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PROCESS CONTROL IN THE EDUCATION OF ORGANIC CHEMICAL TECHNOLOGY

Laboratory practices

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RESUMEN

Las prácticas de laboratorio demuestran la importancia de los modernos procesos de control en las tecnologías de química orgánica. Se necesitaba desarrollar un sistema que une las ventajas de los calorímetros de reacción con las de modelo de los reactores controladas de la industria. El diseño de hardware y de software se permite trasladar el programa desarrollado en el laboratorio para el nivel industrial. El algoritmo general para las reacciones de diazotación y clormetilación es aplicado para el sintésis del cloruro de benzo-diazonio y cloruro de dietoxi-benzil en las prácticas de laboratorio.

Palabras claves: Química orgánica asistida por computador, Equipo de laboratorio, Enseñanza de proceso computarizado de control, Química farmacéutica

ABSTRACT

Laboratory practices for demonstrating the importance of advanced process control methods in the organic chemical technologies have been elaborated. It required the development of a system that integrates the advantages of a reaction calorimeter and a model system of industrial controlled reactors. The hardware and software configuration support the transfer of elaborated control programs of reactions from laboratory level to the industrial technology. General control algorithms of diazotization and chloromethylation can be successfully applied in laboratory practices for forming benzenediazonium chloride and diethoxybenzyl chloride respectively.

Key words: Computer assisted organic chemistry, Laboratory equipment, Graduate education, Pharmaceuticals

The digital process control of batch reactors is widely used in industrial organic chemistry, especially in pharmaceutical plants (Cezerac et al., 1995). The higher level utilization of the advantages offered by these reactors, however, is hindered by the lack of knowledge of process control possibilities among the research and development engineers (Molnár, 1995). They elaborate the new technologies using the conventional laboratory tools that are not appropriate for modeling the wider operating flexibility of controlled industrial systems. The need for organic chemists practiced in the modern methods of batch process control is quite apparent.

In order to answer this challenge, organic chemical education has to demonstrate the advantages of laboratory process control for students, using reactors of higher flexibility than the conventional reactors or reaction calorimeters. Such systems could be used for education of organic chemical technology on graduate level and for research on postgraduate (Ph.D.) level. Multi-purpose hardware elements and hierarchic structure of software are the basis of such systems.

The lower level of hierarchy of the controller program allows step by step programming, while on the higher level of hierarchic structure, the development of a 'library' of pre-programmed basic operations (**BO**s) is recommended (Molnár, 1995, Massey et al., 1990, Kendall et al., 1995). In order to avoid the confusing high number of individual controller algorithms for similar organic chemical reactions, the inclusion of an even higher level into the hierarchic structure, offering general programs for typical groups of reactions, has been proposed recently (Csontos et al., 1999).

This approach meets the point of view of organic chemists, who consider the typical groups of reactions as ***unit (or basic) processes*** (Groggins et al., 1958). Most organic chemical reactions have been already classified this way such as alkylation, esterification, diazotization, etc. Our aim was to establish an intelligent system containing knowledge about these unit processes built in the software and to teach its interactive use for the students.

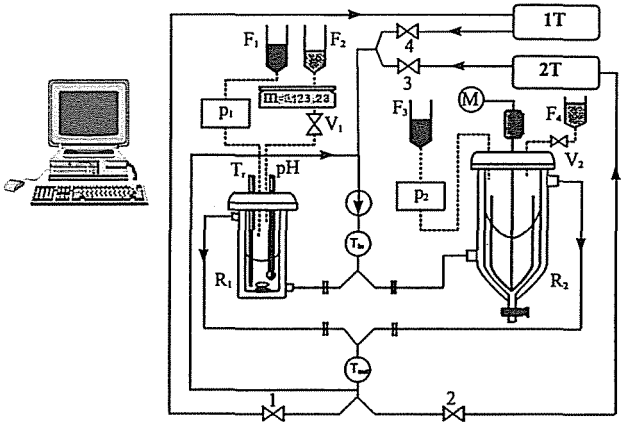
In this paper the basic hardware and software developments are discussed only briefly, further details are given in recent papers (Csontos et al., 1999, Csontos et al., 1998). Examples for using the calorimeter operating mode and simulation are given for diazotization, and chloromethylation unit processes.

EXPERIMENTAL

The computer-assisted laboratory system, as it is used for teaching organic chemical practices and for research, is shown in Figure 1.

The software, developed at the department, is an interactive, menu-driven program allowing to perform nearly all type of chemical reactions. The general structure of algorithms created by the program is shown in Figure 2.

The structure of a basic (master) algorithm is divided to three levels: *Control Instructions* can be given at *Control Step* level. *Control Steps* are operating parallel, while the *Control Phases* (including the basic operations (**BO**s)) follow each other in sequential order. A *Control Part* consist of several *Control Phases*. This level includes the knowledge about the *basic* (unit) *processes* (**BP**s) of organic chemical techno-



1T	*Cold thermostat (min. -13° C*
2T	*Warm thermostat (max. -120° C*
T_R	*Reactor thermometer*
T_m	*Input thermometer*
T_{out}	*Output thermometer*
m	*Digital balance*
pH	*PH-meter*
p1	*Peristaltic pump 1*
p2	*Peristaltic pump 2*
V1,V2	*Magnetic valves*
F1, F2, F3, F4	*Feeders*
1, 2, 3, 4	*Heat-exchanger circuit valve*
M	*Stirrer torque-meter*
⊣⊢	*Flow on/off switch*

Figure 1
Reactors (R1, R2) and auxiliary tools

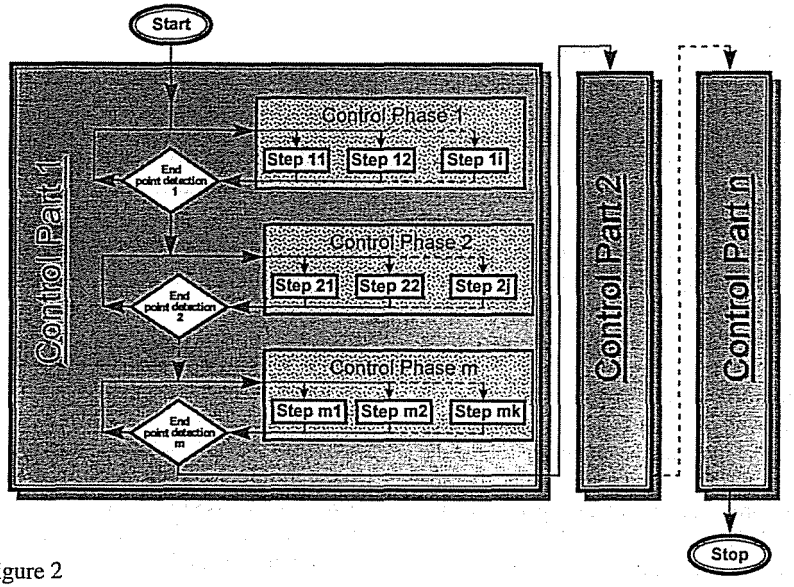


Figure 2
The structure of algorithms

logies as it is described in the introduction. **BP**s are stored in a program library making possible the elaboration of general control algorithms. This upper level includes the *basic operations* (**BO**s), and *Control Steps* characteristic to each typical group of organic reactions, as well as their main parameters. Only the values of these main parameters (temperatures, pH, etc.) are needed to define at formation of the control algorithm of a concrete reaction.

MATERIALS

In diazotization process: aniline distilled, Bp: 184°C; 37 % aqueous hydrochloric acid solution; 30 % aqueous sodium nitrite.

In chloromethylation process: 1,2-dimethoxybenzene, 1,2-diethoxybenzene: colorless materials with characteristic odor, melting temp.: 22.5°C and 43°C respectively; 37 % aqueous hydrochloric acid solution; paraformaldehyde: white powder with a formaldehyde odor, soluble in warm water with the parallel formation of formaldehyde; solvent: benzene; sterogenol: cationic surfactant, light brown powder.

RESULTS AND DISCUSSION

Educational application of the system created

The system constructed is applied for educational purposes at two levels:

- for research work of Ph.D. students and
- for graduate students in chemical and chemical engineering education.

In the laboratory practices of a subject, demonstrating the main unit processes of chemical technologies, the graduate students get acquainted with the general control algorithms of unit chemical processes and with their application to concrete reactions. Two of these unit processes, diazotization and chloromethylation, are shown below as examples.

Practice I: Diazotization

General characteristics of the diazotization unit process:

A diazotization process is widely used for the production of intermediate products of phar-

maceuticals and dyes. It is generally performed at low temperature and in acidic medium. The success of the reaction is highly temperature and pH dependent. The reproducibility of the color of a dye can be essentially improved by application of computer control.

It is of great importance in this process to determine the end of the reaction accurately in order to avoid the feeding of extra HNO_2 that would lead to evolution of poisonous NO_x gases and deterioration of product quality.

A model aided simulation program has been developed and applied for finding a control algorithm that includes the knowledge about the diazotization. (The equations applied for the simulation are given in another papers (Csontos et al., 1998, Szeifert et al., 1995)). The control is carried out by using the mathematical model of the system. The program adjusts the reactor temperature to the required value by

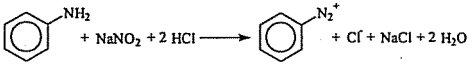
- manipulating the feed rate of $NaNO_2$ solution and using the full cooling capacity when the process is far from the end point and by
- manipulating the flow rate of the cooling water when the end point (according to the calculations) is approached.

This new control algorithm of diazotization is established as follows:

The general control algorithm of diazotization unit process:

1 BO1 Preparations (set of balance, stirrer)
2 BO2 Feeding at constant rate (amine)
3 BO3 Feeding as a function of pH (acid)
4 BO8 Temp. Manipulation (quickest cooling down) + feeding as a function of pH (acid)
5 BO5 Feeding as a function of temperature ($NaNO_2$) + feeding as a function of pH (acid)
6 BO7 Temperature manipulation (total cooling) + feeding as a function of temperature ($NaNO_2$) + feeding as a function of pH (acid)
7 BO8 Temp. Manipulation (keep the temperature) + feeding at constant rate ($NaNO_2$) + feeding as a function of pH (acid)
8 BO20 Unload and cleaning of the reactor

An example of this unit process is the diazotization of aniline:



The algorithm particularized to aniline means that the acid is HCl, the pH value 1.5, the reactor is cooled below 5∞C, the temperature set by feeding of $NaNO_2$ solution. The pH and the temperature control are performed in parallel (BO5). The curves of two runs of diazotization are compared in Figure 3. The first is a conventional method (1) and it is compared to the new procedure requiring shorter time (2).

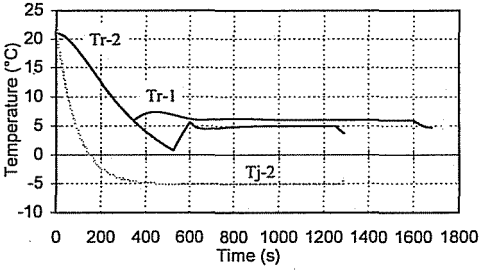


Figure 3
Run of diazotization (Tr: temperature of reactor, Tj: temperature of jacket)

1: Temperature control through the jacket (reference curve, set value = 6 °C)
2: Model aided temperature control (set value = 5 °C)

One of the advantages of the new control method is the much shorter duration of the process, due to the quick feeding of $NaNO_2$ at the beginning. This is reflected by the sharp peak on the heat flow curve in Figure 4. Another important advantage is a sensitive method for detection of the end of the reaction: when 80% of the reaction is completed the feeding is set to the current

value and the temperature is controlled through the jacket (BO8). The lack of heat of reaction at the end results in sharp increase of the jacket temperature that can be used as a signal for termination. In this way the evolution of NO_x gases can be avoided (see in Figure 4).

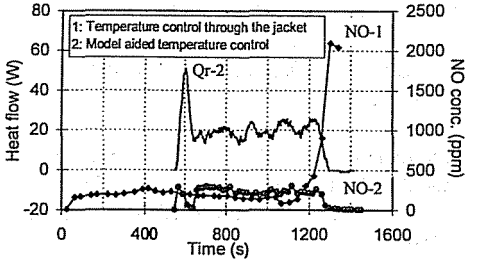


Figure 4
The heat flow (Qr) and NO_x emission at diazotization

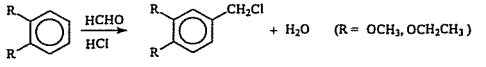
It means that the use of model aided simulation in the unit process of diazotization result in an important advantage in worker and environment protection.

Practice II: Chloromethylation

General characteristics of the chloromethylation unit process:

Chloromethylation is the unit process for replacing a H atom with a chloromethyl group. It is performed in most cases with formaldehyde in acidic medium. The activity of a substrate at chloromethylation depends on the type and number of substituents of the aromatic compound. It determines the temperature and duration of the reaction. These are the variables of the general control algorithm of chloromethylation.

The preparations of dialkoxybenzyl chlorides are of great importance in the pharmaceutical industry.



The reaction takes place in heterogeneous phases, so an emulgeator (appropriate surfactant) is applied in order to achieve intimate interaction between the reaction partners. The preparation of HCl-paraformaldehyde, emulgeator (surfactant) and neutralizing solutions is performed at the beginning of process and then the reaction takes place in a controlled reactor according to the following general process:

The general control algorithm of chloromethylation unit process:

1 BO1 Preparations (set of balance, stirrer)
2 BO2 Feeding at constant rate (substrate, solvent, emulgeator)
3 BO8 Temperature manipulation (controlled heating)
+ feeding at constant rate (HCl solution of paraformaldehyde)
4 BO6 Temperature. Manipulation (keep the temperature)
5 BO6 Temperature. Manipulation (cooling)
6 BO12 Separation of phases
7 BO13 Extraction
8 BO12 Separation of phases
9 BO20 Unload and washing of the reactor

Possible variations: BO10 - Reflux (in special case, when higher temperature is required), BO12 and BO13 - repeated required times to achieve neutral pH.

An example of this unit process is the chloromethylation of diethoxybenzene:

The general control algorithm is applied for this specific case by entering the relating temperatures, times, c_p and enthalpy (for calculating the time of 4th Control Phase (BO6)). A simulation program has been applied for describing the run of reaction and calculating of the concentration of components. (The equations applied for the simulation are given in another papers (Csontos et al., 1998, Stoessel, 1997)). The measured and simulated curves of a chloromethylation reaction are given in Figure 5.

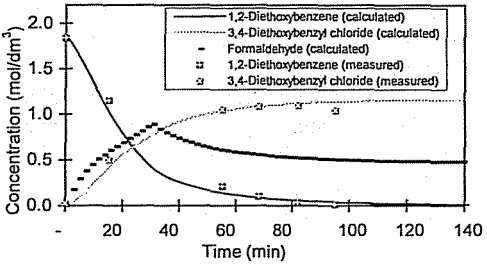


Figure 5
Run of chloromethylation reaction on laboratory scale

The same simulation program can be applied for calculating the curves for industrial reactors. For this purpose the characteristics of the industrial equipment are introduced into the program and the general control algorithm can be specialized for industrial scale by the way of simulation.

CONCLUSIONS

Education of students of organic chemistry being aware of the advantages and possibilities of process control in required the development of a computer controlled reactor that is flexible enough for continuous modification according to the different chemical problems. The flexible, interactive software of the system gave us the possibility to elaborate general algorithms for the main unit processes of organic chemistry (diazotization, chloromethylation etc.). Quantitative determination of the material and heat balance of the reactions have been used for the simulation of the above-mentioned processes, showing the principles of model aided batch process control for the students. Furthermore, the accurately measured heat balances are suitable input data of the prediction or planning of larger scale experiments and shed light on the special rules of scale up procedures, one of the most important aspects of education in organic chemical technology.

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