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Modelling and constraint optimisation of an aromatic nitration in liquid–liquid medium

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Abstract

A methodology, which determines the operating conditions simultaneously optimising the chemical yield and considering the safety aspect, has been developed for a chemical reaction which is carried out batch-wise. To illustrate the methodology, the aromatic nitration of toluene by mixed acid has been chosen as a typical exothermic and non-selective reaction. This reaction takes place in a two-phase medium and, therefore, involves simultaneously chemical reaction and mass transfer phenomena. A kinetic model recently proposed for the slow and fast liquid–liquid reaction regimes was integrated to the mass balance. Nitration experiments were carried out in order to compare experimental composition profiles with simulated ones. Afterwards, an optimisation procedure has been used to maximise conversion, by manipulating the operating conditions subject to safety constraints. The *p*-nitrotoluene yield was chosen as the criterion to be maximised. Experimental validation for the optimisation procedure has been carried out. A monofluid heating–cooling system controlled by a predictive controller was used for the temperature control of the reactor. Simulation and experimental results are presented, discussed and compared.

Keywords: Semi-batch reactor; Modelling; Optimisation; Safety constraint; Toluene mononitration

1. Introduction

Whereas continuous chemical processes have reached an advanced stage of development and modern computer tools are frequently used to optimise these processes, this is not the case for many batch and semi-batch reactors, which remain usually operated manually according to elementary recipes. This may seem surprising since significant benefits can be realised from optimising operating conditions [1,2] and also because batch processes are generally less safe than continuous processes [3].

Specifically, this study deals with the optimisation of batch reactors, which requires knowledge of their dynamic behaviour in order to improve their performance and safety conditions. For an optimised performance, the product synthesis must be performed in the minimum time to lower operating costs. At the same time, to improve the safety of the process, the risk of thermal runaway must be reduced by preventing the accumulation of reactive species and by controlling the cooling devices.

A methodology is developed which determines the best operating conditions by simultaneously optimising the chemical yield and considering the safety aspect of a chemical reaction, which is carried out batch-wise. This methodology can prove to be a useful tool to quickly define safe and optimal operating conditions for new compounds production. It relies on the mathematical description of the chemical process. Coupling of mass balance and kinetics allows determining the composition of the reaction mixture. Kinetic parameters are included in the model, as well as the geometric characteristics of the reactor (volume, heat exchange surface. . .). Once the model is developed, it is integrated in a numerical optimisation procedure.

The aim of this work is to illustrate this methodology with an exothermic chemical reaction that presents selectivity problems, and can be easily performed at a laboratory scale. The toluene mononitration by a mixture of nitric and sulphuric acids called "mixed acid" was chosen for the following reasons. First, this reaction is widely performed in the chemical industries, as it allows the production of useful intermediaries such as primary aromatic amines and azoïc colourings. Secondly, aromatic nitration involves high exothermicity and display numerous side reactions, hence a considerable amount of incidents occur in such processes [3]. Consequently, a better understanding of this kind of processes is of a great importance for the safe and economic design and optimal operation of nitration plants. Also, this reaction takes place in a two-phase medium and, therefore, it involves simultaneously chemical reaction and

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Nomenclature

a	interfacial area (m^2/m^3)
a_{HA}	nitric or sulphuric acid activity (mol/l)
a_{H_2O}	water activity (mol/l)
a_{A^-}	nitrate or sulphate ion activity (mol/l)
$a_{NO_2^+}$	nitronium activity (mol/l)
A	heat exchange area between the reaction medium and the fluid circulating in the jacket of the reactor ($W/(m^2\,K)$)
$d_{impeller}$	stirrer diameter (m)
d_{32}	droplets Sauter mean diameter (m)
$D_{toluene}$	diffusivity of toluene (m^2/s)
E_a	acceleration number
$f(x)$	objective function to minimise
$g(x)$	vectorial application of inequality constraints
$h(x)$	vectorial application of equality constraints
Ha	Hatta number
H_R	acidity function
K	equilibrium constant
k_L	mass transfer coefficient (m/s)
k_2	apparent second-order rate constant related to toluene nitration (l/(mol s))
k'_2	real second-order rate constant (l/(mol s))
$k_{2,1}$	apparent second-order rate constant related to *o*-MNT formation (l/(mol s))
$k_{2,2}$	apparent second-order rate constant related to *m*-MNT formation (l/(mol s))
$k_{2,3}$	apparent second-order rate constant related to *p*-MNT formation (l/(mol s))
m	mass (kg)
m-MNT	mononitrotoluene
M_{feed}	amount of introduced acid (kg)
M_{max}	maximal amount of introduced acid (kg)
n_{int}	number of intervals of the discretization
$n_{toluene}$	initial number of moles of toluene (mol)
$n_{toluene}$	number of moles of toluene remaining in the organic phase (mol)
$n_{toluene(diffusion)}$	number of moles of toluene transferred in the aqueous phase (mol)
N_r	number of reactions
o-MNT	*ortho*-nitrotoluene
p	total number of constraints
p_e	number of equality constraints
p-MNT	*para*-nitrotoluene
q	feed flow rate (kg/h)
Q	heat produced by the reaction (W)
Q_{max}	maximal heat produced by the reaction (W)
r	rate of nitration (mol/(l h))
r_i	rate of reaction i (mol/(l h))
r_R	overall reaction rate (mol/(l h))
t	time (h)
t_j	switching time (h)
t_{op}	operation time (h)
T	temperature (°C)
T_{cf}	temperature of the cooling fluid (°C)
T_j	temperature at the switching time (°C)
T_{max}	maximum instantaneous reaction temperature (°C)
T_{min}	minimum instantaneous reaction temperature (°C)
$T_{reactor}$	instantaneous temperature of the reaction medium (°C)
U	overall heat transfer coefficient between the reaction medium and the fluid circulating in the jacket of the reactor ($W/(m^2\,K)$)
V_t	total reaction volume (l)
w	acid strength
We	Weber number
x	vector of variables to optimise
x_{min}	lower bound on x
x_{max}	upper bound on x
Y	total toluene conversion
Y_i	toluene conversion by reaction i

Greek letters

$\Delta G_{toluene}$	free energy relative to nitration (kJ/mol)
Δt_1	first time interval (h)
$\gamma_{HNO_3 \cdot H_2O}$	activity coefficient of nitric acid in the aqueous phase
ρ	volume fraction of the aqueous phase
$\sigma_{HNO_3 \cdot H_2O}$	surface tension between nitrate acid and water (N/m)
σ	interfacial tension (N/m)
$\rho_{organic}$	density of the organic phase (kg/m^3)

Subscripts

aq	relative to aqueous phase
organic	relative to organic phase

mass transfer phenomena. Such behaviour is commonly encountered in chemical synthesis. Finally, a kinetic model, which uses literature data from homogenous nitration experiments, was recently proposed for the slow [4] and fast liquid–liquid reaction regimes [5].

In this paper, emphasis is given to the validation of the optimisation method. The modelling of toluene nitration is introduced in a first section. The second section deals with the formulation of the optimisation method, and the final section presents the experimental set-up used to validate the optimisation methodology, as well as, the experimental and simulated results.

2. Modelling of toluene semi-batch mononitration

Toluene mononitration takes place in a two-phase liquid–liquid medium. The organic phase is composed of toluene and mononitrotoluene compounds produced during the reaction. The aqueous phase is composed of nitric acid, sulphuric acid and water. Nitration reaction takes place in the aqueous phase. In order to model the toluene mononitration in a semi-batch reactor, the following assumptions are made: the reactor is perfectly stirred with homogenous temperature and concentrations; the reaction only takes place in the aqueous phase; only toluene diffusion is taken into account; mixing heats are not considered.

2.1. Kinetic modelling

The reaction of toluene nitration by mixed acid takes place in the aqueous acid phase and proceeds through the intermediation of the nitronium ion $NO_2{}^+$:

$$\text{toluene} + NO_2{}^+ \xrightarrow{k_2'} \text{products} \tag{1}$$

The reaction rate can be expressed as

$$r = k_2'(NO_2{}^+)\,(\text{toluene})_{aq} \tag{2}$$

The model developed by Zaldivar et al. is used in this study [4]. Toluene diffuses through the organic phase to the interface and into the aqueous phase. Then, it reacts in the boundary layer and/or in the bulk of the aqueous phase with the nitronium ion to form the *ortho*-mononitrotoluene (*o*-MNT), *meta*-mononitrotoluene (*m*-MNT) and *para*-mononitrotoluene (*p*-MNT).

The toluene consumption rate is usually expressed as

$$r = k_2(HNO_3)_{aq}(\text{toluene})_{aq} \tag{3}$$

where k_2 is the apparent second-order rate constant related to toluene consumption, $(HNO_3)_{aq}$ the overall nitric acid concentration and $(\text{toluene})_{aq}$ is the toluene concentration in the aqueous phase.

Homogeneous experiments have shown that k_2 is strongly dependent on the sulphuric acid strength w:

$$w = \frac{m_{H_2SO_4}}{m_{H_2SO_4} + m_{H_2O}}$$

where $m_{H_2SO_4}$ is the mass of sulphuric acid in the mixture water–acid.

So, the formation mechanism of $NO_2{}^+$ has to be taken into account to express k_2. It has been described as

$$HNO_3 \cdot H_2O + HA \rightleftharpoons NO_2{}^+ + 2H_2O + A^- \tag{4}$$

HA represents either sulphuric or nitric acid. Introducing activity coefficients and the equilibrium constant of reaction (4), the concentration of $NO_2{}^+$ can be expressed as

$$(NO_2{}^+) \approx a_{NO_2{}^+} = \frac{K(HNO_3)_{aq} \times \gamma_{HNO_3\cdot H_2O} \times a_{HA}}{a^2_{H_2O} \times a_{A^-}} \tag{5}$$

where $a_{NO_2{}^+}$ is the nitronium ion activity, a_{HA} nitric or sulphuric acid activity, a_{H_2O} water activity, a_{A^-} nitrate or sulphate ion activity, and $\gamma_{HNO_3\cdot H_2O}$ is the activity coefficient of nitric acid in the aqueous phase.

Using this expression and introducing the acidity function H_R, the following expression of k_2 is obtained [4]:

$$\log k_2 \approx \log k_2' + \log K + \log \gamma_{HNO_3\cdot H_2O} - (H_R + \log a_{H_2O}) \tag{6}$$

During nitration, the acid phase composition varies as the reaction proceeds because of nitric acid consumption and water formation and the k_2 value diminishes according to relation (6).

The procedure to compute k_2 is described in [4].

2.2. Overall reaction rate

During nitration, mass transfer, especially at high sulphuric acid strengths may limit the reaction rate. The calculation of the Hatta number (*Ha*) according to Eq. (7) allows evaluating the importance of the mass transfer resistance:

$$Ha = \frac{\sqrt{k_2 D_{\text{toluene}}(HNO_3)_{aq}}}{k_L} \tag{7}$$

According to the Hatta number, three different regimes are considered, and the overall reaction rate r_R is computed according to the following expressions.

- $Ha < 0.3$, slow reaction rate in the acid phase:

$$r_R = \Phi k_2(HNO_3)_{aq}(\text{toluene})_{aq} \tag{8}$$

- $0.3 < Ha < 2$, moderate reaction in the film:

$$r_R = k_L a\, E_a\, (\text{toluene})_{aq} \tag{9}$$

with

$$E_a = \frac{Ha}{th(Ha)}$$

- $2 < Ha$, fast reaction in the film:

$$r_R = a\sqrt{k_2(HNO_3)_{aq} D_{\text{toluene}}} \times (\text{toluene})_{aq} \tag{10}$$

In the case of our experimentation, the reaction starts in a diffusion regime because of a high initial acid strength that enhances the reaction rate. Then, the reaction enters into a reaction regime. Indeed, the reaction leads to water formation and then, to acid strength decrease: the kinetic constant decreases during reaction and, in parallel, the interfacial area increases during the feed of reactants.

So, as it is shown in the Eqs. (8)–(10), the rate of reaction is affected by the characteristics of the system and by the mechanical features of the equipment.

The toluene distribution coefficient which leads to the calculation of $(\text{toluene})_{aq}$ depends on temperature and aqueous phase composition, according to the following equation:

$$\frac{(\text{toluene})_{\text{aq}}}{(\text{toluene})_{\text{organic}}} = \exp\left(\frac{\Delta G_{\text{toluene}}}{RT}\right) \quad (11)$$

The toluene diffusion coefficient in the aqueous phase and all the parameters needed to express the reaction rate in the adapted regime are calculated using the procedure recommended by Zaldivar et al. [4]. The main formulas of this procedure are reminded below:

- The interfacial area (a) depends on the fraction of the dispersed phase and on the Sauter mean diameter:

$$a = \frac{6\Phi}{d_{32}} \quad (12)$$

- Sauter mean diameter can be computed as

$$d_{32} = d_{\text{impeller}} f(\Phi) We^{-0.6} \quad (13)$$

where We is the Weber number.

$$We = \rho_{\text{organic}} N_{\text{r}}^2 \frac{d^3_{\text{impeller}}}{\sigma} \quad (14)$$

We depends on the density of the organic phase (ρ_{organic}), on the rotational speed of the impeller (N_{r}), on the diameter of the impeller, and on the interfacial tension (σ). $f(\phi)$ is a linear correlation of the volume fraction of the dispersed area.

σ is computed from the individual surface tension of organic and aqueous phase.

2.3. Mass balance

The toluene model is a two-phase model including a reaction phase (the aqueous phase) and a non-reaction phase (the organic phase). Toluene has been chosen as the key reactant so that its conversion for each reaction Y_i can be calculated by

$$\frac{\mathrm{d}Y_i}{\mathrm{d}t} = \frac{r_i V_{\text{t}}}{n^0_{\text{toluene}}} \quad (15)$$

where V_{t} is calculated by adding the molar volumes of each compound present in the medium. The overall toluene conversion is given by

$$Y = \sum_{i=1}^{3} Y_i = \frac{n^0_{\text{toluene}} - (n_{\text{toluene}} + n_{\text{toluene(diffusion)}})}{n^0_{\text{toluene}}} \quad (16)$$

The whole reaction is described by Eq. (1) but we have distinguished between the three mononitrotoluene isomers so that three reactions are involved: the kinetics constants $k_{2,i}$ ($i = 1$, *o*-MNT; $i = 2$, *m*-MNT; $i = 3$, *p*-MNT) have the same activation energy but depend on the sulphuric acid strength. They have been calculated as follows:

$$k_{2,1} = 0.96\left(1 - \frac{1}{4.246 - 0.022w}\right)k_2 \quad (17)$$

$$k_{2,2} = 0.04\,k_2 \quad (18)$$

$$k_{2,3} = 0.96\frac{1}{4.246 - 0.022w}k_2 \quad (19)$$

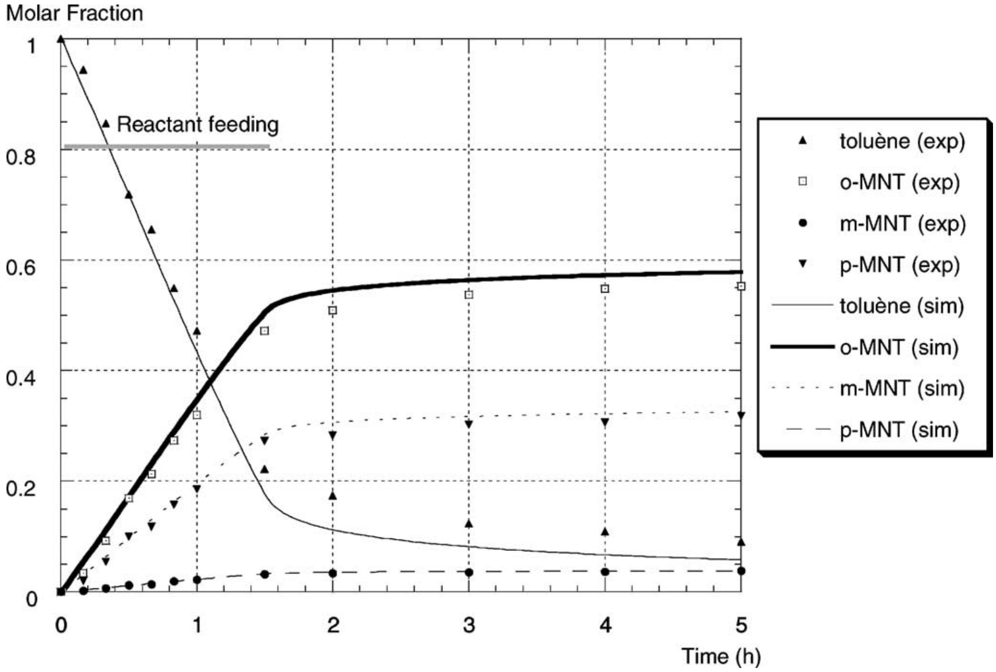

Fig. 1. Evolution of the composition of the organic phase ($w = 72.4\%$, feed time = 1.5 h, experiment 1).

Table 1
Experimental conditions and results for toluene mononitration

Experimental conditions	Experiment 1		Experiment 2	
Operation time (h)	4		4	
Amount of toluene present in the reactor (ml)	150		150	
w	72.4		79.5	
Time feed (s)	5400		5400	
Amount of acid introduced (g)	337		337	
T_{reactor} (°C)	35.9		27.7	
Stirring speed (s^{-1})	16.8		26.6	
	Exp	Sim	Exp	Sim
Simulated and experimental results				
Final composition of the organic phase (mol%)				
o-MNT	54.7	57.9	60.1	59.9
p-MNT	31.6	32.2	35.4	35.8
m-MNT	3.8	3.7	3.8	4.0
Toluene	10	6.7	0.7	0.3
Conversion χ	90	93.9	99.3	99.7
$\Phi_{\max}$ (watt)		40	50	

2.4. Validation of the model

The complete model has been validated for different operating conditions. Two experiments are presented in this paper. Concentration profiles are compared to experimental ones. Operating conditions are listed in Table 1.

For both experiments, the mixed acid was added at a constant flow rate. Figs. 1 and 2 show the simulation (lines) and experimental (points) concentration profiles obtained, respectively for the experiments 1 and 2. Numerical results are also presented in Table 1. A good agreement is found between experimental and simulation profiles. We notice that these two experiments have allowed testing the model under the different regimes. In particular, for Fig. 2, the reaction begins in the diffusion regime, then, the kinetic regime follows. We can deduce from this, that the model describes accurately the chemical reaction under the different regimes.

Nitration experiments have allowed verifying the validity of the model. The following step consists in using this model within the optimisation procedure to find the optimal production under safety conditions.

3. Formulation of the optimisation problem

3.1. Optimisation strategy

The general procedure of optimisation, which has already been described in a previous paper [6], is summarised in this section. This method is characterised by the non-linearity of the variables and constraints. The optimisation problem with bounded and constrained variables takes the form [7]:

$$\begin{cases} \min f(x); & x \in \mathfrak{R}^n \\ h_i(x) = 0; & i = 1, p_e \\ g_i(x) \leq 0; & i = p_e + 1, p \\ x_{\min} \leq x \leq x_{\max} \end{cases} \tag{20}$$

where x is the vector of variables to optimise, $f(x)$ objective function to minimise, $h(x)$ vectorial application of equality constraints, $g(x)$ vectorial application of inequality

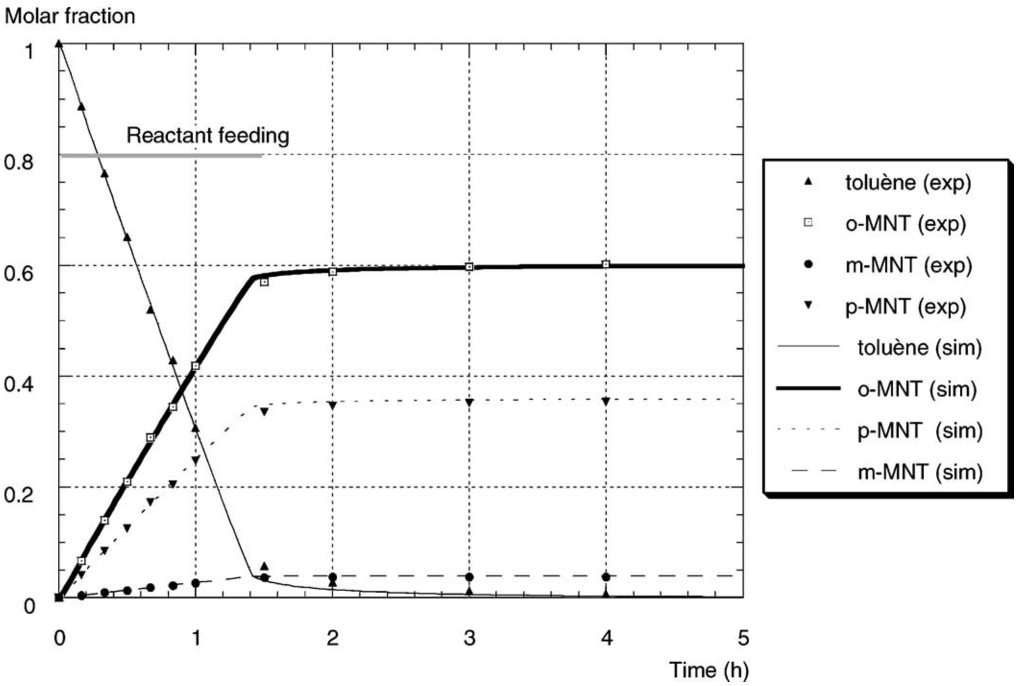

Fig. 2. Evolution of the composition of the organic phase ($w = 79.5\%$, feed time $= 1.5$ h, experiment 2).

constraints, p total number of constraints, p_e number of equality constraints, $x_{\min}$ lower bound on x, and $x_{\max}$ is the upper bound on x.

The optimisation problem consists in determining the operating conditions which will maximise the final yield of the reaction whilst respecting the constraints. The temperature, the feed profile, the operation time, etc. can be defined as the optimisation variables. This non-linear problem is solved by means of the "Successive Quadratic Programming" or "SQP" developed by Schittkowski and using the BFGS method (Broyden–Fletcher–Goldfarb–Shanno) for the evaluation of the Hessian matrix [8].

To solve the problem, the operation time t is divided into a finite number n_{int} of subintervals. The different states of the system are calculated by integration of the differential equations on each interval, by a Runge–Kutta–Merson fourth-order procedure with variable step integration size. The problem consists, then, in determining the $n_{\text{int}+1}$ temperatures at each bound of each time interval. The temperature is assumed to be a linear function versus time in each subinterval, and the final temperature of the interval j is assumed to be equal to the initial temperature of the interval $j-1$ (j varies from 1 to n_{int}). Then, the temperature variations in the range (t_{j-1}, t_j) is given by

$$T = T_{j-1} + (t - t_{j-1})\left(\frac{T_j - T_{j-1}}{t_j - t_{j-1}}\right) \tag{21}$$

The problem is treated in a different manner to determine the feed profile. The program determines the run mass in each subinterval, assuming that the flow rate remains constant within the interval. In this manner, the variables to optimise are the n_{int} run masses in each subinterval.

If the operation time is a fixed parameter, the n_{int} intervals have the same length. In this study, the total operation time and the length of the first time interval are both defined as variables. In this case, all the intervals have the same length except the first one. An example of temperature and feed profile discretization is given in Fig. 3.

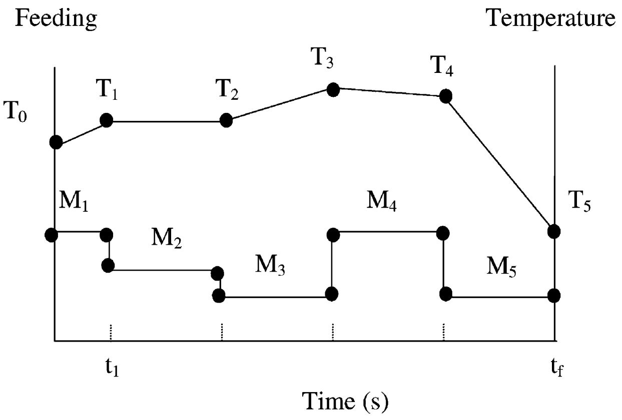

Fig. 3. Example of temperature and feed profiles.

All the variables of the problem are upper and lower bounded. The bounds correspond to the limits of the process, which depend on the chemical reaction and the equipment set-up. For example, the temperature will be limited by the minimal temperature of the reaction and by the critical temperature that could result in a runaway reaction. Moreover, the amount of introduced reactant depends on the volume capacity of the reactor. At last, the feed time is limited by the maximal feed rate of the pump and by the maximal amount of reactants that can be introduced. The slopes of temperature profiles are limited to take into account the cooling and heating capacities of the system, which depend on the heating–cooling system.

3.2. Application to nitration

Optimisation procedure described in the previous part is applied to the specific case of toluene mononitration and illustrated in this section.

3.2.1. Objective function

As the *p*-nitrotoluene is an important intermediary for industrial applications, it was decided to optimise the conversion in *p*-nitrotoluene. Its selectivity increases with the acid strength, w [9]. However, increasing w results in faster kinetics, temperature increases and runaway reactions can occur. For these reasons, the aim of this optimisation problem is to adapt the feeding profile and the temperature of the reactor to the acid strength used, in order to remain between acceptable temperature and generated heat ranges.

The criteria to maximise is the *p*-nitrotoluene yield at the end of the reaction [6]:

$$\min\left(-100 \times \frac{\text{number of moles of } p\text{-MNT} \atop \text{at the end of the reaction}}{\text{initial number of moles of toluene}}\right)$$

3.2.2. Optimisation variables

Five types of variables are used for this optimisation problem: the optimiser is asked to compute the optimal feed rate and temperature profiles, the acid strength, the total time of operation and the first time interval. The total operation time is divided into five subintervals; the first one is considered as a variable to optimise and the four other ones have the same length.

3.2.3. Constraints

Operating constraints are activated in order to obtain safe operating conditions and to correspond to the technology of the process [10].

The following constraints are added to the problem:

- The amount of introduced acid is limited to 767 g:

$$M_{\text{feed}} \leq M_{\max} \quad (M_{\max} = 0.767\,\text{kg})$$

- The maximal feed flow rate is equal to 0.627 kg/h: $q \leq 0.627$ kg/h.
- $Q \leq Q_{\max} \quad (Q_{\max} = 40\,\mathrm{W})$.

This constraint is placed upon the heat produced by the reaction. For the system to be safe, the cooling system should be able to remove all the heat produced by the reaction. Otherwise, heat accumulation will occur and, hence, the reactor temperature will increase. This may trigger a runaway reaction due to the high exothermicity of aromatic nitration; $Q_{\max}$ is the maximum instantaneous thermal flux produced by the reaction, that could be removed by the cooling system. This flux is calculated according to Eq. (22), with a minimal overall heat transfer coefficient equal to 200 W/(m^2 K), a minimal heat exchange surface (0.02 m^2) and a difference in temperature between the cooling fluid and the temperature of the reaction equal to 10 °C.

$$Q_{\max} = UA(T_{\mathrm{cf}} - T_{\mathrm{reactor}}) \tag{22}$$

where U is the overall heat transfer coefficient between the reaction medium and the fluid circulating in the jacket of the reactor (W/(m^2 K)), A heat exchange area between the reaction medium and the fluid circulating in the jacket of the reactor (m^2), T_{cf} temperature of the cooling fluid (°C), and T_{reactor} is the temperature of the reaction medium (°C).

- $T_{\min} \leq T_{\mathrm{reactor}} \leq T_{\max}$, where $T_{\max}$ is the maximum instantaneous reaction temperature. This constraint avoids the temperature of the reactor reaching a critical value. The value given for $T_{\max}$ is 50 °C because dinitration begins to be appreciable above this temperature. The reactor should neither be allowed to reach a temperature below $T_{\min} = 20$ °C, in order to prevent the accumulation of nitric acid in the reaction medium in case of slow reaction.
- 60% ≤ acid strength ≤ 80%.

  To increase kinetics, it is interesting to reach high values of acid strength. This is the reason why w must be more than 60%. But, too high values would result in an increase of temperature and in the production of dinitrotoluene compounds. Hence, the mononitration model, which does not take into account the dinitrotoluene formation, would not be valid anymore. Finally, w must be lower than 80%.
- The first time interval is limited: $1.22\,\mathrm{h} \leq \Delta t_1 \leq 4\,\mathrm{h}$. The 1.22 h corresponds to the maximal amount of reactant introduced at a maximal feed rate (=0.767/0.627).
- The total operation time is upper bounded too: $1.22\,\mathrm{h} \leq \Delta t_{\mathrm{op}} \leq 4\,\mathrm{h}$.

3.3. *Optimisation results*

The optimiser determines an acid strength equal to its upper bound (80%). Concerning the optimal feed profile, approximately 100% of the mixed acid is injected in the first interval which lasts 2 h 50 min, with a moderate flow rate (167 ml/h). An isotherm at 30 °C is found to be the optimal profile for the temperature of the reaction medium. In these conditions, the heat flux rapidly reaches a value around 40 W during feeding, which corresponds to the constraint fixed on the flux (Fig. 4). The resulting yield of *p*-nitrotoluene is 36% after 4 h of operation (Fig. 5). These optimal operating conditions are listed in Table 2.

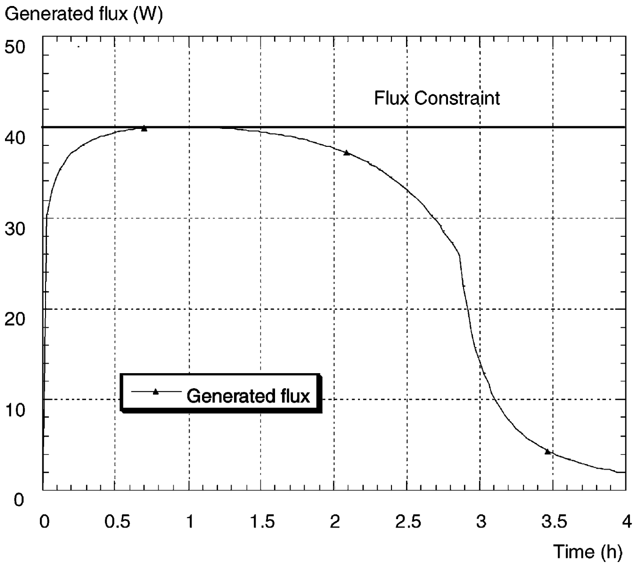

Fig. 4. Simulated temperature profile in the reactor and reactional heat flux.

Table 2
Results of the simulation

	Optimal solution
Initial acid strength (%)	80
Operation time (h)	4
Length of the first time interval (h)	2.87 h (2 h 52 min)
Feed time (h)	2.87 h (2 h 52 min)
Total mass of acid injected (kg)	0.767
T_{reactor} (°C)	30
$Q_{\max}$ (W)	42

To illustrate the performance of the methodology and to validate it, an experimental application is needed. For that aim, a specific pilot plant developed by Bouhenchir et al. [11], which allows a direct control of the temperature inside the reactor is used.

4. Experimental section: validation of the optimisation method

4.1. *Description of the reactor*

The experimental device consists of a 1.5 l jacketed reactor, fitted out with a monofluid heating–cooling system. The monofluid is a glycol–water mixture in ratio of 50% circulating in the jacket at a high flow rate (1000 l/h), it is maintained at a predifined temperature by means of a resistance and heat-exchangers. A sketch of the pilot plant

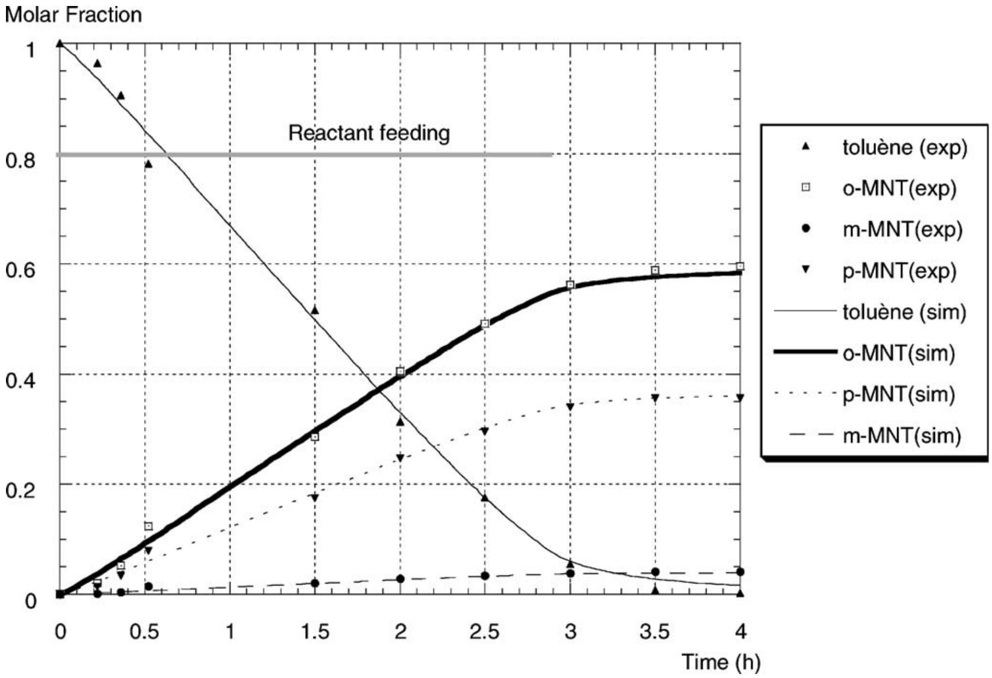

Fig. 5. Evolution of the organic phase composition—comparison between simulated and experimental results for the optimal conditions.

is given in Fig. 6. The mixed acid can be added to the toluene through a peristaltic pump which is able to deliver a constant flow rate. A propeller ensures a good stirring. The temperature of the reaction medium is measured with a thermal probe and automatically controlled. A condenser has been added to avoid nitrous vapour evolution.

The heating–cooling system was precisely studied and described by Bouhenchir et al. [11]. It includes a 2000 W electrical resistance and two plate heat-exchangers, one using cold water (at about 15 °C) and the other using a mixture of glycol–water in ratio 50% (at a temperature of −10 °C). The monofluid flow rate is measured by means of two flow meters, one installed on the main thermal loop and the other on the secondary thermal loop. Temperatures of the monofluid and of the utility fluids are also controlled at any critical point of the thermal loop. Three on–off valves allow the fluid to be heated or cooled.

A computer equipped with input–output boards provides real-time data acquisition, automatic start-up and operation control. Supervision and control programs are implemented on a PC. A predictive controller based on Predictive Functional Control [12] is used to compute the necessary thermal flux to be exchanged between the reactor content and the fluid flowing in the jacket (manipulated variable). This controller is based on a model representation of the process. On the other hand, the maximal and thermal capacities of the different apparatus (electrical resistance, heat-exchangers) are computed and used to select the "right" thermal element with a priority to the device currently used.

Then, the predictive controller computes and applies to the process the manipulated variable by minimising the square errors between the future set points (reference profile) and the output predictions (temperature in the reactor) on a receding horizon.

4.2. *Typical run*

The reactor was first fed with toluene (259.8 g). Stirring and cooling jacket temperature (30 °C) were then set. Once the medium temperature had been stabilised, the mixed acid was added at a constant flow rate. The medium temperature was recorded every 30 s and samples were taken from the medium to follow each product concentration. The exact conditions given by the results of the optimisation were followed. The experiment was performed twice to verify the validity of the results (experiment 3). The conditions are presented in Table 2.

4.3. *Analysis*

Samples of the reaction medium were collected during the runs in order to follow the concentrations of toluene, mononitrotoluenes and eventually dinitrotoluenes: once every 10 min during the first hour, then once every 30 min. They were diluted with cold water to stop the reaction and washed several times with distilled water in order to eliminate acids. The organic phase was then analysed by gas chromatography [13], using a 25 m HP-1 non-polar capillary column and an ionisation flame detector. Response coefficients of each compound were previously determined, taking toluene as the reference compound.

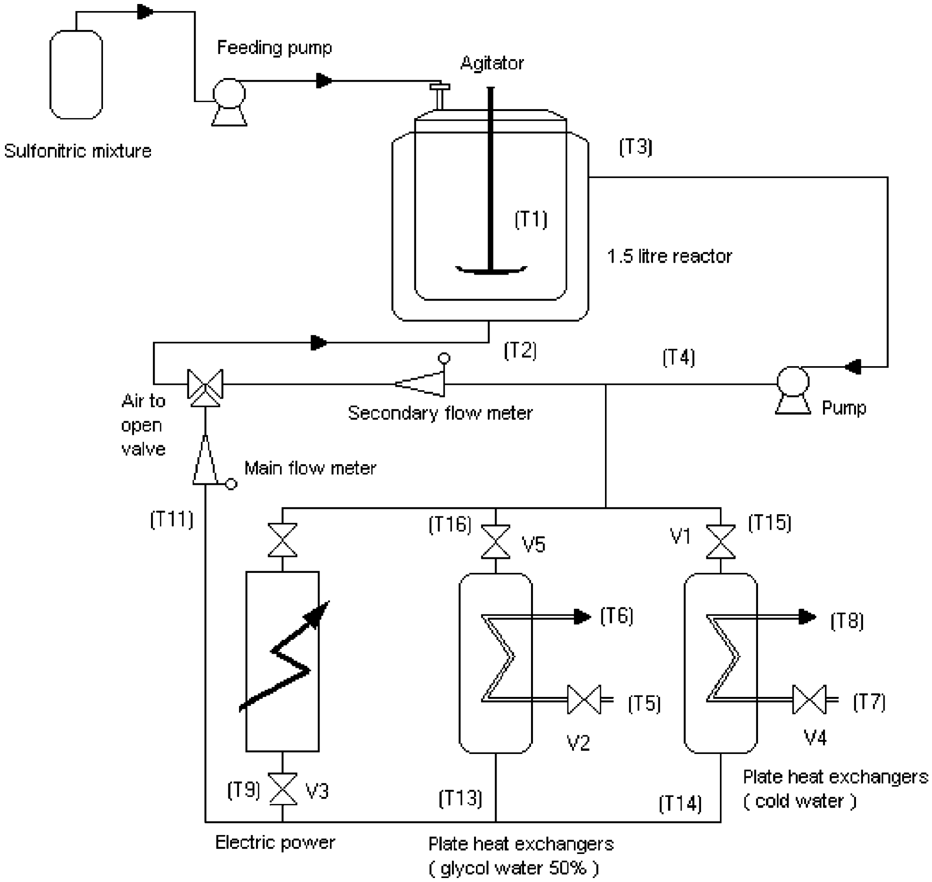

Fig. 6. Reactor linked to the heating–cooling system—experimental set-up.

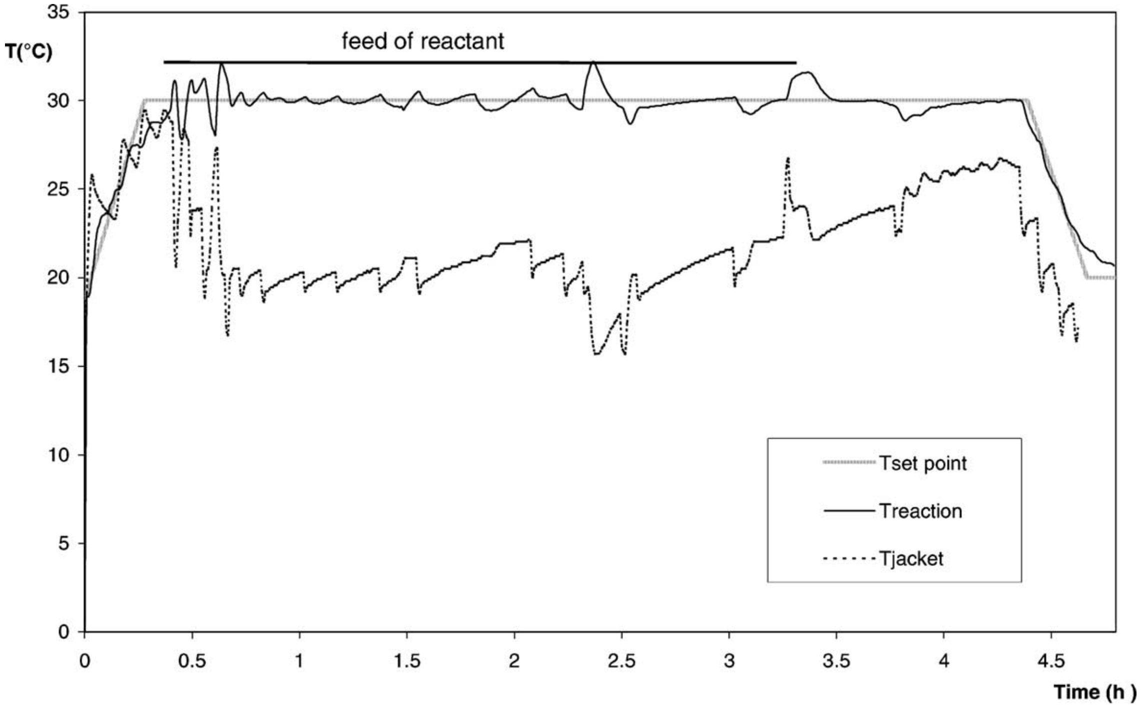

Fig. 7. Temperature profile of the reaction medium (experiment 3).

4.4. Results and discussion

Fig. 5 represents the molar fractions of toluene and of the products of nitration as a function of time. Both simulated and experimental graphs are plotted on this figure and can be compared. The results of experiments are in good agreement with the model used for the simulation. The final yield is equal to 35.6%.

The temperature profile is represented in Fig. 7. The expected temperature is programmed according to the following phases:

- a heating period from 20 to 30 °C during 0.27 h,
- a constant period at 30 °C between 0.27 and 4.38 h with feed of reactant between 0.38 and 3.25 h,
- a cooling period from 30 to 20 °C during 0.27 h,
- a constant period at 20 °C during 0.13 h.

The temperature of the fluid circulating through the jacket, at the exit of the jacket and the temperature inside the reactor are also represented in Fig. 7. By analysing this figure, the following remarks can be given: the fluid in the jacket is heated before the introduction of the acid in the reactor. Then, the reaction starts which results in a quick quenching of the monofluid by activating either one of the plate heat-exchangers either the electric resistance. At 2.5 h, when the rate of the reaction decreases and that less heat is released, the temperature of the fluid in the jacket is increased until the beginning of the cooling period. We can also notice that the set-point profile is correctly tracked during the entire experiment except in a few points: these overshooting correspond to samples taken in the reactor that slightly disturbed temperatures.

Results using the optimisation procedure show that it is possible to obtain the highest *p*-MNT yield (35.6%) by reproducing operating conditions given by the optimisation procedure (experiment 3). Applying these optimal operating conditions allows to carry out the reaction under safer conditions since the maximal heat flux generated limitation is more severe (40 W instead of 50 W for experiments 1 and 2). Comparison between simulated and experimental results validates the methodology presented in this paper.

5. Conclusion

The objective of this study was to integrate the model developed by Zaldivar et al., describing mathematically the chemical process of a nitration by mixed acid in a semi-batch reactor, in a numerical optimisation procedure. From the comparisons between simulation and experimental results, it can be concluded that it is possible to use such a methodology to control and optimise nitration. The application of the optimal operating conditions allows obtaining good efficiencies and safe conditions of operation. This validation can legitimate the application of this procedure to the same reaction in an adiabatic mode, which could represent the case, sometimes met in the industry, of a cooling failure occurrence [14].

Further work will be devoted to the integration of dinitration in the kinetic model, which will lead to a competitive/consecutive reaction. This will allow to work between 80 and 100% acid strength and to obtain a better selectivity of *p*-MNT. But dinitrocompounds formation will then be favoured and safety constraints will be decisive to ensure the process operability.

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