pre-exponentials, reducing the number of random variables to four (three reaction pre-exponentials and one decision variable, the ratio of catalyst surface area to reactor volume) (Lee et al., 2011).

Function evaluation is initiated by evaluating the sensitivity matrix for each sample and for this evaluation, each element of the parameter set (θ) is perturbed one at a time and the model is solved to quantify the change in output with respect to the perturbed parameter. As suggested by Wei et al. (2004), sample average approximation (SAA) is used to evaluate the expected objective function value. It approximates a value by taking the mean of the samples generated by the methodology explained above. For $2^4 = 16$ combinations (four random variables and two sampling areas):

$$\hat{f}\,(\mathrm{X}) = \mathrm{E}\,(\mathrm{J}(\mathrm{X})) = \frac{1}{16}\sum_{k=1}^{16} J(\,\mathrm{X}, \varepsilon_k) \tag{14}$$

where $\hat{f}$ denotes the estimate of f(X), J is log(det(FIM)) and X represents the decision variables.

3.3. Optimization scheme and constraints handling

Particle swarm optimization (PSO) is preferred for implicit problems to avoid gradient calculations. PSO can be likened to the social behaviour of bird flocks or schools of fish and is accepted as a relatively robust technique (Jia et al., 2011). PSO has two phases: initialization and evolution. During initialization, the population (known as a swarm) is initialized with uniformly distributed random particles within their search space. In the evolution phase, particles search for the optima by updating themselves based on their current and past information. After random selection of particles, the update is based on velocity vectors.

Table 5: Parameters used in the particle swarm optimization (PSO) algorithm

Parameter	Value
N_{pt} : Number of particles	20
N_d : Number of search dimensions	1
N_p : Number of parameters to be estimated	8
C_1 : Weight parameter	$2(0.99)^i$
C_2 : Weight parameter	$2(0.99)^i$
W_{int}: Weight parameter	$(0.99)^i(2r-1)$
r denotes a random variable in the range [0, 1].	

The velocity vector changes its direction and magnitude based on the difference between the current and best particle position globally as well as locally in the swarm. New positions are found by adding velocities to the old positions as given in eqns. (15) and (16)

$$x(j+1) = x(j) + v(j+1) \quad (15)$$

$$v_{p,d,j}^{j+1} = W_{int} v_{p,d,j}^{j} + C_1 r_1 \left(x_{p,j}^{ind} - x_{p,d,j}^{j}\right) + C_2 r_2 \left(x_j^{glo} - x_{p,d,j}^{j}\right) \quad (16)$$

where W_{int}, C_1, C_2, r_1 and r_2 are defined in Table 5 along with other parameters. $x_{p,j}^{ind}$ and x_j^{glo} are individual and global best positions respectively.

Apart from these parameters required for the PSO, the parameter β is chosen from 0 to 100 to explore a wide range of weights for the variance. In this study, iterations are terminated when relatively small or no improvement is observed in the objective function over 100 iterations (Zielinski and Laur, 2006).

There are two types of constraints considered; i) inequality constraints for restricting all the variables in the desired range, and ii) an equality constraint forcing the sum of the mole fractions to be unity. (Chu and Hahn, 2009) proposed the following methods to handle constraints: random, absorbing and reflecting. The random method assigns a random value to a particle to bring it back to the boundary. The absorbing method, as the name suggests, absorbs the particle at the closest boundary and the reflecting method involves reflection of point back to the range as a mirror image. The linear equality constraints are difficult to handle because they have to be combined with the PSO algorithm to allow the natural flow of the swarm of particles. In this study, inequality constraints are solved by absorbing particles that lie outside the bounds in the unconstrained PSO to the boundary after each iteration and a velocity adaption method is proposed for the equality constraint.

Initial values (j=1) are chosen such that the sum of the mole fractions is unity. In order that the sum of mole fractions remains unity in further iterations, the sum of velocities applied in the direction of mole fractions is restricted to zero.

for $j = 1$; $\sum x_i = 1$ (17)

for $j \neq 1$;

$$\sum x_i(j+1) = \sum x_i(j) + \sum v_i(j+1) \quad (18)$$

However, the constraint that needs to be followed all the times is:

$$\sum x_i(j) = 1 \quad (19)$$

$$\sum x_i(j+1) = 1 \quad (20)$$

This further means that

$$\sum v_i(j+1) = 0 \quad (21)$$

The mole fractions are selected in the order of hydrogen (v_1), nitrogen (v_2), ammonia (v_3) and argon (v_4). In order to keep the sum of the velocities equal to zero after each iteration, the fourth one is calculated using the first three. The fourth one was chosen such that it corresponds to the inert gas mole fraction particle velocity. However, the absorption technique cannot be combined with velocity adaption as absorbing after velocity adaption will alter the velocity settings. Hence, to constrain mole fractions within their individual maximum and minimum limits, new velocities were calculated using a scaling factor. Their directions remain the same (i.e., towards the best global solution) but only the magnitude of velocities is re-calculated by:

$$v_{i_{new}} = r v_i, \quad i = 1, \ldots, 4 \quad (22)$$

where r, the scaling factor, is chosen by the method explained below.

In Figure 1, the indices 1,2,3,4 refer to the mole fraction of the species in the order illustrated above. As an example, it is shown that at iteration j +1, the mole fraction of species 1 and 4 move out of the boundary but in the opposite directions.
The following quantities are defined for particles outside the boundary:
Deviation distance: The distance of a particle from an initial position (at x = j) to the closest boundary (0 or 1).
Deviating ratio: The ratio of deviation distance and velocity at x = j.

In order to make sure that all the particles outside the boundaries are contracted inside by using a single scaling factor, the minimum deviating ratio is taken to be the rescaling factor for that particular iteration. This ensures that individual mole fractions remain within the range (0, 1), the sum of mole fractions is equal to one and the velocity direction is not changed.

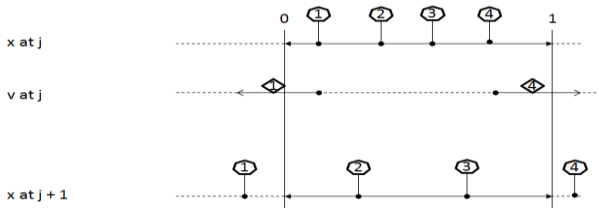

Figure 1: Description of out of boundary particle

4. RESULTS AND DISCUSSION

The decision variables considered in this optimization problem are outlined in eqn. (8). Uncertainties in the variables are accounted for in stochastic optimization and hence, the solutions obtained using the optimization can be implemented in spite of the presence of uncertainties. Using the stopping criteria mentioned above (Zielinski and Laur, 2006), iterations were performed until no change was observed in the last 100 iterations as shown in Figure 3 for β = 0, 0.01, 0.1,1,10 and 100. It is seen that the value of the objective function is maximum for β = 0. This represented the case with minimum weight to variance in J. It is also clear that the maximum value of the objective function decreases with an increase in β, which provides an increase in robustness to uncertainty. Also, variations in the objective function with pressure and temperature for β =0 are shown in Figure 4. Optimal design variables are summarized in Table 6 for stochastic and deterministic optimization. The term 'unconstrained' refers to stochastic optimization with β = 0 and the sum of mole fractions not being constrained to unity. It is clearly observed that the sum of the mole fractions is not unity in that case, i.e., the constraint is not maintained. All the mole fractions can be normalized to make their sum unity; however, that will not be an optimal solution.

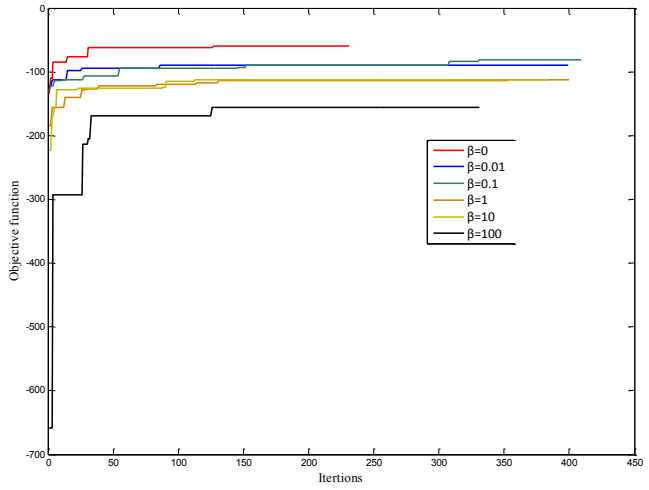

Figure 2: Change in value of the objective function with iterations

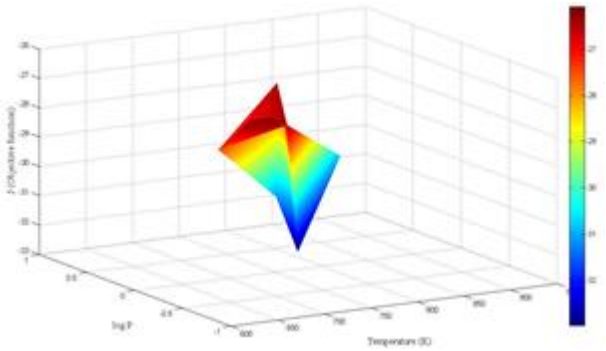

Figure 3: Variation of objective function with temperature (K) and pressure for stochastic optimization with β =0.

In our method, the robustness of the optimal design is achieved by the inclusion of the variance along with the expectation in the objective function (eqn. 10). Also, the optimal experimental conditions identified in Table 6 represent nominal values in the region where experiments need to be conducted to obtain accurate parameter estimates. Multiple experiments will need to be conducted in this region to generate data to obtain the parameter estimates.

5. CONCLUSIONS

Experiments are designed for parameter (pre-exponential factors) estimation for a model of the catalytic decomposition of ammonia. In this study, stochastic optimization techniques are applied to maximize the determinant of the FIM in order to find the optimal input conditions for the experiments. The two main reasons for pursuing stochastic optimization are: (1) the knowledge of nominal values of parameters may not be accurate enough for the best D-optimal experimental design, and (2) it may not be always possible to dial in the exact values of variables determined by the optimizer while performing the experiment and errors may occur while doing so; hence, uncertainty in the decision variables should be taken into account. Sample average approximation was used for approximation of the expectation operator in the evaluation of the objective function, based on the log of the determinant of the Fisher information matrix. Nonlinear constrained particle swarm optimization was also incorporated and a method based on rescaling velocities was proposed for the same that can be extended to other optimization problems.

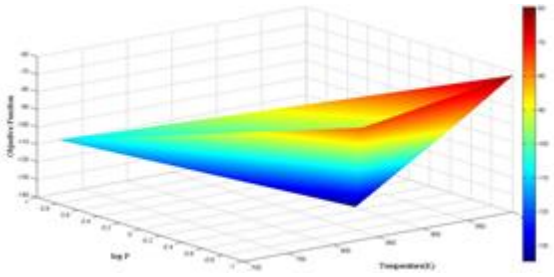

Figure 4: Variation of objective function with temperature (K) and pressure for deterministic optimization

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Table 6: Optimal conditions for experimental design

Result	β =0	β = 0.01	β =0.1	β =1	β =10	β =100	Deterministic	Unconstrained (β = 0)
$T(K)$	1000	839	1000	1000	840.548	1000	631.54	1000.00
$P(atm)$	-1	1	-1	1	-1	-1	-1.00	-1.00
$\tau(s)$	2.17	4.176	4.176	4.176	4.176	2.176	2.18	4.18
$a_v(1/cm)$	-1.301	0.699	0.699	0.699	-1.301	-1.301	-1.30	0.70
$x_1(NH_3)$	0.369	0.79	0.810	0.873	0.411	0.063	0.08	0.76
$x_2(H_2)$	0.001	0.001	0.012	0.001	0.007	0.218	0.00	0.01
$x_3(N_2)$	0.236	0.045	0.170	0.008	0.001	0.105	0.00	0.99
$x_4(Ar)$	0.393	0.163	0.008	0.118	0.580	0.615	0.92	0.28