

BATCH REACTOR OPTIMIZATION BY USE OF TENDENCY MODELS

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Abstract—Batch processes suffer from variation in the quality of the product. This is due to the lack of fundamental understanding about the reactions and their kinetics. As a result, batch processes are not operated as optimally as they could be. Traditional optimization tools require a detailed process model. In most cases a detailed model is not economically attractive to develop.

To account for these difficulties, this publication proposes a new optimization approach by the use of tendency models, with direct application to several batch processes. This strategy accounts for the lack of detailed *a priori* knowledge about the chemical reactions involved. The approach includes the identification of the stoichiometry of a small set of reactions and their approximate kinetic models which fit the available batch data best. The estimated model is used to optimize the next batch and the new data collected is used to update the model until no additional improvement of the process is possible.

Experimental results on the optimization of an example reaction of industrial interest are reported in which the preliminary application of the algorithm is demonstrated.

1. INTRODUCTION

Batch processing is an important segment of the chemical process industries. A growing proportion of the world's chemical production by volume and a larger proportion by value is made in batch plants. In contrast to continuous processes, batch processes related to the production of fine and speciality chemicals, pharmaceuticals, polymers and biotechnology are characterized by the largest present and future economic growth among all sections of the chemical industry (Anderson, 1984). This trend is expected to continue over the next decades as the industry pursues the manufacture of low-volume, high-value added chemicals, particularly in developed countries with few indigenous raw materials.

In comparison to continuous processes, batch reactors are characterized by a greater flexibility of operation and a rapid response to changing market conditions. Typically, a single piece of process equipment may be used for manufacturing a large variety of products utilizing several different unit operations such as reaction, distillation, extraction, etc. As a result, batch plants have to be cycled frequently and monitored carefully, thereby requiring higher labor costs per unit volume of product throughput. Thus most of the batch processes, particularly those related to the production of fine and specialty chemicals, are characterized by significant price differences between the reactants and the products.

Unlike continuous processes, batch processes seldom operate at a steady state, resulting in a lack of reproducibility. Most batch processes suffer from batch-to-batch variation in the quality of the product due to imprecise measurement and control of operating conditions. In the case of continuous processes, the off-specification material produced during the startup and transient operation of the plant can be either reprocessed or blended with the good products during normal operation. Batch processes do not enjoy this luxury. The batch process is in transition most of the time, and the limited time cycle of a batch does not allow for many corrective actions. Often a batch does not result in making a product of desired quality and has to be discarded. Because the added value of the product in relationship to the reactants is so high, the process economics are dependent more on whether the batch made an acceptable product rather than whether the amount of energy or reactants used was the minimum possible. Thus significant economic benefits can be realized from the optimization of a great variety of batch and semibatch processes.

Batch processes are characterized by small annual volumes of production. Typically, the annual requirement for a particular product can be manufactured in a few weeks. The plant is then adapted, and if necessary reconfigured, to produce the next product. This makes the development of detailed kinetic models for each process or product economically unattractive. The frequent process changes that

characterize this technology seldom provide enough time for the development of detailed kinetic models. In the absence of kinetic information, most batch reactors are currently controlled by means of conventional temperature controllers, and in some rare cases, by energy balance control strategies (Juba and Hamer, 1986; Jutan and Uppal, 1984). In almost all cases one lacks any information as to how much the process operation can be improved.

On the other hand, traditional optimization tools aiming to maximize the yield or selectivity of a desired product require complete knowledge of the kinetics of the process under consideration. Development of kinetic models may require several man-years of laboratory investigation and may still lack accuracy and robustness due to impurities and procedural variations found in the plant environment.

To account for some of these difficulties we have initiated the investigation of a general-purpose modeling and optimizing control strategy, which will be directly applicable to several batch processes. This strategy aims to properly account for our lack of detailed process knowledge and the great variety of batch or semibatch reactors. At the same time it takes advantage of the plant data collected during the process operation to update the model. In the present communication we give details of this strategy.

2. BACKGROUND

Since the initial and pioneering work of Bilous and Amundson (1956) on the optimum temperature profile for consecutive reactions and the work of Denbigh (1958) on reversible reactions, several articles have addressed the problem of batch reactor optimization. A recent excellent review paper of Rippin (1982) provides a very useful synopsis of past work.

Two general comments can be made about previous publications in the area of batch reactor optimization and control. Firstly, the considerable emphasis on optimization has also generated a parallel interest in batch reactor control, either through the manipulation of the coolant or heating medium to control the reactor temperature, or through the manipulation of flowrates to control the addition of one or several reactants and/or the removal of products. Secondly, a major fraction of past studies has repeatedly assumed that a process model is always available. This is not true in most cases of practical interest. To remove the limitations imposed by this assumption, the modeling activity should become an equally important and challenging partner to the activities of optimization and control.

Another important practical consideration is the desire to bound the state variables of the process model between an upper and a lower bound. State constrained optimization problems are very challenging to solve, but some results already have been presented in the literature. For example, Newberger

and Kadlec (1971) and Burghardt and Skrzypek (1974), studied the optimum profile of temperature, bound between a maximum and a minimum value, while aiming to maximize the production of product *P*, in a concurrent-consecutive reaction network.

Other authors (Szepe and Levenspiel, 1968; Pommersheim and Chandra, 1975; Pommersheim *et al.*, 1980; Grezik and Skrzypek, 1983; Buzzi-Ferraris *et al.*, 1984; Hatipoglu and Rippin, 1984; Crescitelli and Nicoletti, 1973) used Pontryagin's maximum principle to calculate the temperature profile that would optimize a process performance criterion of reactors with different reaction schemes. They examined cases when the used catalyst was susceptible to deactivation, or where the performance criteria took into account the cost of the reactants, the value of their products and the duration of the batch. An important and very realistic study was reported by Binns (1969).

Certain authors, aiming at a more realistic approach to the problem, did not calculate the optimum temperature profile but the optimum heat flux profile to maximize the performance criterion. To do this, they used a reactor model that included the reactor heat balance equation along with the material balances. In their seminal work, Siebenthal and Aris (1964a,b) treated the problem for a reversible reaction and accounted for the value of the maximum cooling available. A similar study was also reported by Newberger and Kadlec (1971). Marroquin and Luyben (1972, 1973) considered a more detailed heat-transfer model and examined the effect the thermal inertia of the wall had on the effectiveness of the control strategy.

Contrary to the optimization of reactor temperature, the optimization of feed rate has not been the object of many publications, perhaps because it implies that the reaction network should be more complex than the simple and popular reaction of A reacting to produce B. Jackson and Senior (1968) is widely considered as one of the most important studies of the optimum feed profile problem. They constrained the flowrate between a low value of zero and an upper value and maximized a criterion *J* which was defined as a weighted sum of the final compositions. In one of the reaction examples considered, they concluded that the optimum feed policy was to introduce all the reactants at the beginning, while at the second example they calculated an optimal feed rate profile.

When, in the last decade, realtime process control computers became more available, a number of industrial publications have indicated an interest in batch computer control: Allen and Phillips (1971), Allen (1977), Bacher and Kaufman (1970), Spellman and Quinn (1975) and Tsai and Lane (1982) described the improvements observed in existing industrial installations when the procedure was equipped with a computer to manage the traditional analog controllers and collect data, permitting a better understanding of the process. In some cases the computer

allowed better adjustments of the PID parameters and the majority of authors noted the better quality and reproducibility characteristics of the product as well as increased reliability in the operation.

It must be also pointed out that in many of the industrial publications, process regulation is achieved by the use of the classic PID control algorithm in a control structure where each measurement is acting as a single control input. The possibility of interaction between several measured and manipulated variables is ignored, which, in certain cases, could have an important detrimental effect to the control and thus the amount of process optimization possible.

3. PROCESS CHARACTERISTICS

The goal of the strategy developed is to guide the operating conditions of a batch process in order to optimize its performance with respect to an appropriate criterion. This could be, for example, related to the maximization of the product yield or selectivity, or to the minimization of a cost criterion that is affected by the operational and capital costs of the process, as will be the case of interest here. The processes of interest are ones that are carried out in a semibatch reactor in which both liquid- and gas-phase reactants and products are considered.

The main premises of the strategy are the following

A. Use all available process information—This means the inclusion and use of all accurate process data from previous runs as well as all other knowledge about the process. This also implies that the models to be used should not be input-output correlation models, which are usually linear ones, but rather structured nonlinear models, as it will become more clear later.

B. Optimize process in an evolutionary approach—Because the accuracy of the models developed will not be known, process optimization cannot take place in a single step. The initial data and process knowledge can be used to provide an initial model and an optimum expected operation for the next batch. As additional data are collected from subsequent batch runs, the updating of the model will inevitably lead to a further optimization of the process and an increased accuracy of the model.

In our concern to approach real industrial conditions, we developed our strategy influenced by the following hypotheses:

- Batch processes are usually carried out in a multipurpose environment. Devices which measure the actual concentrations during a run are rare and, when they do exist, are highly-specialized and sensitive requiring specialized personnel for their operation. They are not rugged enough for operation in the plant environment. Hence our first hypothesis: it is not realistic to expect time dependent concentration data for reactants and products. The only possible

exception that might be cited is the one concerning the use of gas or liquid chromatography. These measurements are more often used in laboratory rather than production scale reactors and, quite often, will not provide a complete analysis of all reactant and product compositions.

- The production rates of products manufactured in batch processes are not very high and a single reactor might be used to produce more than one product. Furthermore, the production technology of such products is undergoing frequent changes. These conditions do not allow enough time and do not justify the economic expenditure for a detailed study of the chemical kinetics of the process. Consequently it is not accurate to assume that a detailed model is available for the process optimization. Laboratory studies are usually brief, hence the second hypothesis: the reaction mechanism and the kinetics are known only approximately.

- The reactor is usually fed with known quantities of reactants, hence the third hypothesis: the initial concentration in the reactor is known.

- Flow regulators and flow meters are devices proven reliable and present in industrial installations. Hence the fourth hypothesis: the flow of reactants introduced is known.

- At the end of the run an analysis of the reaction mixture is possible in order to determine the quantity of product produced, the quantity of reactants remaining and, when possible, the quantity of all other easily-analyzed byproducts present. Clearly the concentration of several compounds in the product mixture will remain unknown. Their existence might be known but their quantity will be estimated. In the case of organic synthesis, they are generally the "heavy components". In the reaction models that will be used here these byproducts are lumped together and considered as one constituent. The fifth hypothesis is, therefore: the final concentration of the most important constituents in the product mixture is measured, that of others is estimated.

- Batch installations can be easily equipped with thermocouples or temperature transmitters linked to a computer or simple recorder to monitor the reaction temperature, hence the sixth hypothesis: the reaction temperature is known during the entire run.

- Through appropriate calculations or separate experiments, it is possible to know the heat transfer coefficients between the reaction mixture and the cooling or heating medium. The seventh hypothesis is, therefore: the heat transfer coefficients are known so that a heat balance can be accurately closed.

The first six of the above hypotheses lead us to define the following measurements of the system:

- Rate of introduction of liquid reactants
- Reaction temperature
- Initial composition
- Duration of the batch

The above measurements are complemented with available measurements of the final composition of the reaction mixture. In exceptional cases, of laboratory but not industrial reactors, one might also have available concentration data of key reactants and products at different time instances during the reaction.

The set of model parameters to be estimated is made up of the stoichiometric coefficients of the allowed reactions, the corresponding reaction orders, the pre-exponential factors and activation energies. In the case where the seventh hypothesis is taken into account, the added measurement of the time dependence of the heat removal away from the reactor is available and then the enthalpies of the reactions can be estimated.

The approximate model then includes all the available information about the process. But this information might not be complete as it usually is in predictive or white models. The approach adopted here is referred to as tendency modeling, or as a gray model approach. It is contrasted to the black box approach, in which a linear input-output correlation model is constructed to just fit the available experimental data without any attempt to incorporate the physical characteristics and existing understanding of the process.

4. PROCESS OPTIMIZATION

Taking into account those restrictions, we can now develop our method in more detail. It consists of four steps.

4.1. First step: experimentation

This step relates to the collection of the preliminary experimental data if they are not available from previously existing batch runs. The type of data available were described earlier.

4.2. Second step: initial estimation of a representative model(s)

This step consists of exploiting the available experimental data to the maximum to obtain a simple reaction network that will adequately represent the concentration changes in the reaction mixture. No attempt is made to have the model satisfy atomic balances, because in most cases at least one of the reaction byproducts in the model will represent a mixture of several compounds.

Taking into account that only limited information is available, several stoichiometric models might be able to fit the data equally well. Certain of them might be eliminated as contradicting prior knowledge about the reaction. In many cases this might not result in eliminating all but one of the possible reaction networks. Here we suppose that two or more reaction networks are retained.

Besides the identification of the stoichiometric coefficients, the kinetics of each model must be

identified. Determining the correct reaction order with respect to each of the reactants for each reaction is not attempted in the present version of the algorithm. In most cases they are chosen *a priori* to be proportional to the stoichiometric coefficients of every reactant, unless prior knowledge indicates differently. The pre-exponential factors, the activation energies, and the reaction enthalpies, if a heat balance is available, remain to be determined.

Details of the identification procedure used to estimate the above parameters have been given by Filippi *et al.* (1986). Because this identification procedure to a specific process might result in more than one kinetic model, methods for the selection of one of the possible reaction networks are needed. Such methods have not been postulated clearly yet.

4.3. Third step: implementation of optimum control

With the available tendency model, the optimization problem can be solved by the use of Pontryagin's maximum principle, in order to determine the optimal variation of the control variables that minimize the performance index.

In order to implement the solution of the process optimization problem, one has to select the available manipulation variables. This is often needed because the "control variables" with respect to which the optimization is performed might not be available for direct manipulation. For example, a calculated optimal temperature profile can only be achieved experimentally by the manipulation of the flowrate of the cooling or the heating medium or both.

The approach taken here implements a simple PID algorithm in the actual control of process. This does not preclude the need for more elaborate algorithms if the application is expected to benefit from it. The uncertain accuracy of the available tendency model suggests the use of the simplest control algorithms until the accuracy of the models improves.

4.4. Fourth step: preparation of the next run

Taking into account the tendency character of the model that is identified, one might anticipate that the calculated optimum trajectory for the following batch run is perhaps different from that applied in the previous run and possibly quite different from the real optimum of the process that we aim to eventually calculate and implement. Thus, the application of the newly-calculated optimal control policy might lead the process to operating conditions beyond the range of all previous data. Until confidence builds up about the accuracy of the model, drastic changes in the operational strategy of the batch process might result in very undesirable consequences, such as the production of an inordinate amount of byproducts, an explosion or product contamination. For the above reasons, we propose to gradually introduce the newly-calculated control strategy as follows:

$$U_n = U_0 + \phi(t)(U^* - U_0) \quad \phi = \exp(-t/\tau).$$

Here U_0 designates the control profiles applied in the preceding run and U^* the newly-calculated optimum profile. The function $\phi(t)$ is a scheduling function that aims to start the new batch run with a control strategy identical to U_0 and to gradually shift it to the U^* . This gradual shift is characterized by a time constant equal to τ . Initially the value of τ is set equal to one third of the batch time of the previous run. As confidence on the process model builds up, the value of τ should be decreased. It is not as yet clear whether this change should be made with the use of heuristic rules or whether an algorithmic approach will provide a better solution to the problem.

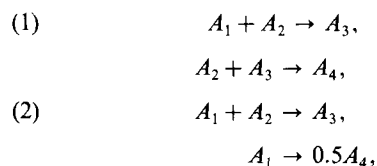
With the above steps addressed, the new batch should be run and the new experimental data collected should be appended in the process data-base, ready to influence the following cycle of model identification, process optimization and control strategy.

After repeating the above cycle a sufficient number of times, the model is expected to become increasingly more accurate and the process optimized. Since it is deemed very difficult to provide a general mathematical proof that the proposed algorithm will always succeed, one can not exclude the possibility that in some cases it might fail to guide the process to a more optimum operation. The application of the proposed procedure to several pilot plant and process examples is expected to shed ample light to this and thus help modify the algorithm to account for a far larger number of contingencies than it presently does.

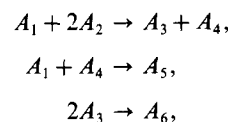
5. SIMULATION RESULTS

The effectiveness of the above procedure was first tested on known kinetic models. From the known kinetic model, fictitious experimental results were generated in the form of tables of initial and final concentrations for the substances considered. Such sets of data were generated for different temperatures or temperature profiles. From the simulated "experimental results" and the application of the algorithm, the original model was successfully retrieved.

While the following kinetic models were initially tested:



it is the identification of the following third reaction network:



that will be detailed here.

A member of the research group (J.V.) wrote a simulation for the above reactions in a batch reactor. This simulation used seven experiments of the reaction system containing six constituents, A_1, A_2, A_3, A_4, A_5 and A_6 . Species A_1 and A_2 react together to give as products the remaining four species. The desired product is A_3 . Table 1, consisting of the initial and final concentrations of the simulated batch runs, was furnished to another member of the group (C.F.-B.).

Given sufficient experimental data, the algorithm can estimate the stoichiometric coefficients of as many reactions as the true elementary steps of the reaction. Taking into account the limited number of experiments available for this process and the number of constituents, the maximum number of reactions that were identified is three.

The successive iterations were as follows:

5.1. First iteration: $R = 1$, one reaction

At Step 4 of the algorithm (Filippi *et al.*, 1986), the computer generated the following stoichiometric coefficients:

$$(-0.987, -1.812, 0.685, 0.816, 0.080, 0.110),$$

respectively for A_1, A_2, \dots, A_6 . In order to make the stoichiometric coefficients be simple integers, the user of the algorithm made the following approximations:

$$(-1, -2, 1, 1, 0, 0).$$

The desired model precision was not attained because the error parameter E_3 was not less than 10^{-3} . On the other hand, $E_2(1), E_2(2), E_2(4)$ and $E_2(5)$ were less than E_4 and thus A_1, A_2, A_4 and A_5 were masked in the next iteration.

5.2. Second iteration: $R = 2$, two reactions

At Step 4 of the algorithm the following coefficients were calculated for the second reaction:

$$(0, 0, -0.764, 0, 0, 0.382),$$

and the user made the following approximations:

$$(0, 0, -1, 0, 0, 0.5).$$

Table 1. Temperature and initial and final concentrations of the simulated data for seven different batch runs

	T (K)	Concentrations A_6A (mol l ⁻¹)							
		C_1^0	C_2^0	C_1^f	C_2^f	C_3^f	C_4^f	C_5^f	C_6^f
1	300	1.000	2.000	0.141	0.351	0.657	0.795	0.032	0.083
2	300	1.000	1.000	0.504	0.102	0.386	0.400	0.048	0.032
3	300	1.000	3.000	0.018	1.080	0.644	0.940	0.021	0.158
4	300	0.500	1.000	0.099	0.221	0.345	0.380	0.011	0.022
5	320	1.000	2.000	0.174	0.594	0.378	0.522	0.120	0.162
6	340	1.000	2.000	0.189	0.846	0.225	0.345	0.231	0.176
7	280	1.000	2.000	0.188	0.402	0.741	0.780	0.016	0.027

Table 2. Energies of activation and frequency factors obtained from identification

	1	2	3	4	5	6	7
E_1^+ (J mol ⁻¹)	74540	56720	62570	63290	45470	42850	43600
E_1^- (J mol ⁻¹)	94860	86270	79640	97670	77160	77555	60800
E_2 (J mol ⁻¹)	48270	68790	41570	45500	58770	49080	48950
E_3 (J mol ⁻¹)	69560	76675	57520	75190	43530	52730	44870
k_1^{0+} [(mol l ⁻¹) ^{-0.5} h ⁻¹]	1.959×10^{12}	1.928×10^9	5.601×10^{10}	2.657×10^{10}	3.651×10^7	2.298×10^7	3.160×10^7
k_1^{0-} (h ⁻¹)	8.615×10^{14}	2.852×10^{13}	8.603×10^{12}	1.193×10^{15}	2.676×10^{12}	6.110×10^{12}	7.590×10^9
k_2^{0-} [(mol l ⁻¹) ⁻¹ h ⁻¹]	6.890×10^6	2.869×10^{10}	1.180×10^6	2.486×10^6	3.365×10^8	8.079×10^6	1.300×10^7
k_3^0 [(mol l ⁻¹) ⁻¹ h ⁻¹]	3.051×10^{10}	8.279×10^{11}	2.641×10^8	5.086×10^{11}	1.118×10^6	2.701×10^7	2.300×10^6

The stoichiometric model precision was still not attained. On the other hand, $E_2(2)$, $E_2(3)$ and $E_2(6)$ were less than E_4 , so now A_2 , A_3 and A_6 were masked from the next iteration.

5.3. Third iteration: $R = 3$, three reactions

At Step 5 of the algorithm, the computer generated the following stoichiometric coefficients for the third reaction:

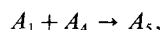
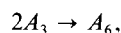
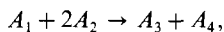
$$(-0.557, 0, 0, -0.617, -0.550, 0),$$

which were approximated by:

$$(-0.5, 0, 0, -0.5, 0.5, 0).$$

After this iteration the desired model precision was attained and no further reactions were identified.

Therefore, the final model obtained is:



which is identical to the correct one. The last two reactions were rewritten by multiplying the stoichiometric coefficients identified by the algorithm by a factor of 2 which does not change the character of the reaction network.

The present version of the algorithm cannot determine whether a reaction is reversible or not. Consequently, all reactions are initially assumed as irreversible.

In the data at our disposal, the batch time is the same for all runs. We also observe that the final concentration of substance A_2 does not decrease monotonically as the initial temperature of the reaction mixture increases, as it would have been expected if the first reaction were irreversible. Therefore, we have written the first reaction as reversible. Notice that the model obtained is identical to the model used initially to generate the data.

It can then be concluded that the algorithm at hand can determine a simple stoichiometric model, but not necessarily the correct one, from the initial and final concentrations of the constituents. Now the activation energies and pre-exponential factors must be determined.

In order to test the method developed for the estimation of the kinetic parameters (Filippi *et al.*, 1986), additional information was added to that

of Table 1. This consisted of temperature profiles (see Figs 4-6-4-12 of Filippi-Bossy, 1987) of the seven simulated experiments described in Table 1 by their initial and final compositions.

The reaction order with respect to constituent A_1 is assumed as equal to 0.5 in the first reaction and equal to 1 in the third. The reaction order with respect to A_2 is assumed as equal to 1 and the order with respect to A_3 is assumed equal to 0.5 in the reverse path of the first reaction and equal to 2 in the second reaction. The order of A_4 in the reverse path in the first reaction is assumed equal to 0.5 and equal to 1 in the third reaction.

For each of the seven experiments, the temperature profiles have been used to identify the activation energies and the pre-exponential factors for each reaction.

To assess the accuracy of the model predictions we look at the values of the relative difference between the measured, C_j^f , and the calculated concentration, C_{jc}^f , for constituent j in each experiment. This difference was expressed as:

$$e_j = \frac{|C_j^f - C_{jc}^f|}{C_j^f}.$$

As a group the calculated relative differences are rather small. Only four among them are greater than 10%, and these refer to very small concentrations.

Table 2 gives the activation energies and the pre-exponential factors identified from the data of each run separately. Some dispersion of the values of the pre-exponential factor is observed. Table 3 gives the mean and the standard deviation, for the values estimated from each run, for the activation energies and the logarithms of the pre-exponential factors. A dispersion on the order of 15% is observed for each of these parameters, implying that a more accurate, but slower computationally, method should have been involved to identify these parameters from the data of all runs simultaneously.

Table 3. Mean values and standard deviations for the activation energies and the pre-exponential coefficient estimated for the 7 simulated runs

i	E_i (J mol ⁻¹)	$\sigma(E_i)$	$\overline{\log(k_i^0)}$	$\sigma[\log(k_i^0)]$
1 ⁺	55680	11190	9.310	1.786
1 ⁻	81990	11510	13.071	1.619
2	51560	8530	7.473	1.414
3	60010	12870	8.910	2.282

Table 4. Percentage difference between the estimated and initial value of the activation energy

Run No.	1	2	3	4	5	6	7
ΔE_1^+	79	36	51	52	9	3	5
ΔE_1^-	14	4	4	17	7	7	27
ΔE_2	16	65	0	9	41	18	18
ΔE_3	67	84	38	81	5	27	8

It is interesting to compare the identified parameters to those of the initial model used to generate the simulated data.

The values for the activation energies used in the simulation runs are as follows:

$$E_1 = 41421 \text{ J mol}^{-1}, \quad E_{-1} = 41421 \text{ J mol}^{-1},$$

$$E_2 = 82843 \text{ J mol}^{-1}, \quad E_3 = 41421 \text{ J mol}^{-1}.$$

The pre-exponential factors were defined in the model though the use of a reference reaction time $t(i0)$ as follows:

$$t_{i0} = 1/K_{i0},$$

where:

$$K_{10} = k_{10} \exp(-E_1/RT_r) \{C_1^0 + C_2^0\}^{0.5},$$

$$K_{1,-1} = k_{-1,0} \exp(-E_{-1}/RT_r),$$

$$K_{20} = k_{20} \exp(-E_2/RT_r) \{C_1^0 + C_2^0\},$$

$$K_{30} = k_{30} \exp(-E_3/RT_r) \{C_1^0 + C_2^0\}.$$

The values for the t_i parameters used in the first simulated run are:

$$t_{10}^+ = 1, \quad t_{10}^- = 10, \quad t_{20} = 10, \quad t_{30} = 10.$$

The corresponding ones for the other experiments are obtained by substituting in the above equation the appropriate values of the initial concentrations.

Tables 4 and 5 give the relative deviations ΔE_i and Δt_{i0} between the value of these parameters in the simulated runs and those obtained from the identification. There are important differences between the two values which are explained by the large number of parameters identified and the small number of available data. We will later see that this imprecision is not at all detrimental to the overall approach.

6. EXPERIMENTAL

6.1. Introduction

In the preceding sections we presented the individual steps of the proposed algorithm. For each of them simulation results were given. It is now important to examine the performance of the overall approach when it is applied to an experimental test.

Table 5. Percentage difference between the estimated and initial value of the reaction time

Run No.	1	2	3	4	5	6	7
Δt_{10}^+	180	84	62	7	31	27	29
Δt_{10}^-	281	268	15	750	2	48	49
Δt_{20}	23	26	95	12	69	45	14
Δt_{30}	41	40	426	19	13	87	6

The chemical reaction studied was proposed by Rhone-Poulenc, the sponsoring company. Because the specific reaction studied and the results arrived at are of commercial interest to Rhone-Poulenc, only the generic characteristics of the studied reaction will be presented here. The overall reaction involves the partial oxidation of reactant A by an oxidation agent B to produce two main products C and D, of different commercial value. At the same time the reaction produces heavy byproducts that will be denoted as E.

This reaction is of interest because the feed rate of B and the temperature of the reaction mixture have important effects on the amount of products C and D produced and on the progress of the unwanted reactions to byproducts E. These byproducts are difficult to analyze and their quantity can only be estimated by an approximate total material balance. Very little is known about the exact mechanism of the reaction.

The choice of this reaction was essentially motivated by its physical-chemical properties. In particular one wishes to maximize the production of products C and D over byproduct E. Of equal importance is the ability to selectively increase or decrease the amount of C over that of D. Although the experimental conditions under which this reaction was studied are not identical to the industrial ones, the results obtained are of substantial practical interest to Rhone-Poulenc, which performs the reaction industrially.

The chemical transformation is quite exothermic. It evolves on the order of 60 kcal mol⁻¹ of reactant converted. A preliminary overall reaction rate model was furnished by Rhone-Poulenc, but no values of the kinetic constants and the corresponding activation energies were made available. This model was given only as an illustrative example, and is not used as a constraint for the performance of the algorithm.

Depending on production schedules different catalysts favor the reaction to one or the other of the main products C or D. Our approach here was different. The catalyst used was fixed and we acted on the temperature of the reaction mixture and the feed rate of reactant B to affect the desired mix of products.

6.2. Analytical techniques

Appropriate analytical measurements were used to measure the composition of the reactant A and B and products C and D at the end of the batch.

In particular the amount of reactant A is known by weighing its storage tank before and after the reactor is charged. Since it is in large excess we do not measure A at the end of the batch. The amount of reactant B fed in the reactor is calculated by the flowrate used and the feeding time. The amount of reactant B that is left at the end of the batch is measured by wet chemistry methods. On the other hand, the amount of products C and D produced at the end of the batch is measured by high-pressure liquid chromatography.

6.3. The experimental setup

The batch reactor facility consists of a 2 l vessel (Fig. 1) having a jacket around it so that the thermal losses are minimized. At the same time the reactor has a cooling coil that is introduced inside the reaction mixture and which is used to control the reactor temperature by heat removal. The amount of heat removed is proportional to the flowrate used and to the temperature difference between inlet and outlet coil temperatures, which are measured.

The stirring system used is formed by a stainless steel axle and a stainless-steel six-blade helix covered with Teflon. The system is guided by ball bearings.

The feed system for reactant B consists of a Teflon capillary tube with an i.d. of 0.8 mm pierced by a stainless-steel tube. Injection is made near the stirrer, which allows excellent incorporation of the feed stream into the reaction mixture.

A thermal bath (Thermomix 1441 by Braun) was used to circulate constant temperature cooling

fluid in the jacket in order to establish the desired reactor temperature and to reduce the heating losses of the reactor to the ambient environment. The fluid used was ethylene glycol. A Masterflex pump was used to circulate cold water in a cooling coil immersed inside the reactor. The pump characteristics are linear in the flow range in which it was used.

A burette (electroburette by Tacussel) was used to feed the reactor with reactant B. It is controllable by voltage, which acts on the frequency of the stepper motor driving the piston of the syringe. We often noted a difference of 8% between the desired and achieved flowrate of reactant B. This alters the yield of the desired product from that expected from the calculations. To compensate for this inaccuracy, the reactant B flowrate was controlled manually in the optimization experiments.

Platinum probes, Pt 100, were used to measure the reactor temperature at two different locations, their resistance varying linearly with the temperature of the surroundings in which they are immersed. The temperature of the reaction mixture was taken equal

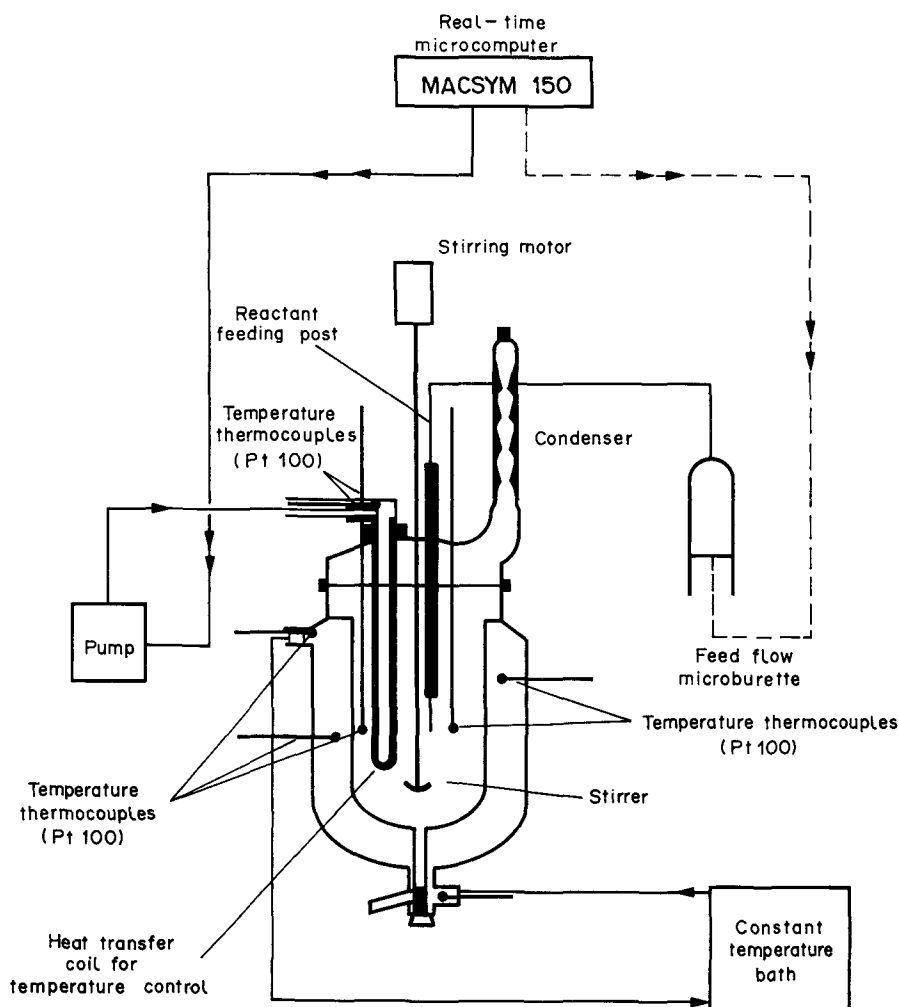


Fig. 1. Schematic representation of the experimental reactor.

to the average of the two measurements. Other temperature probes measured temperature at two inside locations and at the inlet and outlet of the jacket and at the inlet and outlet of the cooling coil. These measurements will be used to write the energy balance of the reactor.

Analog to digital converters were used to convert the voltage signals of the probes to a digital number to be sent to the microcomputer. A Macsym 150 microcomputer from Analog Devices Inc. was used to perform the data acquisition and control of the process. It is equipped with an analog input card (AIM 100) for data acquisition and an analog output card (AOT 100) to control the pump and burette. The control of the temperature of the reaction mixture was performed by a proportional-integral controller (PI) by use of the cooling coil flowrate as the manipulated variable.

6.4. Characteristics of the experiments

All the experiments were carried out with the following characteristics:

- The mass of reactant A introduced is of the order of 109 units of weight. To determine the amount of reactant used, the bottle of reactant A was weighed before and after the filling of the reactor. Thus we know exactly the mass of reactant A introduced, but obviously it is impossible to have always exactly 109 units. Operating in this manner one aims to avoid contact with the reactant as much as possible, because it is dangerous and because it solidifies at ambient temperatures.
- Two additional chemicals, acting as catalysts, are introduced. The first in the amount of 0.11 units and the second in the amount of 0.14 units.
- Once reactant A is introduced in the reactor and it attains the desired temperature, the experiment begins. At that time the feed of the second reactant and the control of the reaction temperature is initiated.
- A sample of the reaction mixture is taken at the end of the experiment while the agitator is still working.
- The concentrations of reactant B and products C and D in the final reactor mixture are analyzed by use of the techniques described above. The quantity of reactant A remaining and the amount of heavy products E are unknown. Reactant A is in excess and this is why it is not accounted for in the reaction scheme we will propose next.
- There is no simple technique to identify and measure the heavy products. Only an estimation of their quantity is used. From an understanding of the chemistry involved we decided to use the following approximate method. The difference between the number of moles of B consumed and the number of moles of C and D produced is taken as equal to the number of heavy byproduct mol equivalents produced.

7. RESULTS AND DISCUSSION

7.1. Optimization index

In this part we describe the steps we followed to apply the developed tendency modeling and control strategy developed to the experimental problem described above. Of particular interest is to detail: (i) the criterion chosen to optimize the batch reactor with; (ii) the experiments performed to initialize the model; (iii) the method used to identify a first stoichiometric model; and (vi) the various optimization steps.

The optimization index J to be minimized represents a technical-economic criterion expressing the goal of maximizing the production of product C in the smallest time possible. It consists of two terms.

The first term is the proportional cost (PC) of the operation. It depends on the amount of product C produced and the quantity of reactant B introduced. To minimize this cost, it is necessary to produce the maximum amount of C and the minimum amount of E while introducing the minimum amount of B. We thus need to maximize x_C while minimizing the ratio x_E/x_C . The cost to be minimized can be expressed as proportional to:

$$\frac{1 + \gamma x_E}{x_C},$$

where x_C and x_E are equal to N_C^f/N_B^i and N_E^f/N_B^i , respectively and γ is a factor expressing the relative weight of the two terms.

The other term is called the nonproportional or fixed cost of operation. It takes into account personal and maintenance expenses. It depends on the yield to product C, x_C and the duration of the operation t_B . To minimize this cost, it is necessary to produce the maximum amount of C while introducing a minimum amount of B and performing the reaction in a minimum time. The term in the cost to be minimized can be expressed as proportional to:

$$\frac{\beta t_B}{x_C},$$

where β is a weighting factor. The overall criterion we seek to minimize is, therefore, the following:

$$J = \frac{1 + \beta t_B + \gamma x_E}{x_C}.$$

The optimization is done with the following values: $\beta = 174$ dimensionless units and $\gamma = 1$.

Note that these values of the parameters imply that the duration of the run is more important than the quantity of byproduct E formed.

7.2. Initial experiments

In order to initialize the model building part of the optimization algorithm, six experiments were performed under different conditions. An initial not very accurate method of reactor temperature control did not permit the realization of transient temperature profiles. Consequently, the experiments were carried

Table 6. Data describing the six initial experiments used for the estimation of model parameters

Run	Temperature	N_B^i/N_A	Feed time	Batch time	N_B^f/N_A^0	N_C^f/N_A^0	N_D^f/N_A^0	N_E^f/N_A^0	J index
1	1.2465	5.645E-02	222.2	355.6	6.1554E-04	9.3938E-02	2.6366E-02	2.0072E-02	20.16
2	1.2326	5.504E-02	222.2	355.6	1.8077E-03	1.2237E-02	2.7764E-02	1.3232E-02	14.57
3	1.2674	5.833E-02	222.2	355.6	1.3458E-04	1.0141E-02	2.6841E-02	2.1216E-02	19.31
4	1.2151	5.887E-02	222.2	355.6	2.1460E-03	1.5217E-02	2.7931E-02	1.3589E-02	12.48
5	1.1855	5.824E-02	202.6	355.6	5.8366E-03	1.3149E-02	2.5968E-02	1.3287E-02	14.30
6	1.1890	5.399E-02	200.7	355.6	4.9076E-03	1.2975E-02	2.2354E-02	1.3755E-02	13.54

out isothermally at different temperatures T . Table 6 reviews the experimental conditions as well as the principal results obtained for each run. The data are presented in dimensional form. Temperature is made dimensionless by dividing its value in K by the value also in K of a reference temperature close to the ambient temperature.

Since the mass of reactant A introduced into the reactor was not always constant, the number of moles of each of the other reactants and products is given in reference to the initial number of moles of reactant A which is always in excess. The dimensionless concentration change for reactant B is defined as follows:

$$Y_B = \frac{N_B^f - N_B^i}{N_A^0}$$

For the products C, D and E we also have:

$$Y_C = N_C^f/N_A^0,$$

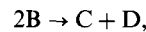
$$Y_D = N_D^f/N_A^0$$

and

$$Y_E = N_E^f/N_A^0.$$

The values of the Y variables can be easily obtained from Table 6.

The stoichiometric model derived by the algorithm is:



7.3. Batch optimization

The value of the technical-economical criterion J was calculated for each of the six preliminary runs. The best value of this criterion is obtained for run 4, so the optimization will be initiated by assuming run 4 as the starting point.

By use of the model and the optimization strategy we will be calculating desired optimal runs. These predicted runs might be denoted by the letter O and an appropriate number. When such a strategy is implemented the reactor might not behave as it was predicted by the tentative model. Thus a different

symbol and number might be used to denote the actual run.

In order to simplify the first experimental test of the algorithm, it was decided to restrict the search domain of optimization. The following constraints were then introduced:

The temperature of the reactor is considered constant and fixed. Furthermore, the ratio of the total moles of B introduced in the reactor over the moles of A charged in the reactor at time zero is kept constant.

Consequently the optimization will be performed by varying the feed time (t_F) for reactant B. Note that since the total amount of B is fixed, an increase in the feed time (t_F) will result in a decrease of the feed flowrate of B. The sensitivity to the batch time (t_B) is also examined. For this variable the changes are not calculated by the algorithm but rather imposed by the user.

From the final composition and the temperature profile of experiment 4, we have determined the activation energies and the pre-exponential factors of the stoichiometric model previously identified. The reaction order of reactant B in the first reaction is taken to be equal to 2. The order of the reaction in the second reaction is taken to be 1. The orders, therefore, are assumed equal to the apparent stoichiometric coefficients.

For a fixed ratio of moles of B over the moles of A used, and equal to 0.05887 and a batch time equal to 347.8 dimensionless units, we obtained the optimum constant feed rate and the feed time needed to introduce in the reactor the amount of reactant B.

The first optimized batch run was performed and the collected data were used for the re-identification of the activation energies and pre-exponential factors. The new kinetic model was then used to find the optimum feed duration of reactant B for the same total amount but for a batch time reduced to 275.36 dimensionless units.

The second optimized batch was performed and the third optimized batch was prepared making use of the same principle. Table 7 below summarizes the results obtained for the three successive optimize

Table 7. Experimental data of the optimized runs indicating improvement in the performance index

Run No.	Batch time	Optimal feed time	Obtained feed time	Time error (%)	x_C	x_E	Y_C/Y_D	J	Improvement (%)
E ₄	347.83		217.39		0.2585	0.2308	0.5448	12.48	
O1	347.83	323.19	313.04	-3.14	0.2800	0.1531	0.5951	11.26	9.78
O2	275.36	242.75	251.74	3.70	0.2623	0.1670	0.5829	10.48	6.93
O3	253.62	229.71	228.48	-0.54	0.2891	0.2154	0.6560	9.23	11.93

Table 8. Difference in the estimated kinetic constants for the two assumed reaction orders

Dimensionless kinetic parameters	First reaction order = 2	First reaction order = 1
E_1/RT_r	7.81	16.63
$k_1 \times \text{ref time}$	826.90	5325.70
E_2/RT_r	30.41	81.46
$k_2 \times \text{ref time}$	1.39E + 08	1.36E + 26

ations. The notation of O1, O2, O3 is used to denote the optimized experimental runs.

Note that there is a true improvement in the criterion for each step of the optimization. Between the two first runs, the batch time remained the same, and optimization with respect to the feed rate and thus the feeding time improved the criterion by 10.8%. In the two subsequent runs, the decrease in the batch time strongly contributed to an improvement in the criterion. The temperature profile of the third optimization presents a nonnegligible peak. This resulted from a temporary malfunction of the regulating pump. On first sight one might believe that it contributed to the improvement in the criterion, but in reality we believe that it contributed very little. When this experiment was rerun with the pump functioning correctly, without the peak in temperature, the criterion obtained was equal to 9.185. One can, therefore, conclude that the peak had no influence on the observed improvement.

7.4. Influence of assumed kinetics

The initially assumed order of the approximate reaction was equal to the stoichiometric coefficients of the reactions. In particular the first reaction was assumed as second-order and the second reaction was

assumed to be a first-order reaction. To study the effect of the reaction order on the optimization results of the overall algorithm, the assumed reaction order of the first reaction was changed to first. Run 4 was used as the base case here as it was done before. The temperature was kept constant at 1.213 dimensionless temperature units and the batch time was equal to 347.8 dimensionless units. The ratio of the moles of B fed to the reactor over the moles of A initially charged in the reactor remained equal to its value at run 4.

With the use of the previously collected data, runs 1–6, the kinetic constants and the activation energies were estimated in both cases where the first reaction was assumed to be first- or second-order. The estimated values of the kinetic constants are reported in Table 8. The batch optimization results are reported in Table 9. In this table we present the expected value of the performance index after the optimization calculation was concluded and the optimization index achieved after the next experiment was performed. We observe that the experimental values of J were always slightly larger than expected from the optimization calculations. Run E indicates that this change in reaction order does not result in an improvement of the performance index. Consequently, we assumed that there was no apparent benefit to motivate the change of the first reaction order to first.

7.5. Influence of the number of reactions

To examine the effect of the number of reactions, the tendency model was allowed to have an additional reaction. With the help of the total of 17 experimental runs available, summarized in Table 10,

Table 9. Sensitivity of experimental results on the assumed kinetics

Run No.	Temperature	Batch time	Optimum feed time	Expected J	Achieved feed time	x_C	x_E	Y_C/Y_D	Achieved J	Improvement (%)
E ₄	1.21	347.83			217.39	0.2585	0.2308	0.5448	12.48	
O ₄	1.21	347.83	323.19	10.55	313.04	0.2800	0.1531	0.5951	11.26	9.78
O ₅	1.21	347.83	290.51	11.54	297.10	0.2442	0.1978	0.5143	13.70	-21.67

Note: Run O₄ with assumed second-order kinetics on first reaction.

Run O₅ with assumed first order kinetics on first reaction.

Table 10. Summary of all experimental runs used to estimate the three reaction models

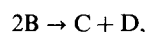
Run No.	N_B/N_A	Batch time	Feed time	Temperature	Y_C	Y_D	Y_E	N'_B/N'_A	$(N'_B - N'_B)/N'_A$
E ₁	5.64E-02	347.83	217.39	1.24	9.390E-03	2.637E-02	2.007E-02	8.200E-04	-5.583E-02
E ₂	5.50E-02	347.83	217.39	1.23	1.224E-02	2.776E-02	1.383E-02	1.810E-03	-5.323E-02
E ₃	5.83E-02	347.83	217.39	1.27	1.014E-02	2.684E-02	2.122E-02	1.300E-04	-5.820E-02
E ₄	5.89E-02	347.83	217.39	1.21	1.522E-02	2.793E-02	1.359E-02	2.150E-03	-5.672E-02
E ₅	5.82E-02	347.83	198.19	1.19	1.315E-02	2.597E-02	1.329E-02	5.840E-03	-5.240E-02
E ₆	5.56E-02	347.83	132.75	1.19	1.481E-02	2.498E-02	1.069E-02	5.080E-03	-5.047E-02
E ₇	5.40E-02	347.83	196.38	1.19	1.298E-02	2.235E-02	1.375E-02	4.910E-03	-4.908E-02
E ₈	6.27E-02	347.83	298.55	1.19	1.437E-02	2.491E-02	1.669E-02	6.770E-03	-5.597E-02
E ₉	6.06E-02	347.83	323.19	1.21	1.605E-02	2.763E-02	1.306E-02	3.860E-03	-5.674E-02
E ₁₀	6.49E-02	275.36	255.80	1.21	1.575E-02	2.593E-02	1.589E-02	7.120E-03	-5.780E-02
E ₁₁	7.02E-02	253.62	237.68	1.21	1.502E-02	2.628E-02	1.739E-02	1.147E-02	-5.869E-02
E ₁₂	6.23E-02	347.83	323.19	1.21	1.649E-02	2.798E-02	1.247E-02	5.480E-03	-5.685E-02
E ₁₃	6.09E-02	276.30	273.91	1.21	1.600E-02	2.533E-02	1.377E-02	5.790E-03	-5.510E-02
E ₁₄	5.89E-02	347.83	313.04	1.21	1.649E-02	2.771E-02	9.020E-03	5.670E-03	-5.322E-02
E ₁₅	5.89E-02	275.36	251.74	1.21	1.845E-02	2.680E-02	9.840E-03	7.100E-03	-5.179E-02
E ₁₆	5.89E-02	253.62	228.48	1.21	1.703E-02	2.596E-02	1.269E-02	3.220E-03	-5.567E-02
E ₁₇	6.44E-02	217.39	141.30	1.19	1.807E-02	2.657E-02	1.494E-02	7.870E-03	-5.559E-02

Table 11. Batch runs optimized with the three reaction model. Run O6 is the expected one from optimization, run O7 is the obtained one experimentally

Run No.	Batch time	Feed time	Temperature	Y_C	Y_D	Y_E	Y'_B	Y_C/Y_D	J
O3	253.62	229.71	1.22	1.703E-02	2.596E-02	1.269E-02	3.22E-03	0.6560	9.23
O6	253.52	232.61	1.22	2.035E-02	2.528E-02	9.600E-03	3.65E-03	0.8050	7.58
O7	253.62	240.36	1.22	1.456E-02	2.461E-02	1.392E-02	5.80E-03	0.5916	10.90

we estimated the stoichiometry and the kinetic parameters of the new tendency model for the reaction.

The reaction network obtained is:



The assumed reaction orders are second, first and first, respectively. The sequence of the optimization runs performed with the previous two-reaction model was repeated with the three-reaction model. Run 3 of Table 11 was used as a base case.

The results are reported in Table 11. The results are a bit disappointing from the experimental point of view because they did not produce the expected performance improvement for the reactor. At the same time the encouraging observation is that the model calculations indicated that there is a smaller value possible for the performance index.

The concerns raised here about the experimental and algorithm parts of the problem are presently examined in detail. On the experimental side, steps are taken to more effectively stop the reaction in the measurement sample once it is withdrawn from the reactor. This is crucial so that the composition measurement obtained represents a state of the reactor more accurately. This correction may very well account for the systematic undesirable difference between the projected value of the performance index and the experimentally obtained one. Additionally, the time varying feed rate of reactant B and time varying temperature profiles are also presently considered. Progress in these areas will be reported in future communications.

8. CONCLUSIONS

We believe that the proposed novel method for the involvement of tendency models in the optimization and control of batch reactors has substantial promise in becoming a very useful tool in a research area of increased economical importance. This communication has demonstrated very successful experimental results related to an important industrial process. However, several important questions remain open and need additional work. For example, we assumed the order of the reaction rates and we have shown that this choice has an important effect on the success of the algorithm. More systematic methods need to be employed for the identification of the correct

reaction order. Two additional open areas relate to the assumption of perfect mixing and the design of the initial and follow up experiments for the statistically-accurate estimation of the model parameters. Hopefully our excitement about the proposed approach will be shared by others who will decide to also contribute to the problem.

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