Research paper

Modeling & simulation of micro reactor with nitration of 2–methyl–4,6–dihydroxy–pyrimidine

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Abstract

Nitration of 2–methyl–4,6–dihydroxypyrimidine (MDP) using concentrated sulfuric acid and nitric acid as nitrating mixture is a highly exothermic and hazardous reaction. Conducting such reaction in a batch reactor follow an unsteady state and its trajectory depends on various important parameters such as initial reactor temperature, initial composition of reaction mass, temperature of circulating coolant, etc. However, over all productivity, process control and safety of the batch process is highly restricted due to lower surface to volume ratio. In the present work, an effort has been made to over come the limitations of batch reactor by using the novel micro reactor device. Micro reactor is having extremely high surface to volume ratio, which has been explored to carry out nitration of MDP both numerically as well as experimentally and the results were compared with conventional batch reactor.

The micro reaction system has been modeled using two dimensional (2–D) heat flow and mass transfer equations. The kinetic rate equation for nitration of MDP has evaluated experimentally by differential method which is used in modeling of the micro reactor. The numerical results from the 2–D model for conversion and temperature profile along the length and radius of micro reactor have been compared with corresponding results obtained from batch reactor.

In order to validate the model, several experiments were conducted in micro reactor set–up with the variation of flow rate, residence time, concentration, temperature, etc. The experimental results from micro reactor revealed that nitration of MDP takes place even at much lower concentration and lower residence time with better control of temperature profile. Also, the reaction takes place in laminar region compared to turbulent region in corresponding batch reactor setup.

Keywords : 2–methyl–4,6–dihydroxypyrimidine, micro reactor, 2–D modeling, batch reactor

1. Introduction

1,1–Diamino–2,2–dinitroethene (FOX–7) is a futuristic insensitive high explosive and a potential candidate to replace cyclotrimethyl trinitramine (RDX). Due to its chemical and thermal stability, it has created significant interest in the recent past. At High Energy Materials Research Laboratory (HEMRL), FOX–7 is prepared by adopting a two step batch process, viz., nitration of 2–methyl–4,6–dihydroxypyrimidine (MDP) to get nitrated intermediate followed by acid catalyzed hydrolysis of nitrated MDP to get FOX–7. Nitration of MDP is highly exothermic and the heat of reaction evaluated by reaction calorimeter (RC)[1] is about 460 kJ/mole of FOX–7. Control of operating parameters like temperature, flow rate, etc. is difficult in conventional stirrer tank reactor, therefore the higher productivity is difficult to realize mainly because of lower surface to volume ratio. Since the problem has not yet been addressed/reported in open literature by any researcher so far it was thought appropriate to overcome this problem with a novel approach by using micro tubular

reactor. It has high surface to volume ratio, efficient heat and mass transfer characteristics which vastly improved fluid mixing etc. in addition to provision of precision control of reaction with resulting in improved conversions, selectivity, etc. The reaction time is less compared to conventional reactors with less degradation of side product. Also the optimization and scalability are significantly easier.

Modeling and simulation of micro tubular reactor for the above nitration reaction have been studied and subsequent validation to access the feasibility by conducting the experiments in micro tubular reactor have been presented in this work. The kinetics for the nitration have been studied in detail and the reaction rate have been developed[2] by differential method is given in equation (i). The same rate equation has been utilized here for modeling and simulation.

$$\frac{dC_B}{dt} = -0.014C_B^{2.19} \quad \text{(i)}$$

In the present work, a tubular reactor surrounded by a cooling media/ambient atmosphere is considered for modeling and simulation. A few investigators/researchers[3)-9)] have described the analogous models of packed tubular reactor in which both radial and axial gradients of temperature and concentration were taken into account. Ahmed et al.[5)-6)] previously solved such two dimensional (2−D) model by converting partial differential equations into ordinary differential equations. However, in the present work the partial differential equations are solved step wise by converting it in to difference form. Besides, information about advantages of micro reactors is also reported by various other authors[10)-12)].

2. Modeling

2.1 Reaction

Nitration of MDP is a highly exothermic reaction, where a mixture of concentrated sulphuric acid, H_2SO_4 (98%) and nitric acid, HNO_3 (98%) are used as nitrating agent. MDP is first dissolved in sulfuric acid at desired concentration. Concentrated nitric acid and MDP is allowed to mix in a micro mixture and then allowed to flow through micro reactor at desired flow rate in the molar ratio of [MDP] : $[HNO_3] : [H_2SO_4] = 1 : 5.1 : 10.1$. The temperature of the mixture is maintained at the desired level. The overall reaction is shown in Scheme 1.

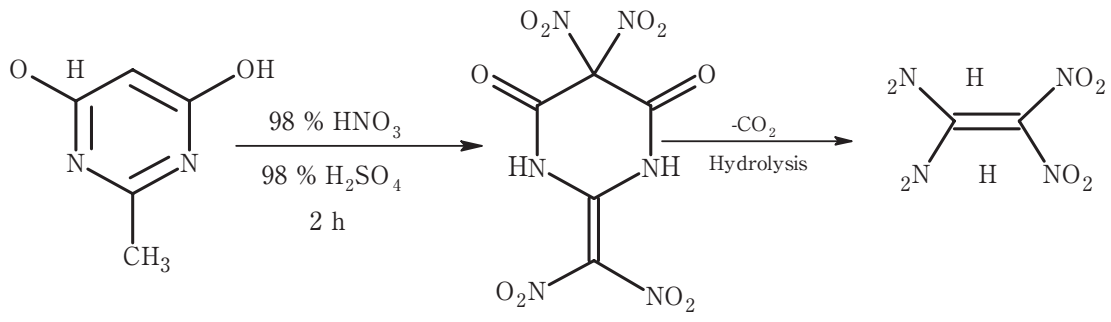
2.2 Micro reactor

Micro reactor implies a reaction chamber whose dimensions are typically in the range of micrometers (μm) with volumetric capacity in the range of microlitres (μl) and l/d ratio at least > 2000. The possibility of reduction in dimensions with small volumes of reaction zone would allow application of high temperature or concentration with significant ease of process control and thermal management. This would, therefore, allow previously infeasible regimes of operation possible with improved performance. Richardson and Rase (1978)[11)] reported a continuous stirred micro reactor for liquid−liquid reactions where by adjusting inputs and operating conditions it was possible to delineate the chemical steps from intervening transport efforts. In the present study, the metallic reactor of about about1mm diameter with L/D > 2000 has chosen for the modeling and simulation.

2.3 Modeling of tubular reactor

The overall reaction rate equation used has been reported by Mandal et al[2] for a batch reactor. The rate equation reveals how much reaction has taken place at any time in the reactor provided the temperature and concentration are known. To evaluate the temperature and concentrations, energy and mass balances are formulated for an entering fluid flowing through the tubular reactor. These balances are in the form of differential equations, the solutions of which gives the temperature and concentrations at any location including the reactor exit. These concentration and temperatures are the solutions to the design problem. The analytical solution of these differential equations is not possible due to prevailing temperature gradient and then the design process entails the numerical solution of a set of coupled differential equations. These differential equations are first converted to a difference form. The procedure adopted is described later.

The reactants are allowed to enter in the micro tubular reactor at a uniform temperature and composition, but as they pass through the reactor and the reaction occurs, the accompanying heat of reaction induces both longitudinal and radial variations in temperatures. In order to make



Scheme 1 Overall reaction

the problem simple, it is assumed that the entire reactor operates isothermally and the rate is a function of concentration. However, practically the rate will vary along the reactor because of concentration and temperature change in both radial and longitudinal directions. The integration of the mass balance requires the numerical solution technique. The calculation is done on the basis across the incremental diameter of the reactor tube for a small longitudinal increment and repetitions of the process for each successive longitudinal increment. The radial distribution of velocity would account for radial concentration and the temperature gradient by using Peclet numbers which themselves varied with radial position and would allow for axial dispersion if that were significant.

The following assumptions have been used for2−D model equations.

- The operation is considered to be at a steady state
- Longitudinal dispersion is neglected
- Both mass velocity and Peclet number for mass and heat transfer are constant across the reactor tube
- Velocity is permitted to vary with radial position
- External wall temperature is kept constant, however internal wall temperature is varyin with axial direction
- Effective radial thermal conductivity and radial diffusivity are assumed to be constant
- The temperature gradient at centre line is zero but at wall is determined by heat transfer characteristics
- Considering standard equations for mass and heat balance of reactant in a tubular reactor, following model equations[10] used to represent concentration and temperature profile of micro reactor system as below,

$$\frac{\delta}{\delta r}\left(rE_r\frac{\delta C}{\delta r}\right)+r\frac{\delta}{\delta z}\left(-u_z C+E_z\frac{\delta C}{\delta z}\right)-r_c r=0 \qquad (1)$$

$$\frac{\delta}{\delta r}\left(rk_r\frac{\delta T}{\delta r}\right)+r\rho c_p\frac{\delta}{\delta z}\left(-u_z T+k_z\frac{\delta T}{\delta z}\right)-r_c r\Delta H=0 \qquad (2)$$

In the experimental reactor which is modeled in this work, the wall temperature is maintained by means of jacket of cold water circulation and drop across the wall could be assumed negligible. Therefore, the wall temperature, Tw was taken as constant and equal to the coolant temperature, T_c, then the boundary conditions are,

$$r=0,\ \frac{\delta C}{\delta r}=0,\ \frac{\delta T}{\delta r}=0 \qquad (3)$$

$$r=r_w,\ \frac{\delta C}{\delta r}=0,\ T=T_w \qquad (4)$$

$$z=0,\ C=C_i,\ T=T_i \qquad (5)$$

2.4 Dimensionless variables

Unlike radial position, the axial / longitudinal diffusion in the tubular reactor is neglected, the length of the reactor plays the same role as the axial position z and hence it is not required to be used as characteristic length. The tube radius, r_w is used as a characteristic length and The dimensionless reaction rate is defined as

$$r_c^* = r_c/r_{ci}$$

where r_{ci} is the rate of reaction at starting feed condition (T=T_f and x=0). In addition to the above, using T_f, C_0, $<u>$, $<E_r>$, $<k_r>$ as characteristic value, and dimensionless axial distance $\zeta = zr_{ci}/<u_z>C_0$, then the equations (1) and (2) becomes

$$u^*\frac{\delta x}{\delta\zeta}-E^*\frac{1}{D_{am}}\left(\frac{1}{r^*}\frac{\delta x}{\delta r^*}+\frac{\delta^2 x}{\delta r^{*2}}\right)-r_c^*=0 \qquad 1(a)$$

$$u^*\frac{\delta T^*}{\delta\zeta}-k^*\frac{1}{D_{am}L_e}\left(\frac{1}{r^*}\frac{\delta T^*}{\delta r^*}+\frac{\delta^2 T^*}{\delta r^{*2}}\right)-r_c^* H^*=0 \qquad 2(a)$$

where, $H^*=\frac{\Delta HC_0}{\rho c_p T_f}$, $L_e=\frac{\rho c_p<E_r>}{<k_r>}$, $D_{am}=\frac{r_w^2 r_{ci}}{<E_r>C_0}$

are dimensionless adiabatic temperature rise, Lewis number and modified Damkohler number respectively, The dimensionless boundary conditions become,

$$atr^*=0,\ \frac{\delta x}{\delta r^*}=0,\ \frac{\delta T^*}{\delta r^*}=0$$

$$atr^*=1,\ \frac{\delta x}{\delta r^*}=0,\ T^*=T_w^*$$

$$at\zeta=0, x=0,\ T^*=T_f^*$$

2.5 Solution of partial differential equation

Equation1 (a) and 2 (a) are solved by a stepwise numerical procedure, starting at the entrance to the reactor. The equations are first written in difference form. Let n & L represent the number of increments in the radial and axial directions respectively, and δr^* and $\delta\zeta$ be its magnitude, so that

$$r^*=n\Delta r^*$$

$$\zeta=L\Delta\zeta$$

The conversion and temperature at any point in the tubular reactor can be written using second difference form in r and z direction are,

$$x_{n,L+1}=x_{n,L}+\frac{E^*\Delta\zeta}{D_{am}u^*\Delta r^{*2}}\left[\frac{1}{n}(x_{n+1,L}-x_{n,L})+x_{n+1,L}-2x_{n,L}+x_{n-1,L}\right]+\frac{r_c^*\Delta\zeta}{u^*} \qquad 1(b)$$

$$T^{*}_{n,L+1}=T^{*}_{n,L}+\frac{k^*\Delta\zeta}{L_e D_{am}u^*\Delta r^{*2}}\left[\frac{1}{n}(T^{*}_{n+1,L}-T^{*}_{n,L})+T^{*}_{n+1,L}-2T^{*}_{n,L}+T^{*}_{n-1,L}\right]+\frac{H^*r_c^*\Delta\zeta}{u^*} \qquad 2(b)$$

The indeterminate form of the equations at n=0can be avoided by using the special expressions

$$x_{0,L+1}=x_{0,L}+\frac{2E^*\Delta\zeta}{\Delta r^{*2}u^*D_{am}}(2x_{1,L}-2x_{0,L})-\frac{r_c^*\Delta\zeta}{u^*} \qquad 1(c)$$

$$T^{*0,L+1} = T^{*0,L} + \left(\frac{2k^{*}\Delta\xi}{u^{*}L_e D_{am}\Delta r^{*2}}\right)(2T^{*1,L} - 2T^{*0,L}) - \frac{H^{*}r_c^{*}\Delta\xi}{u^{*}} \quad 2(c)$$

Equation 1(b) and 2(b) were solved stepwise to obtains the Conversion and Temperature profile during the course of reaction. The first step was to compute the value of ζ(zeta) and x across the diameter.

For the first step $\xi = 1 * \nabla\xi$, therefore L=1. Which is to be calculated from the previous value of L=0 (initial condition). Then continue to the next step in longitudinal direction at L=2. The indeterminate form of equation at n =0 can be avoided by using the special expression (derived from the' L hospital rule ; limit $Cos\, x/(x-\pi/2)$ [3]

$$X \rightarrow \pi/2$$

3. Simulation

The conversion and temperature profile during the exothermic nitration of MDP in micro tubular reactor at any point (except at n=0) were obtained by solving the equation 1(b) and 2(b). The equation 1(c) and 2(c) were solved to get the temperature and conversion profile at the entrance where n=0. The reaction term in the equation 1(b) and 2(b) affects both temperature and conversion ; since the rate depend upon these terms. The average value for the increment L to L+1is known only after the equation 1(b) and 2(b) are solved by trial and error procedure. During the simulation of MDP nitration reaction, the problem is considered and computed with the radial variation taken into account for a fixed position/ increment along the axial position. The rate equation used in simulation, was earlier generated experimentally during the kinetic study[2] of the same.

Simulation steps mostly followed are,

For 2-D problem T^{*}, x and r_c^{*} are represented as $T^{*}_{r*,\xi}$, $x_{r*,\xi}$ and $r^{*}_{Cr*,\xi}$ The conversion at the entrance will be zero at all radial position and also the temperature at the entrance is considered as feed temperature. Now, initial value of $r_{c\,(1,0)}$ is obtained from the initial feed temperature and initial feed conversions (i.e. x=0).

The steps followed for simulation are as follows,

1. Assume a value of $r_{c\,1,1}$ after obtaining $r_{c\,1,0}$
2. Compute $T_{1,1}$ and $x_{1,1}$from equation 1(b) and 2(b)
3. Evaluate rate $r^{*}_{c\,1,1}$ at the end of the increment
4. Average $r^{*}_{c\,1,1}$ & $r^{*}_{c1,0}$ and compare the result with assume $r_{c\,1,1}$.If agreement is not obtained repeat the sequence with revised value of $r_{c\,1,1.}$

Thus the computation have been first made across the radius of the micro-tubular reactor at L=1 and Δz=0.5. The successive calculation with increments L=2 *to 10* have been made across the radius to get the temperature and concentration profile.

3.1 Simulation result

The code for the above equations were developed in MATLAB and the 2-D model for micro tubular reactor derived for nitration of MDP has been solved across radius & length of reactor using the parameters selected as shown in Table 1. The conversion of reaction in tubular reactor along the radius of reactor is shown in Fig. 1. Fig. 2 is the 2D profile of conversion along the length and radius of reactor. The simulated temperature profile in micro tubular reactor along radius is shown in Fig. 3. It is seen that temperature varies along radius ; it finally reaches to wall temperature. Fig. 4 is the 2D profile of Temperature along the length and radius of micro-reactor. The product conversion variation with temperature is shown in Fig. 5. Simulated conversion along the dimensionless length of micro reactor is shown in Fig. 6. Comparisons of the experimental and simulated variation of conversion at different reaction temperature of 5, 15, 25°C is made and shown in Figs. 7, 8 and 9 respectively.

Table 1 Parameters used for simulation of the micro tubular Reactor for nitration of MDP.

Physical parameters	Parameters Value
Feed temperature, T_f	15°C
Wall Temperature, T_w	10°C
Heat of reaction, ΔH_R	460 kJ/mole
Activation energy, E	10000 cal
Universal gas constant, R	2cal
Arrhenius constant, $k_0$at 15°C	$1.49*10^{6}$
Reaction feed rate, r_{ci}	0.042 moles/l.sec
Initial feed concentration, C_0	1.84 moles/lit
Radius of the tube, r_w	$1.5*10^{-3}$m
Velocity along tube length, u_z	0.007 m/sec
Cross sectional avg. velocity along length	$5*10^{-6}$
Density without dilution, ρ	2.5 g/cc
Specific heat, C_p	1.5 J/g°C
Radial thermal conductivity, k_r	0.08 W/ m K
Lewis nos. Le	0.9
Cross sectional average k_r	0.2
Radial diffusivity, E_r	$1.1*10^{-7}$
Cross sectional average radial diffusivity	10^{-7}

4. Model validation

The model has been validated by conducting experiment on nitration of MDP in micro tubular reactor. The details of the experimental set up and procedure followed is described here along with analysis result.

4.1 Experimental setup

The typical experimental setup involves two fluid metering pump (make-FMI, USA) hooked-up with a 'T' to function as a micro mixer, which was subsequently connected to SS 316 micro tube. The micro tube (reactor) immersed in thermostat (Make-JULABO, Germany) and nitrated reaction mass coming out of tube was collected in glass jacketed reactor fitted with electrically driven motor having agitator, temperature indicator etc. Experimental setup for nitration of MDP in micro tubular reactor is shown in Figs. 10 & 11. FMI pumps of low flow rate were selected for pumping reactant at low flow rate for nitration reaction. It consists of mainly two parts, pump drive module, and pump head module. The pump selected

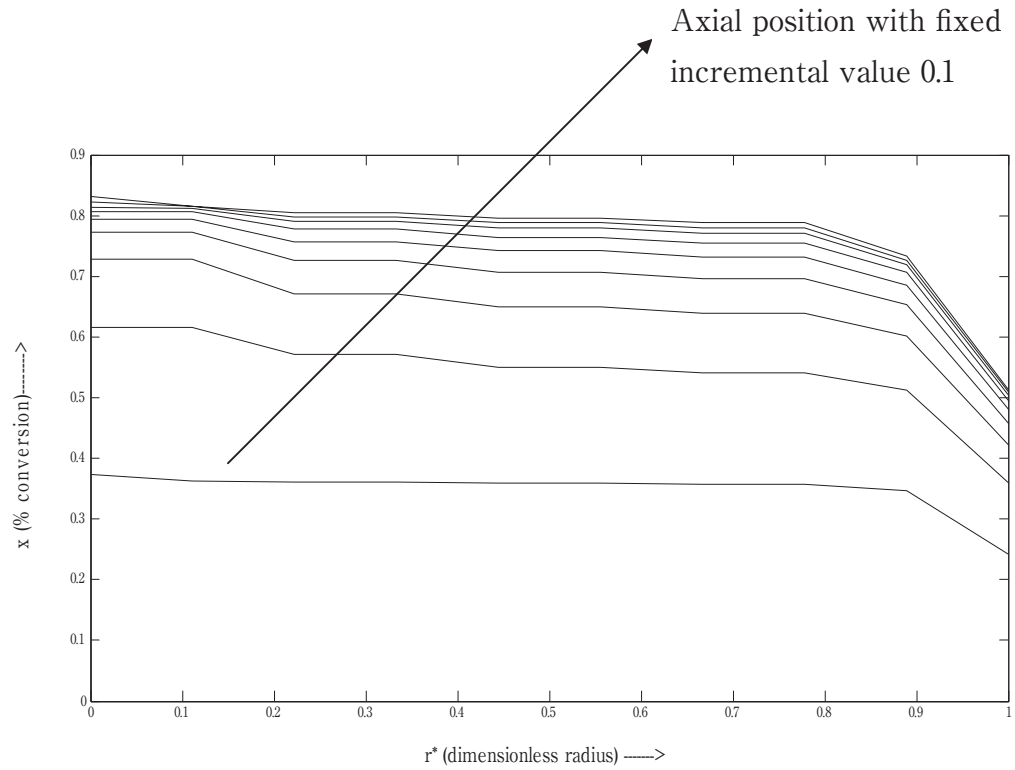


Fig. 1 Simulated conversion of reaction in micro reactor along the radius.

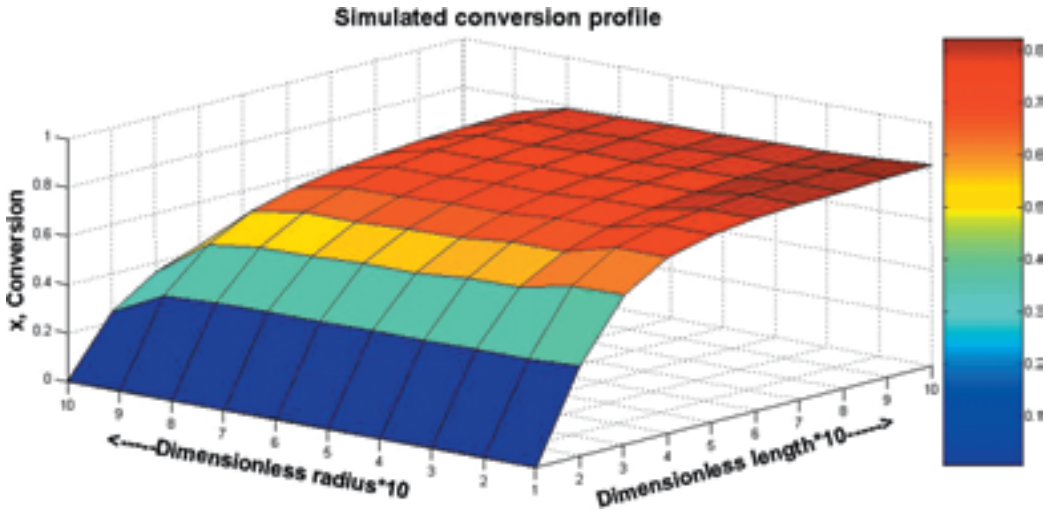


Fig. 2 2D Profile of conversion along the length and radius of reactor.

is a valve less pumping device and operates by synchronous rotation and reciprocation action. One complete piston revolution is required for each suction / discharge cycle. The pump has excellent chemical resistance to most acids, caustic, and solvents with some exceptions including acetone, methyl ethyl ketone (MEK) and methylene chloride. It is designed for flow rate of 0 to 5 ml/minute, infinitely adjustable through pump head rotation controller. Casing is made of PVDF and stroke cylinder is ceramic. 'T' joint of SS 316 and I.D (about 2 mm) was used as micro mixer for mixing MDP solution and Nitric acid.

4.2 Experiments in micro reactor

Experiments were conducted in micro tubular reactor ; initially MDP solution was prepared by using in sulfuric acid at desired concentration. The MDP solution & HNO_3 acid were allowed to mix in 'T' shaped micro mixer at desired flow rate. The reaction mixture comes out from end of tube was quenched into ice followed by hydrolysis under high speed agitation (400 rpm) for 2−3 hrs to get product FOX−7 which was then filtered, washed with water to get final product. The product weight was determined for each run after drying. The product formed was analyzed & characterizes by slandered analytical/ Instrumental method. No literature is available on Nitration of methyl dihydroxy pyrimidine (MDP) in micro tubular rector. Hence, the experiments were planned systematically. Initially efforts were made to carry out the reaction with standard molar ratio of [MDP] : [HNO_3] : [H_2

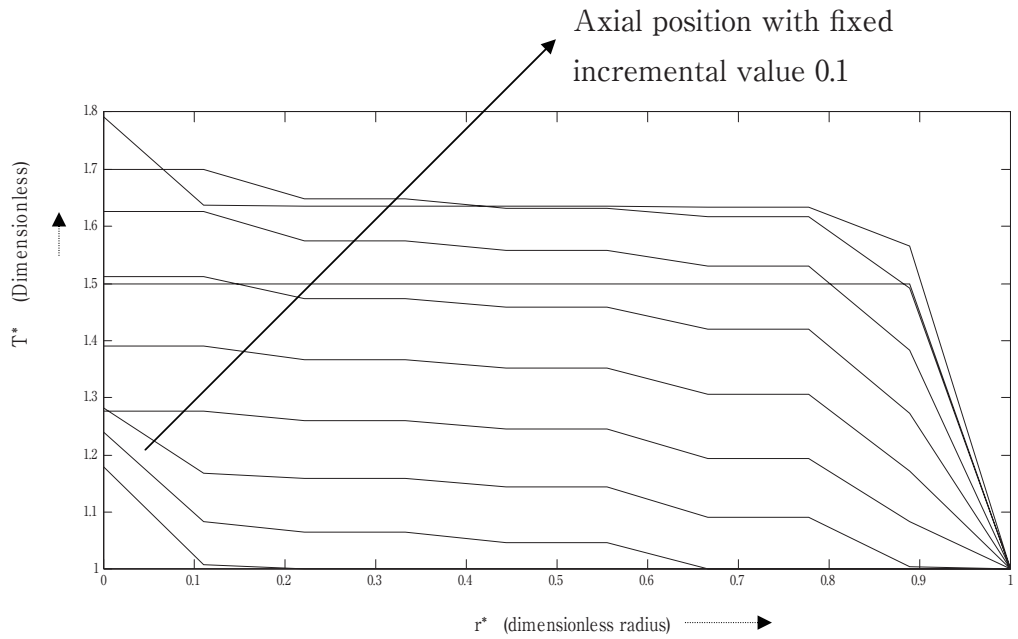


Fig. 3 Simulated temperature profile in micro reactor along the radius.

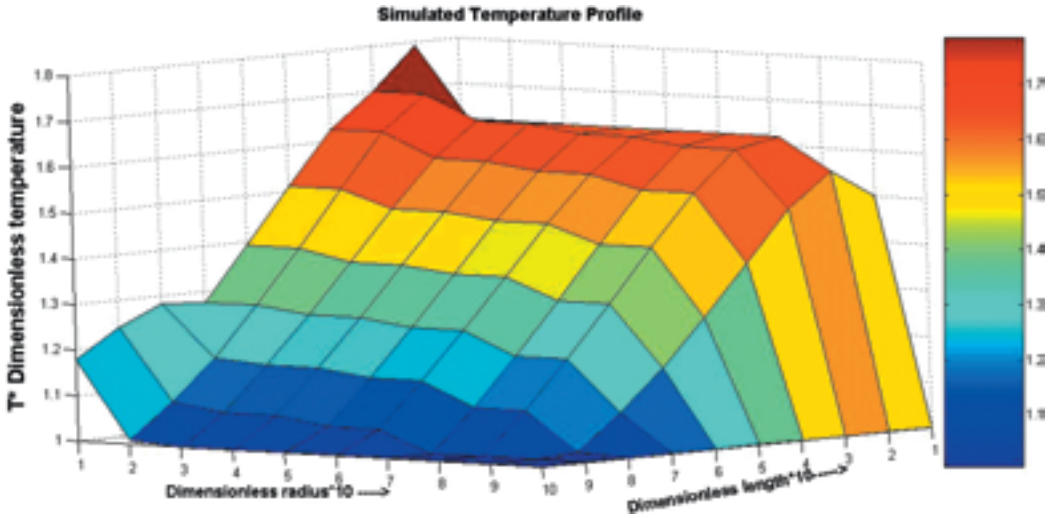


Fig. 4 2D Profile of temperature along the length and radius of reactor.

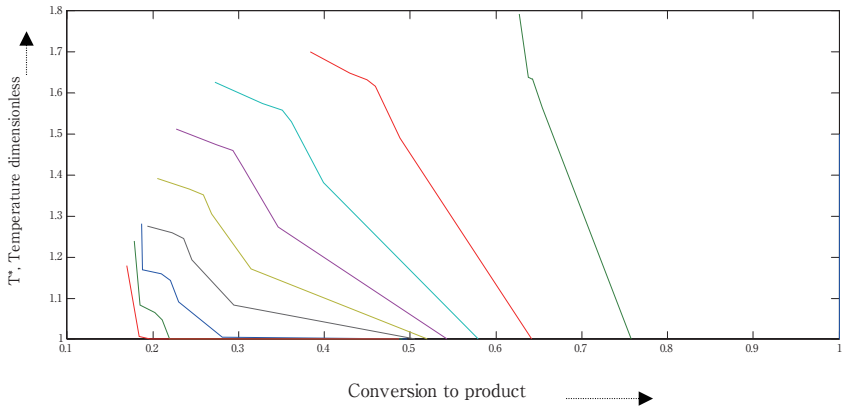


Fig. 5 Simulated product conversion with different reaction temperature.

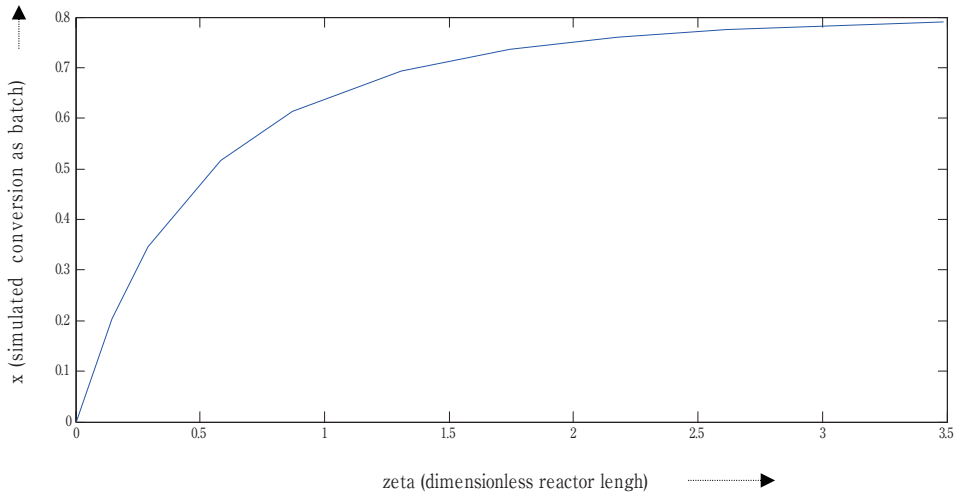


Fig. 6 Simulated product conversion along dimensionless reactor length.

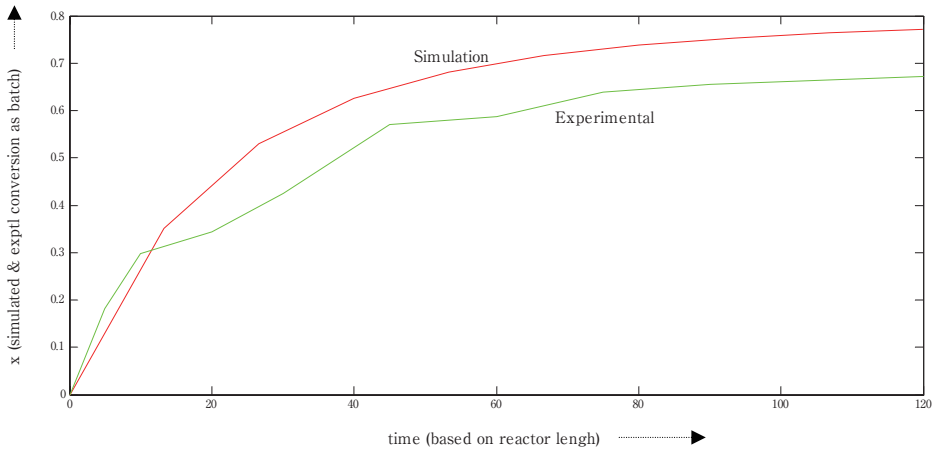


Fig. 7 Comparison of experimental batch and simulated conversion at 5°C.

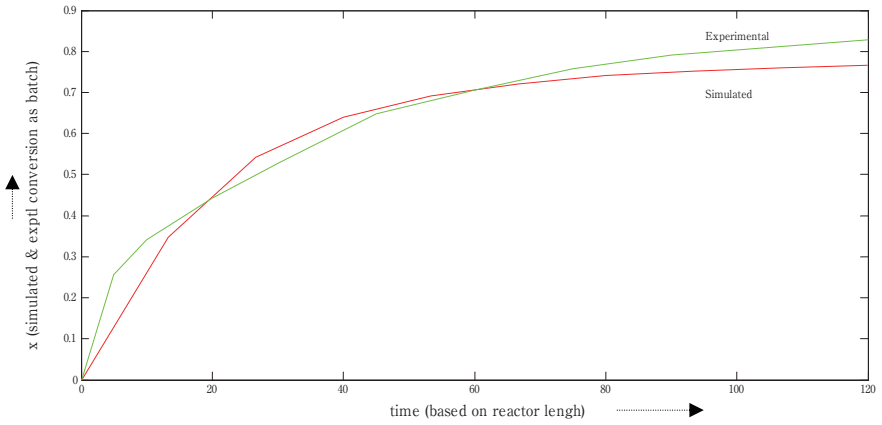


Fig. 8 Comparison of experimental batch and simulated conversion at 15°C.

SO_4]=1 : 5.1 : 10.1 reactant considered for experiment, no product was able to be isolated as tubular reactor get chocked due to formation of nitrated methyl pyrimidine dione (NMPD) at required flow rate. So dilution of reactant at different concentration of MDP of 50%, 75% and 100 % in concentrated sulfuric acid (H_2SO_4) solution was used for experiment and the reaction was conducted in three different length of 1.2 m, 2.7 m and 3.7 m having *L/D* ratio 1000, 2250 and 3000 respectively. Such dilute solution prepared and used immediately. The reaction was carried out with this dilute solution in different length of micro tubular reactor mentioned earlier. During each run in micro tubular reactor, variation of temperature was recorded at different zone along the length of reactor. Temperature variation with time is shown in Fig. 12. It is seen that large heat released is compensated by large area available for heat transfer per unit volume of fluid so very small variation in temperature were observed. Besides, other process parameters were noted and calculated such as rate of formation per minute, amount of product

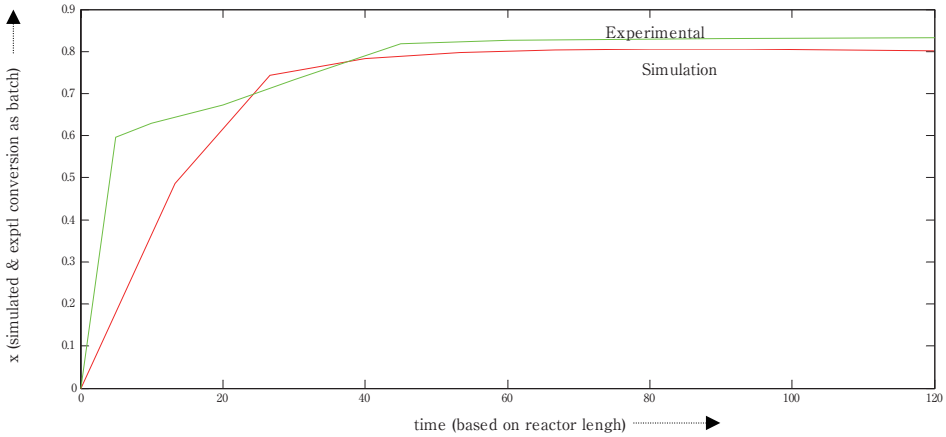


Fig. 9 Comparison of experimental batch and simulated conversion at 25°C.

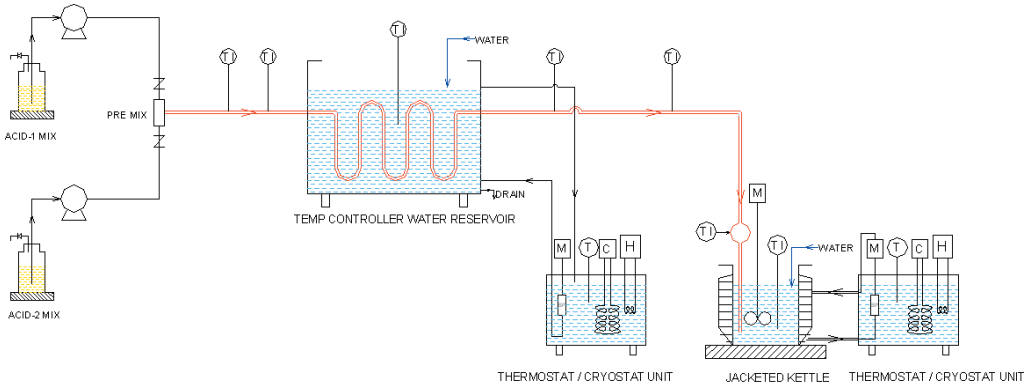


Fig.10 Schematic of experimental setup for nitration of MDP in micro reactor.

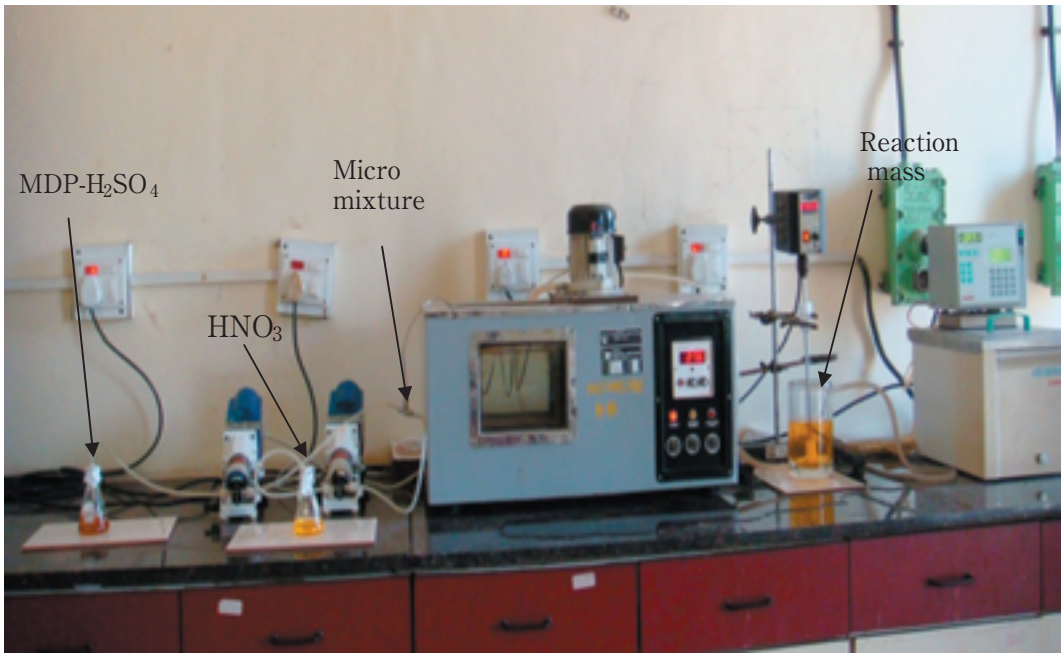


Fig.11 Experimental setup for nitration of MDP in micro tubular reactor.

formed, yield etc. The rate of formation of product per minute at different concentration in reactor with various residence times is shown in Fig. 13. It is seen that the rate of formation of product per minute at different concentration of MDP in reactor is inversely varies with concentration of MDP . The rate of formation of product per minute at different concentration of MDP in reactor with various length of reactor is shown in Fig. 14. The % yield of reaction in micro tubular reactor at different dilution and residence time is shown in Fig. 15 and Fig. 16 respectively.

5. Results & Discussion

Experiments conducted with MDP and H_2SO_4 ratio of 1 :

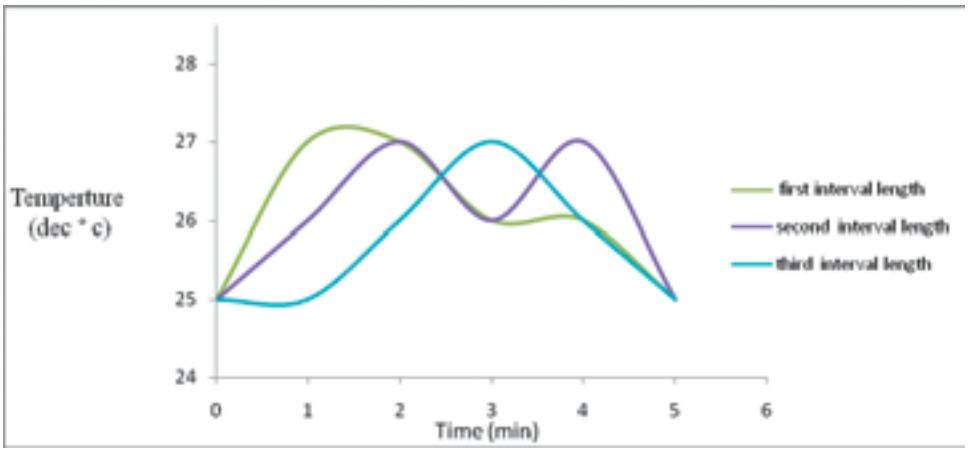


Fig.12 Variation of temperature with time.

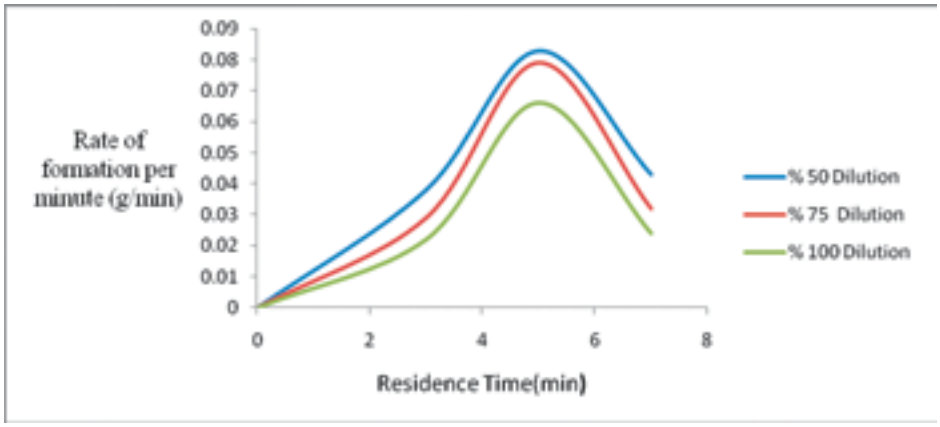


Fig.13 Variation of conc. of MDP on rate of formation at different residence time.

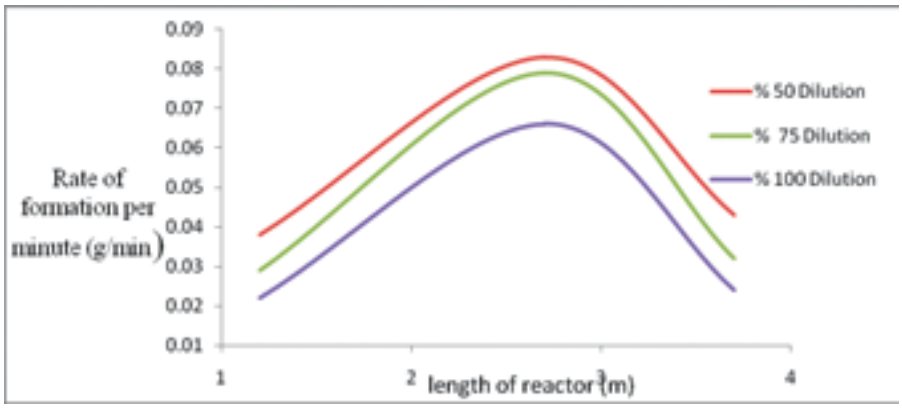


Fig.14 Variation of conc. of MDP on rate of formation at different reactor length.

20.2, 1 : 17.5, 1 : 15.05 gave satisfactory results. The yield observed at 25°C at different residence times for both continuous and batch types are shown in the Tables 2 and 3. The results from the batch experiments were compared with continuous experiment at identical operating conditions. It can be seen that the % yield of FOX−7 in the continuous experiments in micro reactor of about 1mm I.D was as against % obtained in batch experiments. It is observed that, although in the batch as well as the continuous experiments the same mole ratio was maintained, in case of continuous flow experiments (micro reactor) yields higher amounts of product formation. It is also noted that the area available for heat transfer per unit volume of fluid is high in case of micro reactor which was sufficiently high to maintain the constant temperature in the entire length without circulating the cold fluid. Further, rate of formation of product irrespective of the different residence time was higher in case of micro reactor correspond to batch reactoras given in Table 3. The yield of continuous experiment is having similar trend agreed with simulation result. The brief summary of nitration experiments in micro reactor is given in Table 4. The rate of formation of product at 50% concentration is highest and that of 100% dilution is least but, continuous flow of reaction mass is maximum in case of 100% diluted solution.

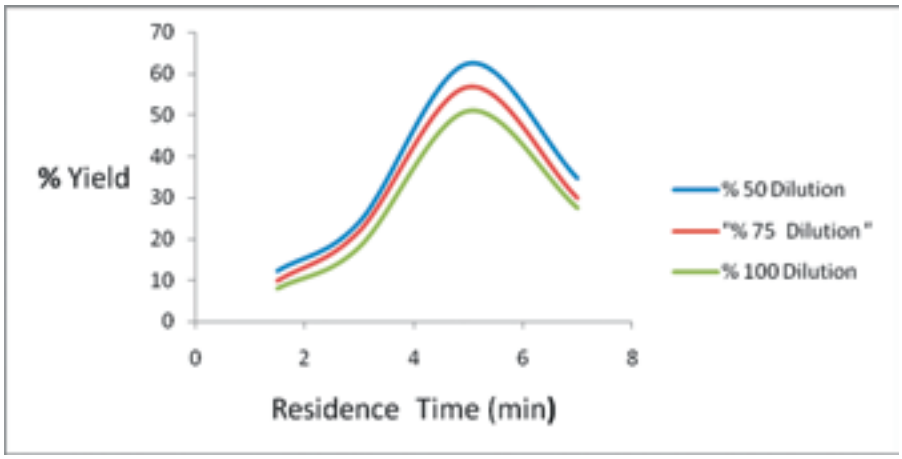


Fig.15 Variation of concentration of MDP on yield at different residence time.

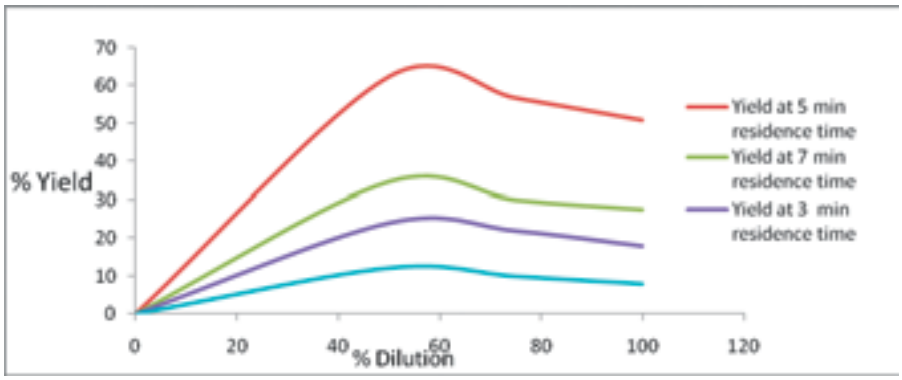


Fig.16 Concentration of MDP on yield at different length of reactor.

Besides, it is also found that during reaction with standard concentration of MDP in concentrated H_2SO_4 (MDP : H_2SO_4=1 : 10.1.), micro reactor including 'T' mixture gets choked and also develops a very high pressure drop (more than 6 kg/cm^2) and practically no product was able to be collected form the micro reactor. This kind of choking was observed even for different orientations (like vertical, horizontal) of the micro tube. In order to overcome such situations, lower concentration of MDP (like MDP : H_2SO_4=1 : 20.2, 1 : 17.5, 1 : 15.05) were used and the experiments were carried out with minimum of choking problem.

5.1 Micro reactor verses batch reactor

Experiment batches were carried out in cylindrical jacketed glass reactor (500 ml capacity) fitted with driving motor, agitator, temperature indicator in the reactor as well in jacket inlet and outlet. The coolant outlet is at the top and inlet at the bottom of glass reactor. The inner diameter of the reactor was 300 mm. It was equipped with a motor driven agitator and heated and cooled by a thermostat and cryostat unit having PID controller (JULABO PT12). Heating medium was a mixture of glycol and water with a viscosity of 2.58 cp. During experiment MDP solution was prepared in sulfuric acid at predefined temperature then concentrated nitric acid was added at controlled rate to MDP solution by maintain the temperature at 12±2°C. Addition of concentrated nitric acid in MDP solution is highly exothermic reaction which leads to runaway reaction. So, it was gradually added to the MDP solution. The reaction temperature was maintained at 25±2°C. After reaction is over, the reaction mass was slowly quenched into ice followed by hydrolysis

Table 2 Comparison of yield in micro reactor and batch reactor

Dilution	Continuous reactor		Batch reactor	
	Residence Time(min)		Residence Time (min)	
	5	7	19	10
	rate formation of product (g / min)			
50%	0.163	0.075	0.022	0.0185
75%	0.113	0.043	0.020	0.017
100%	0.104	0.039	0.018	0.011

Table 3 Comparison of rate of formation in micro reactor and batch reactor

Dilution	Continuous reactor		Batch reactor	
	Residence Time(min)		Residence Time (min)	
	5	7	19	10
	% Yield			
50%	62.5	35	43	12
75%	57	30	38	9
100%	51	28	32	8

Table 4 Summary of the nitration experiments conducted in micro reactor
Micro reactor length : 2.7 m, ID : about 1mm, T : 25°C / room temperature, Pump MOC : Ceramic, Tube MOC : SS316

Sl no.	Date	% dilution of MDP soln with H_2SO_4	Residence time (min)/ continuous flow (min)	Amt of MDP + H_2SO_4(ml) / Wt of MDP (g) taken	Amt of HNO_3 (ml) taken	Flow rate HNO_3/ H_2SO_4(ml/ min)	Density MDP solution (g/cc)	C_{MDP} (moles/lit)	Amount of MDP soln (g) / MDP Passed (g)	Amt of HNO_3 passed (g)	Product formed (g)	Rate of formation per minute (g/min)
1.	06.01.09	50	5/8	15/2.3	20	0.5/0.5	1.82	1.2	14.8/1.26	15.3	0.69	0.086
2.	12.01.09	50	5/10	15/2.3	15	0.6/0.5	1.82	1.2	15.0/1.27	17.0	0.82	0.082
3.	13.01.09	50	5/10	15/2.3	15	0.6/0.5	1.82	1.2	15.5/1.27	15.8	0.84	0.084
4.	14.01.9	50	5/11	15/2.3	15	0.6/0.5	1.82	1.2	16.0/1.36	16.0	0.91	0.083
5.	15.01.09	75	5/17	17.5/2.3	20	0.6/0.5	1.82	1.0	17.7/1.29	18.0	0.88	0.052
6.	19.01.09	75	5/18	17.5/2.3	20	0.6/0.5	1.82	1.0	18.89/1.38	19.5	0.97	0.054
7.	20.01.09	75	5/20	17.5/2.3	20	0.6/0.5	1.82	1.0	21.09/1.54	20.5	1.1	0.055
8.	23.01.09	75	5/19	17.5/2.3	20	0.6/0.5	1.82	1.0	18.90/1.38	19.0	0.97	0.051
9.	22.01.09	100	5/24	23/2.3	25	0.6/0.5	1.82	0.9	20.5/1.31	20	0.91	0.038
10.	27.01.09	100	5/25	23/2.3	25	0.6/0.5	1.82	0.9	22.2/1.42	22	1.0	0.04
11.	29.01.09	100	5/24	23/2.3	25	0.6/0.5	1.82	0.9	19.72/1.26	20	0.86	0.036
12.	30.01.09	100	5/26	23/2.3	25	0.6/0.5	1.82	0.9	22.38/1.43	21	1.01	0.039

under high speed agitation (rpm about 400) for 3hrs to get product FOX−7 which was then filtered ,washed with water to get product. The product weight was determined for each run after drying. The product formed was analyzed and characterizes by slandered technique. % Yield was compared with the corresponding value obtained in micro reactor are shown in [Tables 2 and 3].

6. Conclusion

Application of micro reactor is a novel approach in the synthesis of key pharmaceutical intermediates and fine chemicals where either the reactions are highly exothermic or there are situations where the selectivity of the product is an issue. It is reported in the recent past that several reactions can show the better yield when carried out in micro reactors than in the conventional batch mode operation. The high heat transfer area helps to achieve a better control of temperature variation in the micro reactor. This further helps to maintain the rates of reaction in specific ranges and thus avoids byproduct formation. Besides, the small length scales also help to achieve faster mixing, thereby reducing the possibility of byproduct formation in fast reactions.

In the present work, the micro reaction system has been modeled for nitration of MDP by adopting two dimensional (2−D) heat flow and mass transfer equations. The numerical results from the 2−D model for conversion and temperature profile along the length and radius of micro reactor have been compared with corresponding value obtained for batch reactor. In order to validate the model several experiments on nitration of MDP were conducted in micro reactor setup with the variation of concentration, flow rate and residence time, temperature etc. The measurable findings of studies are,

- The experimental result from micro reactor revealed that nitration of MDP concentrationtakes place even at lower concentration of MDP and lesser reaction time with better control of temperature.
- The nitration of MDP reaction in micro reactor takes place in laminar region. The yield of final product, i.e., FOX−7 is higher in continuous flow micro reactor than corresponding concentration in batch reactor irrespective of reactant concentration.
- The Rate of formation of FOX−7 (g /min) in continuous flow micro reactor is higher than correspond of batch reactor
- The nitration of MDP in micro reactor was found feasible at even room temperature at different flow rate and residence time and results in higher yield in comparison of batch mode and the present study provides adequate information on design of micro reactor system.

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Notations

C = *Concentration*
C_0 = *Initial concentration at the inlet of the reactor*
E_r = *Effective radial diffussivity*
$< E_r >$ = *Cross* sectional *average radial diffussivity*
D_{am} = *Modified Damkohler number* for *mass*, $r_w^2 r_{ci}/(< E_r > C_0)$
H^* = *Dimensionless temperature rise*, $(\Delta H)\, C_0/(\rho c_p T_f)$
k_r = *Effective radial thermal conductivity*
$< k_r >$ = *Cross* sec *tional average radial thermal conductivity*
k_w = *Thermal conductivity near the wall*
k_z = *axial effective thermal conductivity*
k^* = *Dimensionless radial thermal conductivity*, $k_r/< k_r >$
L_e = *Lewis number*, $c_p < E_r > /< k_r >$
P_{em} = *Peclet number* for *mass* $< u > d_p/< E_r >$
r_c = *Rate of the reaction*
r_{ci} = *Rate reaction at feed inlet*
r_c^* = *Dimensionless reaction rate*, r_c/r_{ci}
r^* = *Dimensionless radial dis* tan *ce*, r/r_w
r_w = *Radius of the tube*

T = *Temperature*
T_f = *Temperature at the feed inlet*
T^* = *Dimensionless temperature*, T/T_f
u_z = *Velocity at z direction*
$< u >$ = *Cross sectional average velocity*
u^* = *Dimensionless velocity*, $u_z/< u >$
x = *Factional conversion*
z = *Axial distance*
z^* = *Dimensionless axial distance*

R = *Universal gas constant*
E = *Activation energy*
h = *Heat transfer coefficient*
k_0 = *Arrhenius constant*

c_p = *Specific heat*
α = *Ratio of tube radius to particle diameter*, r_w/d_p
ΔH = *Total heat of reaction*

Greek symbols
ζ = *Dimensionaless axial position*, $zr_{ci}/< u > C_0$
ρ = *Density*
ξ = *Expression having the group* $\left(\frac{H^*\Delta s}{u^*}\right)$
φ = *Expression having the group* $\left(\frac{E^*\Delta\zeta}{D_{am}u^*\Delta r^{*2}}\right)$
ψ = *Expression having the group* $\left(\frac{\Delta\zeta}{u_z^*}\right)$

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