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Multi Objective Dynamic Optimization Study of Butylated Urea Formaldehyde Resin Process in a Batch Reactor

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Abstract: Butylated urea formaldehyde (BUF) is a key intermediate for manufacturing paint and coating. The quality of BUF resins can be measured in terms of the concentration of free formaldehyde in the BUF resins and the extent of butylation. We in this work present an optimal control study to obtain minimum free formaldehyde concentration and minimum butanol concentration at the end of the batch operation. Reactor temperature is used as the manipulated variable and optimum temporal reactor temperature profiles are obtained using control vector parameterization approach. The two aforementioned criteria are observed to be mutually conflicting and hence the multi-objective optimal control problem is solved in this work yielding the pareto optimal curve showing the trade-off solutions of the MOO problem. Such pareto optimal curve helps the operator to choose an operating condition for a desired operation.

Keywords: Multi-objective optimization, butylated urea formaldehyde, batch reactor.

1. INTRODUCTION

Urea formaldehyde (UF) resins are widely used amino resins in paint and coating industry because of their low cost and fast curing property. Urea resins have historically been the resins of choice for making interior panels for goods such as case goods, cabinets, countertops, furniture, and fixtures that are used in interior environments. Because of the lack of resistance to moisture and heat, UF resins have limited use such as on interior goods and as wood adhesives. Hence, UF resins are typically modified using alcohols for imparting weather resistant property. These alcohol modified resins such as Butylated UF resins are used as adhesives, coating substance, and baking enamels etc. In spite of the importance of BUF in the industry, BUF synthesis process modeling was present only very recently. Amin et al. (2017) presented the reaction mechanism and kinetic model of BUF synthesis for addition reaction mechanism. The process model was able to predict the concentrations of urea, formaldehyde, butanol, water, methylol species, and butylated species.

Free formaldehyde in the reaction mixture after the BUF synthesis is not desired since its emission is harmful and can cause eyes and skin irritation (Myers, 1984). Hence, we formulate an optimization problem for minimization of free formaldehyde at the end of the batch operation by optimizing the temporal temperature trajectory. It should be noted that this optimization problem is solved in presence of process dynamics constraints. Hence, such optimization problem is also referred as dynamic optimization. Other than free formaldehyde as the optimization criteria, we also minimize the end point concentration of butanol for achieving high degree of butylation. It was further found that both these optimization criteria, namely minimization of end point free formaldehyde and butanol concentrations are mutually conflicting. Hence, a multi-objective optimization problem with these two criteria is also solved in this work. Solutions of such multi-objective optimization (MOO) problem can help the operator to choose the operating conditions for synthesizing the BUF resins of desired quality.

Process dynamic of BUF synthesis used for the MOO study is summarized in section 2. Multi-objective optimization problem formulation is presented in section 3. Results of the MOO problem are discussed in section 4 and finally, the conclusions are drawn in section 5.

2. PROCESS MODEL

Reaction mechanism and kinetic model of BUF synthesis for addition reactions was developed very recently by

Amin et al. (2018) based on the functional group approach. The reaction mechanism and the kinetic model consist of four types of species, *Aij, Bij, Cij, Dij* and six rate constants (K_1 to K_6) representing all the forward and reverse reactions. Here, A represents mono methyl urea (MMU) and its butylated compounds. Similarly, B and C represent the derivatives of dimethyl urea (DMU), while D represents that of trimethyl urea (TMU). The first index (i) denotes the degree of butylation, while the second index (j) denotes the degree of oligomer. Thus, species A_{01} represents monomer of MMU with no butylation, while B_{12} stands for dimer of DMU with one butyl group.

There are total 31 reversible reactions and 31 reaction species and hence 31 ordinary differential equations (ODEs) representing the transient conditions of the BUF synthesis process in a batch reactor. We reproduce only two ODEs here, for butanol (Bu) and formaldehyde (F) for the sake of brevity. One can refer Amin et. al (2018) for the entire batch reactor model for the BUF resin synthesis in addition step.

$$\frac{d[U]}{dt'} = t_b C_{U0}(K_3[A_{0,1}][H_2O] - 8K_1[U][F]) \quad (1)$$

$$\frac{d[F]}{dt} = [-2F]\left(2K_1(2[U] + [A_{0,1}] + [B_{0,1}]) + K_2([A_{0,1}] + 2[C_{0,1}])\right) + K_3[H_2O]([A_{0,1}] + 2[B_{0,1}] + 2[C_{0,1}] + 3[D_{0,1}]) - 2K_4[A_{0,1}][F] - 4K_4[B_{0,1}][F] - 4K_4[C_{0,1}][F] - 6K_4[D_{0,1}][F] - 2K_4[B_{1,1}][F] - 2K_4[C_{1,1}][F] - 4K_4[D_{1,1}][F] + 8K_6[H_2O][H] - 2K_4[D_{2,1}][F] \quad (2)$$

$$\frac{d[Bu]}{dt} = (K_5[Bu])([A_{0,1}] + 2[B_{0,1}] + [B_{1,1}] + 2[C_{0,1}] + [C_{1,1}] + 3[D_{0,1}] + 2[D_{1,1}] + [D_{2,1}]) + K_6[H_2O]\left[[A_{1,1}] + [B_{1,1}] + 2[B_{2,1}] + [C_{1,1}] + 2[C_{2,1}] + [D_{1,1}] + 2[D_{2,1}] + 3[D_{3,1}]\right] \quad (3)$$

There are six reaction rate constants in the kinetic model as can be seen from the above two equations. The corresponding pre-exponential factors and activation energies are summarized in the form of Arrhenius law in Table 1.

Table 1: Rate constants with activation energy and pre-exponential factor values

$K_1 = e^{(\frac{-7870}{T}+15.88)}$
$K_2 = e^{(\frac{-4515}{T}+5.160)}$
$K_3 = e^{(\frac{-4246}{T}+4.157)}$
$K_4 = e^{(\frac{-11650}{T}-22.21)}$
$K_5 = e^{(\frac{-5009}{T}+6.484)}$
$K_6 = e^{(\frac{-10049}{T}+20.15)}$

3. MULTI-OBJECTIVE DYNAMIC OPTIMIZATION PROBLEM

Free formaldehyde is harmful and toxic in nature. Hence, minimizing its concentration at the end of batch operation is one the optimization criteria. However, minimizing free formaldehyde content leads to more conversion of formaldehyde, which in turn increases the formation of methylol specie, which in turn reacts with butanol. Thus, minimizing free formaldehyde should lead to more butanol consumption. However at very high temperature the reverse reaction of BUF reactions dominate the forward reactions as will be shown in the next section. As a result minimizing free formaldehyde (which may take place at high temperature) leads to low butanol conversion. Thus, the two criteria (minimizing free formaldehyde and butanol) are conflicting in a specific range of temperature values. These aspects are simulated using dynamic optimization for multi-objective optimization problems in this work.

The benefit achieving desired quality of the resin can be can be realized when temporal profile of temperature is optimized for minimization of both the criteria, free formaldehyde and butanol concentrations.

The aforementioned multi-objective optimization problem can be formulated as follows,

$$\min_{T(t)} \left(F(t_f), Bu(t_f)\right) \quad (4a)$$

$$\frac{dx}{dt} = f(t, x, T) \quad (4b)$$

$$298 \leq T(t) \leq 373 \quad (4c)$$

Here, (4a) represents the two objective functions to be minimized; (4b) represents batch process dynamics constraints; (4c) represents the lower and upper bounds on the temperature profile to be optimized. The MOO problem (1) can also be termed as dynamic MOO problem owing to the fact that there are few constraints which are dynamic in nature.

3.1 *Dynamic Optimization Solution Approach*

The dynamic optimization problem (DOP) shown in equation 4 cannot be solved directly using nonlinear programming (NLP) solver. Hence, the manipulated input variable (T) is discretized along time horizon to convert the infinite dimensional problem into a finite dimensional one. Such discretization of the input variable converts the original DOP to a nonlinear programming (NLP) problem. However, a

DAE solver is required to solve the process dynamics equations for evaluating an objective function value. This approach of discretizing the input variables is called control vector parameterization (CVP) Vassiliadis et. al. (1994). Manipulated input variable (u) are discretized along time horizon and approximated by a series of trial function, γ in the CVP approach as follows,

$$u(t) = \sum_{j=1}^{na} a_j \gamma_j (t - t_j) \quad (5)$$

where, *tj* is the *jth* switching instant of the manipulated variable; *na* is the number of temporal switching intervals; and *aj* represents the magnitude of the manipulated variable at time *tj*. The input value at any time instant *t* can be interpolated using lower order interpolating function.

CVP approach has obtained large popularity owing to the certain advantages over the simultaneous approach wherein both, the state and input variables are discretized. These advantages include (1) a smaller sized NLP to be solved, (2) the solution is always feasible for a feasible initial input trajectory, and, (3) initial guess of input vector is required as compared to the need of the initial guess of both, the state and input variables in the simultaneous approach.

3.2 *Multi Objective Optimization Problem Solution Approach*

Conventional approach of solving a MOO problem includes the augmentation/scalarization of multiple objectives to form a composite scalar objective. The resulting augmented scalar objective function is minimized using a single objective optimization (SOO) solver. One such solution for a set of scalarized weighting parameters corresponds to one pareto solution in MOO. Thus, numerous SOO problems have to be solved for generating the pareto solutions in this approach. On the other hand, population based evolutionary algorithms (EAs) have gained significantly popularity in last two decades, which can compute the optimal pareto front in a single run. Non-dominated sorting Genetic Algorithm (NSGA-II) proposed by Srinivas and Deb (1994) is widely used in the literature for solving MOO problems. NSGA and its updated version, NSGA-II (Srinivas and Deb, 2002) have been widely accepted and applied GA for MOO in various fields of science and engineering.

We use CVP based NSGA II in the current work for solving the multi-objective dynamic optimization problem applied to BUF resin synthesis.

4. RESULTS AND DISCUSSION

As mentioned previously in section 3, minimization of the endpoint formaldehyde and butanol concentrations are conflicting in nature at least for a certain range of temperature values. In fact, the rate of BUF formation reaction is observed to be less significant at low temperatures, while the backward reactions dominate at high temperature. Hence, the optimum temperature is found away from the two bounds (273 K and 373K). This can be realized from the temperature dependence plots of the rate constants involved in BUF synthesis as shown in Fig. 1. K_5 is the rate constant for the forward reactions of butanol while K_6 is that for the backward reactions. As can be seen from this figure, the rates of increase of both the kinetic constants with temperature are positive. However, the two graphs intersect at 360 K, beyond which the increase of K_6 dominates the increase in K_5.

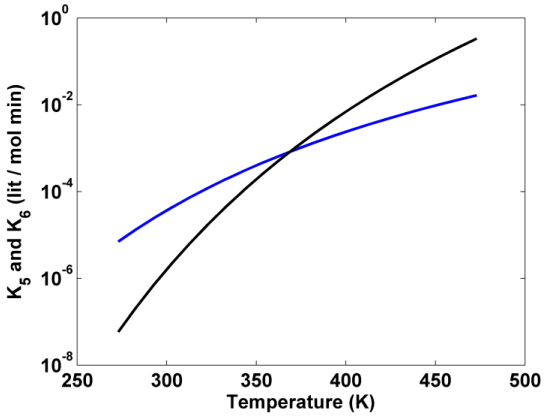

Fig. 1. Temperature dependence plots of rate constants, K_5 (blue) and K_6 (black).

On the other hand the rate of formaldehyde consumption is observed at large values of temperature. This can be realized from the plot of rate constants corresponding to the formaldehyde consumption. These rate constants dominate the rate constants corresponding to the backward reactions as shown in Fig. 2.

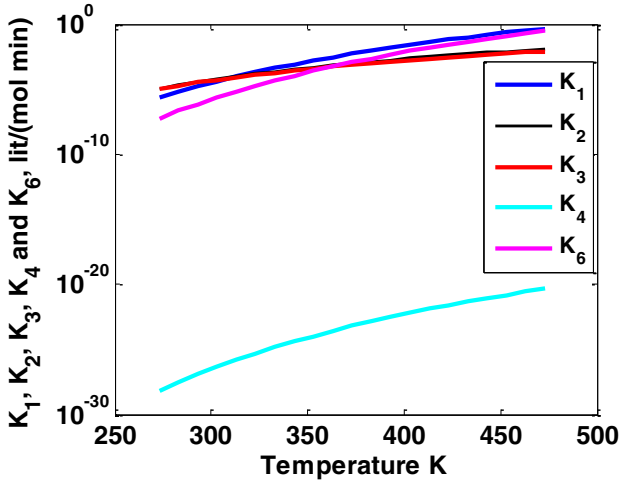

Fig. 2. Temperature dependence plots of all rate constants, K_1 to K_4 and K6

The aforementioned preliminary results motivated us to carry out the multi-objective optimization study. Hence, the multi-objective dynamic optimization problem (1) is solved for the pareto optimal curve using genetic algorithm. The resulting pareto optimal curve is shown in

Fig. 3 representing the trade-off between the two objectives. It should be noted that each point on the pareto curve is an optimal solution and corresponds to an optimum temperature profile at which the reactor can be operated. It is difficult to show the optimum temperature profiles for all the solution pareto points. However, three representative solutions (points A, B, and C) are discussed here, which are also shown on the curve. Point A corresponds to the minimum endpoint butanol concentration, while point B corresponds to minimum formaldehyde concentration. Point C is an equal percentage trade-off between the two objectives. The three representative pareto points are summarized in Table 2.

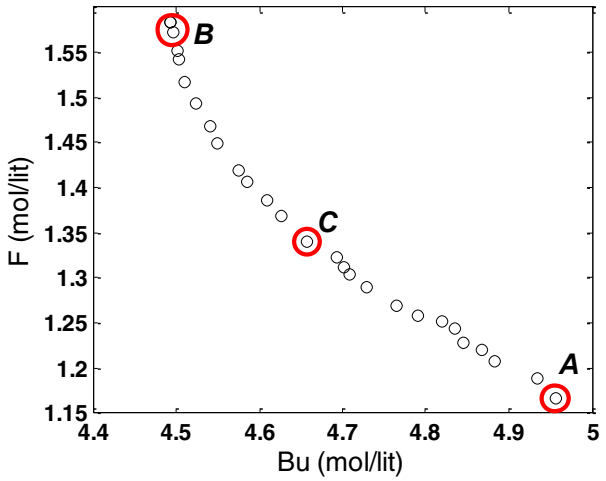

Fig. 3. Pareto optimal curve for the minimization of F(t_f) and Bu(t_f)

Table 2: Summary of the three representative points of the optimal pareto curve

Point on pareto curve	Characteristic of the point	F mol/lit	Bu mol/l
A	Min F(t_f)	1.583226	4.493918
C	Utopia point	1.304733	4.709191
B	Min Bu(t_f)	1.167203	4.955607

Apart from choosing one of the three types of operating points, the pareto curve also helps providing information of the extent of gain in one objective with a compromise in the other function. Thus, the minimum value of the formaldehyde concentration is obtained as 1.164 mol/lit (point B). The corresponding butanol concentration is found to be 4.95 mol/lit. If one can afford to compromise in the minimum possible formaldehyde value by 12% it leads to 5% improvement in the endpoint butanol concentration. Similarly, 2.4% compromise in the minimum butanol concentration leads to 12% improvement in formaldehyde concentration.

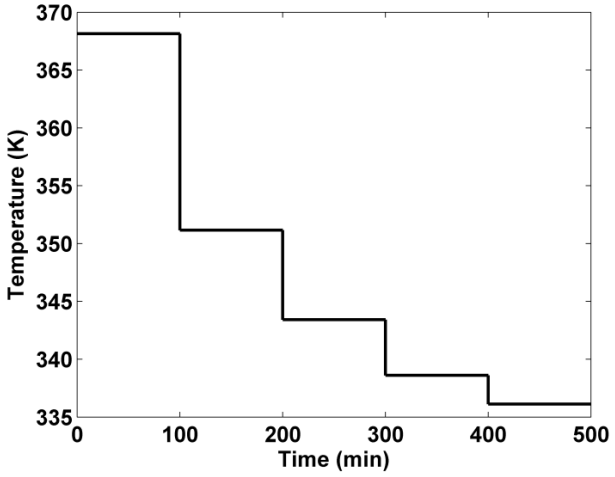

Fig. 4 Optimal temperature profile corresponding to point A (minimum F(t_f)) in Fig. 3

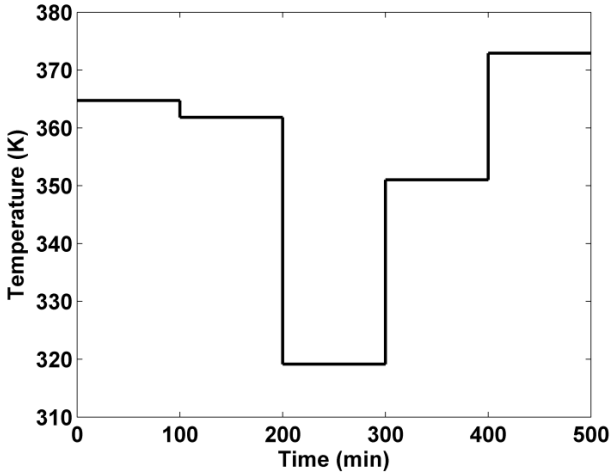

Fig. 5 Optimal temperature profile corresponding to point B (minimum Bu(t_f)) in Fig. 3

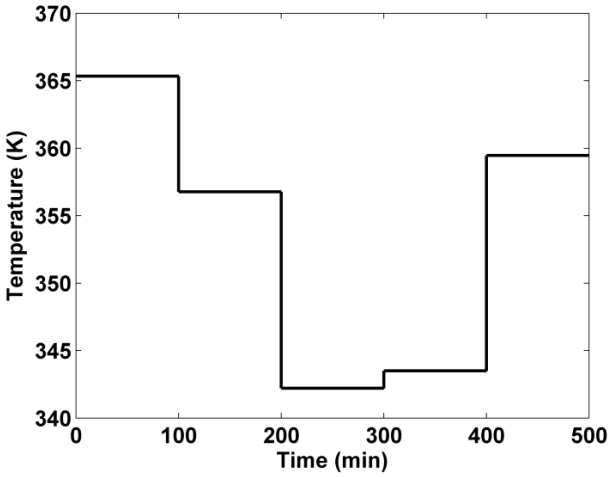

Fig. 6 Optimal temperature profile corresponding to point C (utopia point) in Fig. 3

5. CONCLUSIONS

Dynamic optimization study was carried out to find the optimum temporal trajectory of temperature for non-isothermal batch operation. DOP is solved with two optimization criteria, namely (1) minimization of the end point free formaldehyde concentration and (2) end point butanol concentration minimization. The above mentioned optimization results showed that both the optimization criteria are conflicting in nature. Thus, the endpoint Bu concentration beyond certain temperature starts increasing, while the formaldehyde concentration show decreasing trend. Hence the MOO problem has been solved for temperature profile optimization. The results for the MOO problem of minimizing end point concentration of F and Bu are in the form of pareto optimal solutions. The pareto front shows all the optimized values for formaldehyde and butanol trade-off.

It can be noted that temperature variations do not bring significant improvement in the two optimization criteria in batch reactor. This is also reflected in the MOO results, which do not show significantly large range of values for the two objectives. This can be attributed to the batch mode of operation for BUF synthesis. It is expected that in semi-batch operation for BUF synthesis, continuous removal of water from the reactor can shift the reactions to right and form more BUF leading to more consumption of formaldehyde and butanol. Thus, such dynamic and multi objective optimization activity in semi-batch process can lead to larger span of the endpoint butanol and formaldehyde concentrations. We shall attempt the MOO study of BUF process in semi-batch mode in the future work.

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