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CALORIMETRIC MONITORING OF INDUSTRIAL CHEMICAL PROCESSES

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ABSTRACT

Enthalpimetric methods used in chemical production and in process development are reviewed.

On-line methods are applied to concentration analysis, to safety monitoring and to the control of reaction progress.

The most promising applications of thermal methods are found in process development: enthalpimetric process investigation on the bench scale. Design principles for "process calorimeters" are outlined and applications to a pressure reaction, to a highly unstable radical reaction and to fermentations are shown.

1. INTRODUCTION

Thermometric and enthalpimetric methods have been applied to process control and process optimization for many decades.

The author is active in process development for fine chemicals. With this paper, he hopes to promote applications of thermal analysis which are somewhat neglected by thermal analysts and only occasionally utilized by chemical reaction engineers.

The contribution is confined to enthalpimetric methods in or for chemical production processes; thermal methods based on temperature/concentration-equilibria (e.g. dew point instruments) are not considered. Some literature references are given. However, a thorough literature review is not intended.

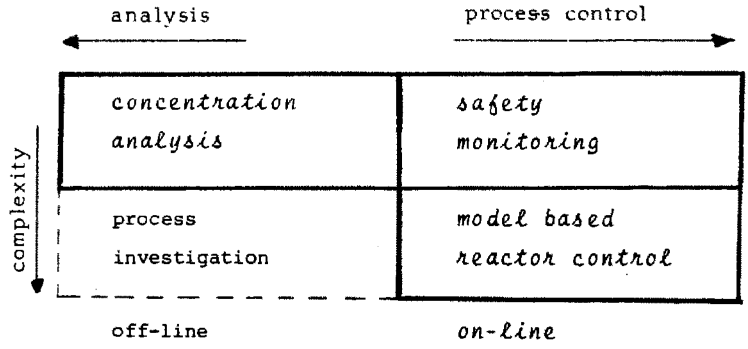

Fig. 1. Enthalpimetric process monitoring

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Applications of enthalpimetric methods to chemical process problems (Fig.1) may be structured according to goals

- analysis (acquisition of information)
- process control (corrective action based on acquired information)

and according to the complexity of the information or performance to be obtained.

On-line methods have been described for

- concentration analysis
- safety monitoring
- reactor control (determination of the extent of reaction based on heat release)

Most efforts on enthalpimetric methods in the process field have been devoted to the design and application of calorimeters for process investigation (simulating process conditions off-line on the bench scale).

2. ON-LINE METHODS FOR CONCENTRATION ANALYSIS

2.1 Liquid process streams

For continuous analysis, the design principle of classical laboratory flow calorimeters may be used (Fig. 2a*).

A side stream from the process and excess reagent (both metered and thermally conditioned) are mixed and reacted adiabatically. The adiabatic temperature rise ΔT is a measure of the concentration to be determined. The reagent should be specific for the component to be analyzed and should react fast.

The method looks simple (compared to spectrometric and chromatographic methods) and thermometric analyzers are available from many instrument suppliers. Also, there is considerable need for on-line analysis in liquid process-streams (e.g. to control the stoichiometric ratio of reaction components). However, few on-line applications have been published. Russian authors (ref.1) described the control of azo-coupling reactions. Scandinavian authors (ref.2) reported on alcali determination and on calorimetric control of a ClO_2-generator, both applied in the pulp industry.

The hesitation to apply flow calorimeters is probably due to handling problems. Plugging is a major problem with small undiluted process streams.

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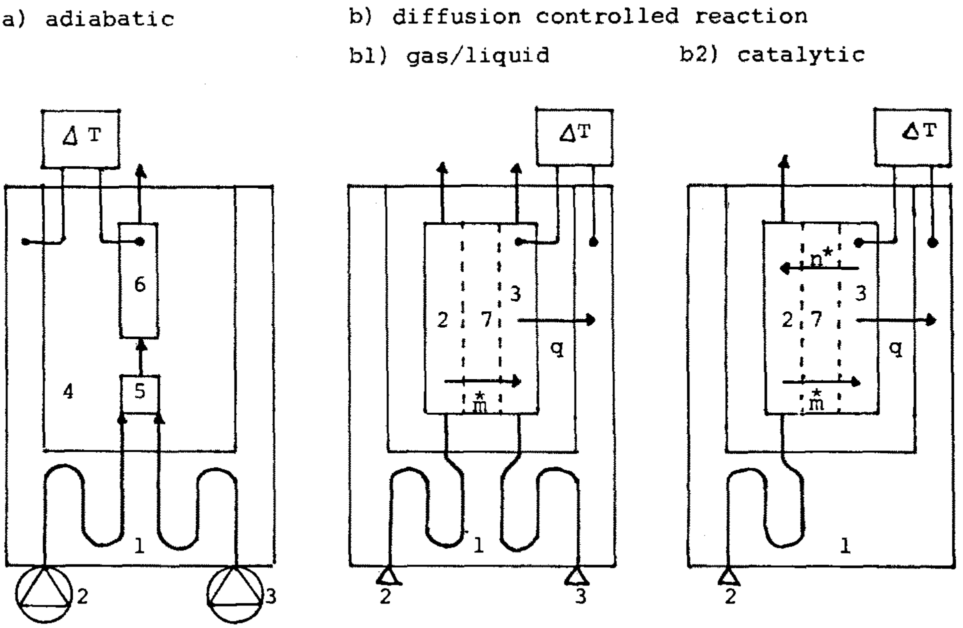
*) For the sake of simplicity, a "single cell" scheme is shown. In practice, differential designs are used.



Symbols:

$\overset{*}{m}$, $\overset{*}{n}$ diffusion flux of reactants and products

q heat flux

1 temperature conditioning system
2 side stream from process
3 liquid reagent (or catalyst)
4 thermal insulator
5 mixing cell
6 adiabatic reactor
7 resistance to mass diffusion

Fig. 2. Enthalpimetric continuous flow concentration analyzers

Therefore, batch thermometric titration might be the method of choice. It is quite easy to separate a sample from the main process stream (Fig.3) and to thermo-titrate it within seconds, e.g. using the "overflow method" described by Becker (ref.3). No reference on process applications of this method is known to the author.

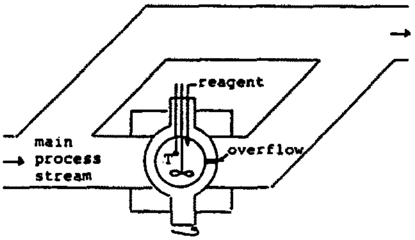


Fig. 3. In-line batch thermotitrator

2.2 Gaseous process streams

Adiabatic temperature rise methods, as described above for liquids, may also be applied to analyse gases. If the reaction is fast and if the reaction zone can be confined to a very small well defined space, then diffusion based methods can be used. They require no (or at least much less accurate) metering of the process stream and of the reagent (Fig.2b)

Recently, a moisture analyser using this operating principle has been anounced (ref.4). It is based on the heat of dilution of H_2O in concentrated H_2SO_4.

Most "combustible gas analyzers" (explosimeters) are based on diffusion controlled reaction. In this case, there is no reagent. The reactants (air + combustible gas) enter the analyzer well mixed, and the reaction zone is the surface of a catalytic wire (Fig.2c).

In both cases (moisture analyser, explosimeter) the mass flux to the reaction zone is proportional to the concentration in the process stream. The heat flux from the reaction zone (and thus its temperature rise above that of the heat sink) is proportional to this mass flux.

3. ENTHALPIMETRIC SAFETY MONITORING AND PROCESS CONTROL

A safety monitor, designed by Hub (ref.5,6) to detect runaway conditions in chemical reactors in an early stage, is based on enthalpimetric principles.

Thermal runaway is characterized by the fact that q, the rate of heat release within a reactor, is rising faster than the rate of heat removal from the reactor. By differentiation of the heat balance equation of the reactor with respect to time, we obtain

$$m\,c_p \underbrace{\frac{d^2T_R}{dt^2}}_{\text{heat accumulation}} = \underbrace{\frac{d}{dt}(q)}_{\text{internal heat release}} - U\cdot A \cdot \underbrace{\frac{d}{dt}(T_R-T_F)}_{\text{heat removal}}$$

rate of change of:

Progressive temperature rise ($d^2T/dt^2 > 0$) may be caused by external heating. However, if it occurs at times when the rate of heat removal is increasing, i.e. when the temperature difference between the reactor contents (T_R) and the heat transfer fluid (T_F) is increasing, then there is proof for increasing and uncontrolled heat release. The computerized instrument (ref.7) will cause an alarm, when $d^2T_R/dt^2 > 0$ and $d(T_R-T_F)/dt > 0$.

The instrument may also be applied to monitor reactions with delicate initiation procedures (e.g. Grignard reactions) where, for a short while, a progressive heat release must occur, before one can proceed to the semibatch addition of the main quantity of the second reactant.

A more sophisticated approach to reactor safety, based on enthalpimetric process information, was developed by Gilles and Schuler (ref.8-10)

Enthalpimetric reaction control, i.e. the determination of the acutal extent of reaction based on the amount of heat released from the reactor, is used e.g. for polymerisations and polycondensations, particularly for operations where the mixture becomes solid, when the reaction is not stopped at the right moment. A patent scheme by Morgan (ref.11) serves as an example. Heat release monitoring is also applied to industrial fermenters (ref.12).

4. CALORIMETRIC PROCESS INVESTIGATION

Thermal and caloric data (heats of reaction, dilution, etc.; heat release rates; heat transfer properties) are useful for plant design and for the adaptation of new processes to existing equipment. They are necessary for the assessment of thermal process hazards, now required in most chemical process industries by internal rules or by public regulation.

Consequently, most chemists and engineers active in processes development are somewhat familiar with calorimetric methods. When they have a good reaction calorimeter available, they do discover, that they get far more than data from such an instrument. It provides immediate insight into the course of a process

- how fast reactions proceed
- how reaction rate is affected by reactant concentrations and catalysts
- whether there is a dangerous accumulation of reactants (which might cause a thermal runaway or trigger an exothermic decomposition)
- when phase transitions take place, etc.

A major problem in process development is analytical capacity. The calorimetric reactor gives excellent indications for sampling (to obtain a maximum of process information from few samples).

In the view of the author, appropriate reaction calorimeters are important tools to cut process development costs.

The ease of obtaining kinetic information by means of heat-flow calorimeters has been demonstrated by many authors (e.g. ref.13,14): Two examples from ref.14 may serve for demonstration:

- the hydrolysis of acetic anhydride
- the isomerisation of trimethyl phosphite

The hydrolysis of acetic anhydride is often used as a performance test for "kinetic calorimeters". The short duration of a single run and the fact that kinetic data are immediately available, permit the determination of a whole set of kinetic parameters (Fig.4) within one single working day.

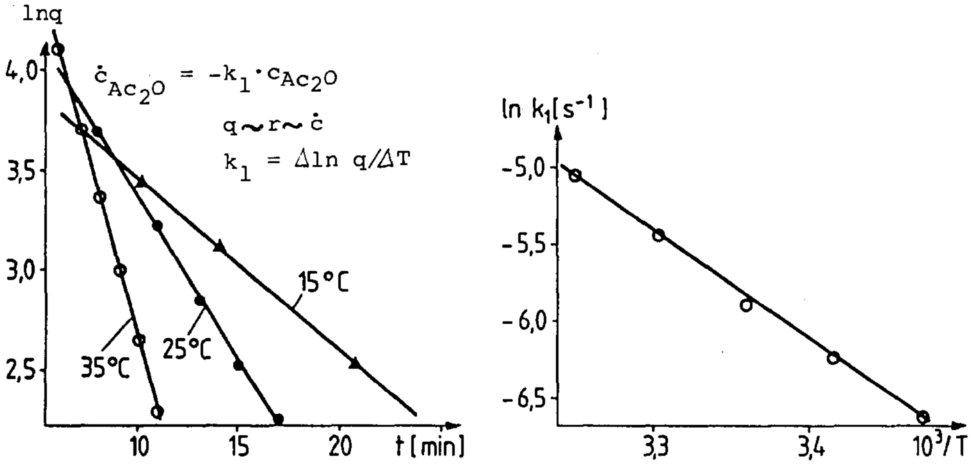
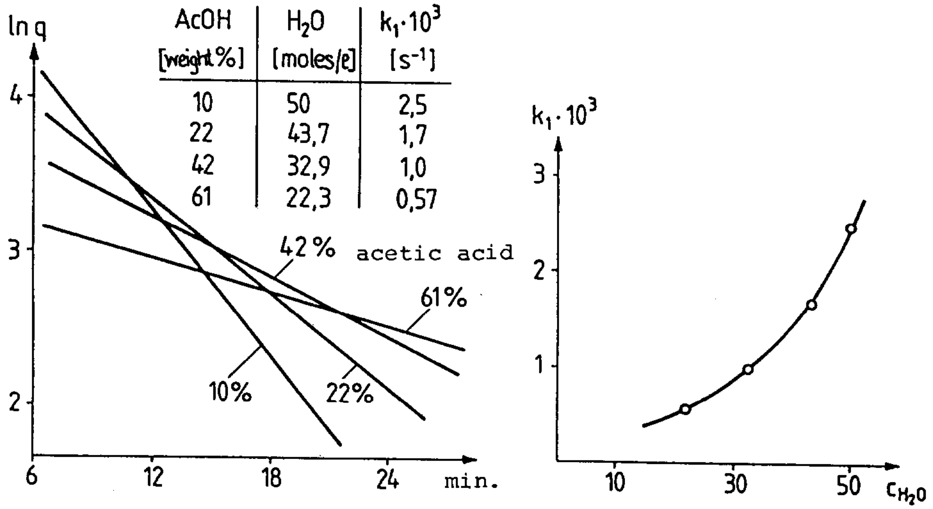


Fig. 4. Thermokinetic investigation of the hydrolysis of acetic anhydride (reaction with a large excess of water)

This ease of experimentation facilitates the investigation of process parameters often neglected: Acetic anhydride hydrolysis is usually done in dilute acetic acid (to provide homogeneous reaction conditions). As shown in Fig.4, the reaction is first order in acetic anhydride; however, it is by no means first order in the second reactant (water) which is usually applied in large excess (Fig.5). One may claim strict bimolecularity and attribute the deviations from the simple kinetics to a "solvent effect" (the water/acetic acid mix is the solvent in this reaction).



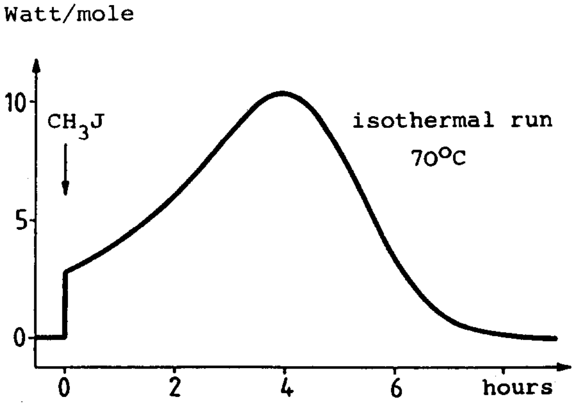
AcOH [weight%]	H_2O [moles/l]	$k_1 \cdot 10^3$ [s^{-1}]
10	50	2,5
22	43,7	1,7
42	32,9	1,0
61	22,3	0,57

Fig. 5. Influence of the reaction medium (aqueous acetic acid) on the rate of hydrolysis

The "solvent effect" approach was applied in the second kinetic example, the isomerisation of trimethyl-phosphite to dimethyl-methanphosphonate, which is catalyzed by CH_3J (ref.15)

$$\underset{\text{TMP}}{P(OCH_3)_3} \dashrightarrow \underset{\text{DMMP}}{CH_3\text{-}PO(OCH_3)_2}$$

Fig. 6 shows the initiation of the reaction by catalyst addition, followed by a heat release pattern which hints at autocatalytic kinetics.



kinetics:

$\dot{c}_{TMP} = -k\ (\varepsilon)\cdot c_{TMP}\cdot c_{cat}$

the rate constant k (ε) strongly depends on the dielectric constant (ε) of the reaction mixture. ε increases with increasing extent of reaction

Fig. 6. Strong solvent effects in the isomerisation of trimethylphosphite

The reason is, however, a tremendous increase of the polarity of the reaction medium. If one evaluates the record shown in Fig.6 using first order kinetics on TMP and assuming a polarity dependent isothermal "rate constant" k_1 (ε) which depends on the dielectric constant, then ln $k_1(\varepsilon)$ is strictly proportional to $(\varepsilon-1)/(2\varepsilon+1)$. In this case, the polarity increase effected by the progress of the reaction causes an increase of the isothermal rate "constant" by a factor of 20.

Substantial polarity changes caused by reaction progress are quite common in industrial processes, making "academic kinetics" obtained in high dilution sometimes worthless for process design. This is a good reason to investigate kinetics under the real process conditions.

The efficiency of calorimetric devices for kinetic work as shown above, is not attributed to a specific calorimetric design. Results similar to those presented may be obtained with many reaction calorimeters described in the literature.

5. CALORIMETERS FOR PROCESS INVESTIGATION

5.1 Requirements

In the view of the author, the following features are of particular importance for process work:

Facility to simulate industrial process conditions

- temperature must be a controlled process variable (this rules out adiabatic calorimeters)
- possibility to feed reactants (gases, liquids, solids) during calorimetric investigation
- operation under vacuum, pressure, reflux
- choice of mixing devices

Adequate calorimetric performance

- sensitivity <1 Watt/l (note: typical heat fluxes in industrial reactors are 10 to 100 Watt/l); this requires an accordingly stable base line
- resonably fast response (a time constant of 30 seconds acceptable for most applications)
- absolute accuracy of heat measurement is less important for process work than for research applications.

Ease of operation

- short duration of preparatory work for experimental runs
- easy access to reactor
- visibility of reactor contents (this helps to guide the experiment and furthermore may provide valuable non-calorimetric information).

Unfortunately, no calorimeter described so far does fulfill all requirements mentioned. Not surprisingly, the readiness to compromise is highly specific for individual experts in the field. A unified view on the required performance features is probably not attainable.

5.2 Design prinicples for process oriented calorimeters

An exhaustive review on design principles and on existing designs was recently given by Karlsen (ref.16). It partially follows older reviews by the author (ref.14,17) which are adopted here.

The requirement, that temperature must be a free process variable, confines the choice to so called "isothermal calorimeters" (heat-flow methods), i.e. it rules out heat accumulation methods.

The need of fast response and the fact that the operational needs mentioned above require a not too small reactor volume, call for active heat-flow calorimeters, i.e. devices with some kind of heat flow controller which causes heat transfer, induced by the slightest deviation of the sample temperature from its set-point.

Active systems have response times which are 5 to 1000 times faster than passive systems. (In passive systems, temperature changes in the sample, caused by partial accumulation of the evolved heat, are the driving force for heat exchange). The degree of response improvement achieved by active heat-transfer control depends on the reactor type required (thin walled vessel/pressure autoclave) and on the method of heat-flow control chosen.

The four ways of heat-flow control and heat-flow measurement which are described in the literature, are discussed here under the headings "Peltier", "compensation heating", "heat transfer"*) and "heat balance".

They are schematically shown in Fig. 7 and discussed in Table 1.

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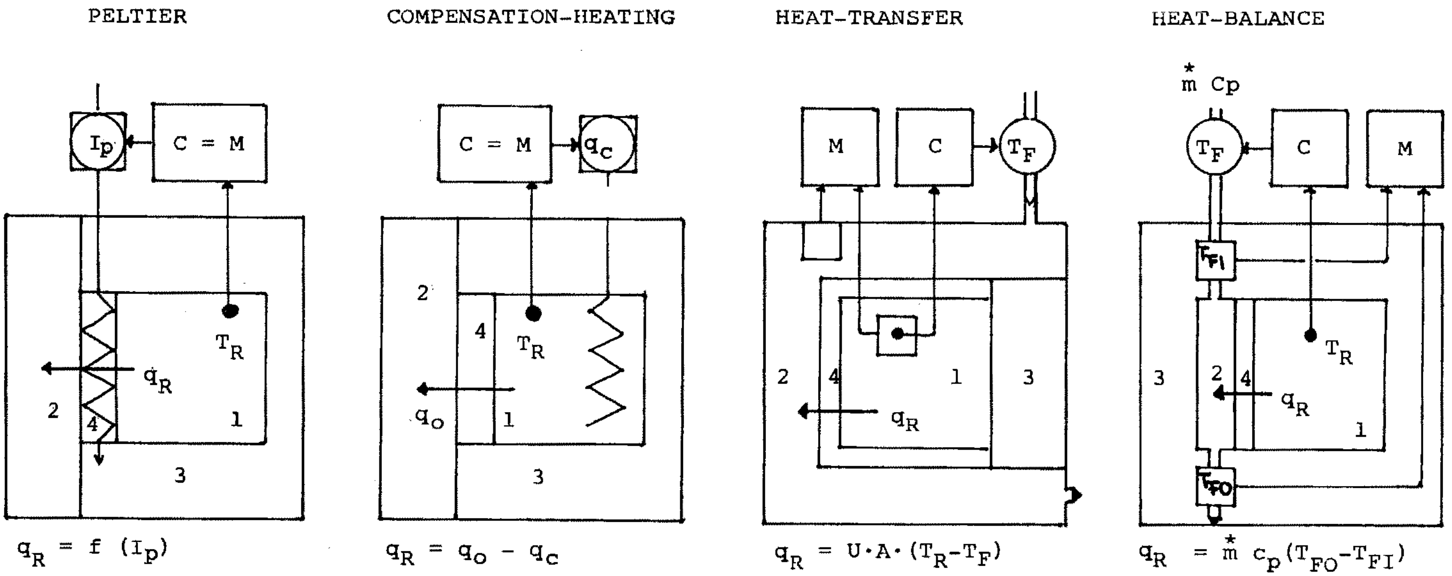
*) The notation "heat transfer" was chosen, because quasi-steady-state heat-transfer conditions at the reactor wall are used to determine heat flow. Since heat transfer is involved in all types of heat-flow calorimeters, a better nomenclature is welcome. "Heat conduction" would be incorrect, as convective heat transfer prevails on both sides of the reactor wall.



○ variable affected by controller C
I_p Peltier current, q_c heater power, T_F temp. of heat transfer fluid

□ variable sensed by primary measuring device M
I_p, q_c, T_F see above, T_R reaction temp.; T_{FI}, T_{FO} inlet/outlet temp. of heat transfer fluid

1 heat source
2 heat sink
3 thermal insulation
4 heat transfer resistance (area A, transf. coeff. U)

Fig. 7. Means of heat flow control and heat flow measurement

Table 1: Classes of active heat-flow calorimeters

Class	PELTIER	COMPENSATION-HEATING	HEAT-TRANSFER	HEAT-BALANCE
control of heat-flow by	Peltier current	power of compensation heater	temperature of heat sink	temperature of heat sink
measurement of heat-flow by	Peltier current	power of compensation heater	temperature difference across reactor wall	temperature change of heat-transfer fluid
advantages	calibration and base-line independent of reactor contents fast response	fast response simple design	ease of operation (no thermal insulation, reactor accessible) choice of reactors	calibration and base-line independent of reactor contents
problems	temperature range reactor shape construction material of reactor	base-line affected by reactor contents construction material of heater	calibration affected by reactor contents slow response	thermal insulation slow response

5.3 Selected design examples of calorimeters for process investigation

It is certainly appropriate to start with a look at the history of the development:

- Quantitative heat-flow calorimetry (passive systems) was brought to a high degree of sophistication by Tian (ref.18) and Calvet (ref.19) in France
- Borchard and Daniels (ref.20) gave momentum to the idea of kinetic interpretation of thermoanalytical records
- The first calorimeter designed for process investigation was developed at the "Institut français du petrole" by Baumgartner and Duhaut (ref.21). It was a passive system with a relatively slow response, later marketed under the name "Thermokinegraph"
- The first active heat-flow control system was, surprisingly, developed for a microcalorimeter, the "Differential scanning calorimeter" of Perkin-Elmer (ref.22)
- The first active single-cell mini-calorimeter was presented by Walisch and Becker (ref.23). It was based on Peltier heat-flow control and was aimed at scientific application.

Below, a list of process oriented heat-flow calorimeters using active heat-flow control is given. It is necessarily incomplete, but hopefully includes the most important developments.

Peltier systems have been described recently by Nilsson, Silvegren and Törnell (ref.24,25).

Compensation-heating systems were presented by Andersen (ref.26), Koehler et al (ref.27), Litz (ref.28), Schildknecht (ref.29) and Igarashi and Katayama (ref.30). Schildknecht pointed out the serious base-line problems inherent in this type of calorimeter. Igarashi and Katayama used a secondary control loop to keep the overall heat flow from the reaction mixture to the heat sink constant. Litz later (ref.31) proposed a solution which combines compensation heating and heat-balance characteristics to solve the problem.

Heat-transfer systems, using the temperature difference across the heat transfer resistance (i.e. the reactor wall and the liquid films on both sides) were designed by Regenass and co-workers (references see below) and recently by Moritz and Reichert (ref.32).

Heat-balance systems were designed by Meeks (ref.34), Hub (ref.4,31), Hentschel (ref.35) and by Nilsson et al (ref.36).

At Ciba-Geigy, we started work in 1965 simultaneously on a heat balance system (ref.37) and on a heat transfer system. We soon abandonned the heat balance system as it was too awkward to operate. The heat-transfer system was first presented in the thesis of H.Martin (ref.15) and later at ICTA 4 (ref.38). When its value for process optimization and hazards assessment was recognized, a substantial number of "Bench Scale Calorimeters" were produced to be used in various development departments and safety laboratories. In 1981 a series of computer controlled bench-scale calorimeters was constructed and made available to third parties (ref.39). Based on this experience, Mettler developed the RC 1 (ref.40). For the moment it seems to be the only process oriented calorimeter available commercially.

One may ask the question, why the heat-transfer design which seems to have as many deficiences as its alternatives (see table 1) has proved more successful. The reason is probably the ease of operation which calorimeters of this class can offer, and possibly the fact that the reactor looks very much like that with which a chemist is accustomed to working.

6. PROCESS INVESTIGATIONS WITH BENCH SCALE CALORIMETERS*

6.1 Multiphase pressure reaction

For a highly exothermic pressure reaction of the type

$$A + B \longrightarrow C + D$$

where A and D are organic components with melting points in the operating range of the process and B is an aqueous solution of a gas, a quantitative hazard assessment was required for scale-up. A temperature programmed run in the pressure calorimeter (Fig. 8) revealed the complex nature of the process and indicated a considerable hazards potential for batch operation (danger of thermal runaway).

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*) For the investigations reported below, "heat-transfer calorimeters" designed by the author and his coworkers were used.

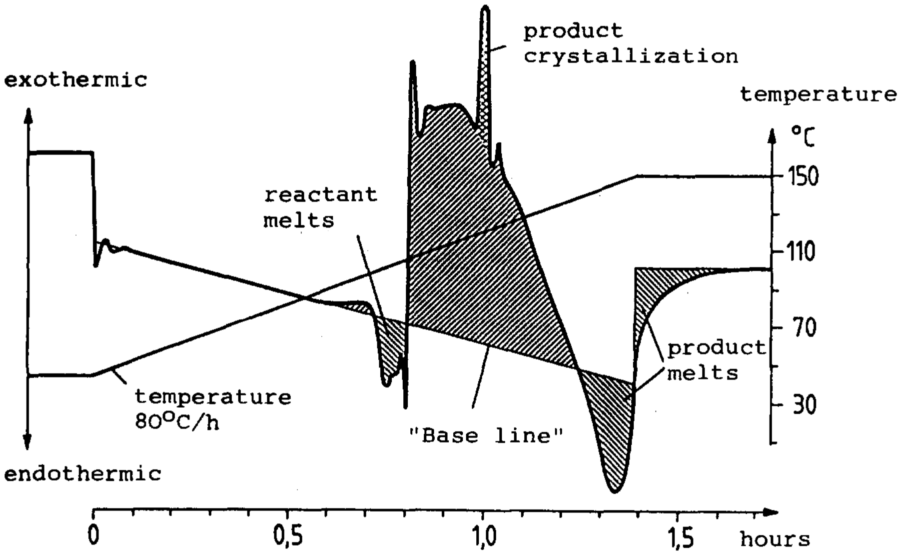
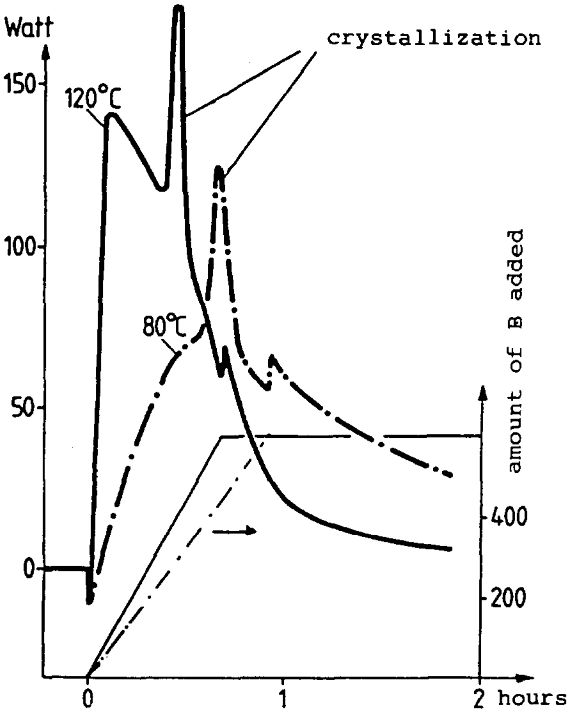


Fig. 8. Multiphase pressure reaction, Temperature programmed batch experiment



Isothermal semibatch runs (Fig.9) provided kinetic data which allowed to simulate the dynamic behaviour of the system and which were the basis of a safe and efficient large scale semibatch process. More information is given in ref. 14.

Fig. 9. Multiphase pressure reaction. Isothermal semi-batch experiments

6.2 Oxidation of 4-Chlorotoluene

Side chain oxidations with molecular oxygen are of considerable industrial importance (e.g. for the production of terephtalic acid). Usually a restricted amount of air is bubbled through the solution of the aromatic compound in acetic acid. Cobalt salts and Bromides are used as catalysts.

Beyrich (ref.41,42) used the heat flow calorimeter to investigate the oxidation of 4-chlorotoluene. Instead of bubbling air through the reactor he used a closed system: a pressure controller supplied the oxygen consumed by reaction from a cylinder (Fig.10). With this experimental set-up strange instabilities of this oxidation reaction were discovered. Under the reaction conditions suggested in the patent literature, a reactions pattern was observed which, after a short induction period, is almost zero order with respect to the hydrocarbon concentration (Fig.11a).

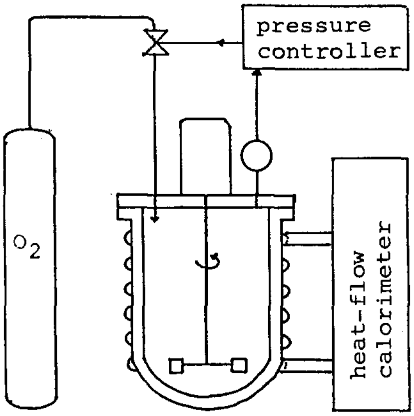


Fig. 10. Apparatus for Oxidation

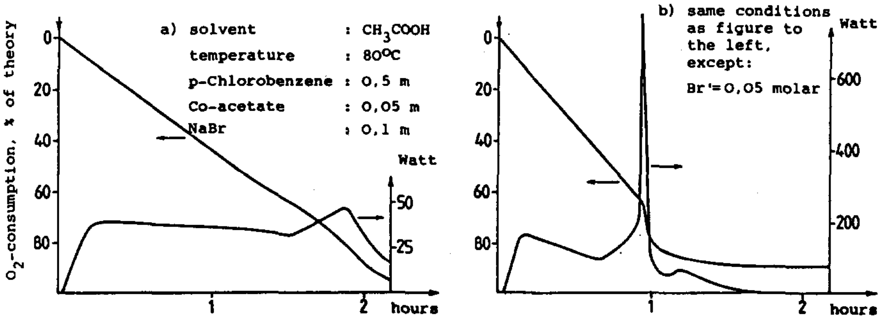


Fig. 11. Oxidation of 4-chloro-toluene

When the bromide concentration was lowered, however, sharp peaks of reaction rate occured (fig.11b). Under certain conditions (ref.41) up to three peaks were found and the peak reaction rate was up to 50 times higher than the quasi-steady-state rate observed before.

6.3 Fermentation

Marison and von Stockar (ref.43) adapted a heat flow calorimeter for fermentation. With this equipment they could trace influences on biological growth. Fig.12 shows how growth is stopped upon depletion of available nitrogen and initiated again by the addition of NH_4^+.

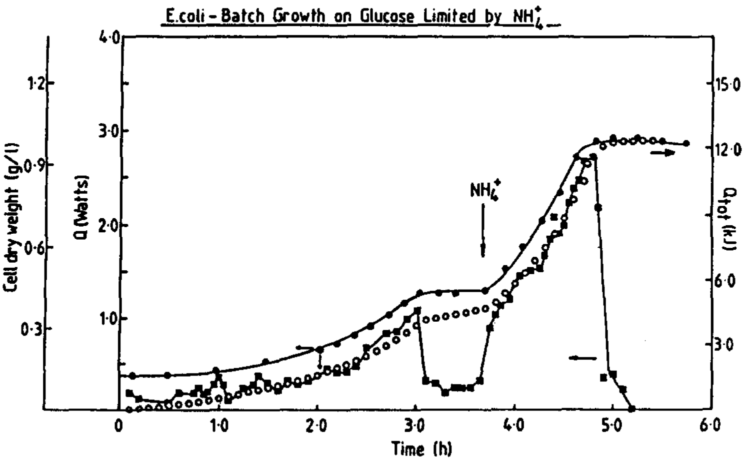


Fig. 12. Nitrogen-limited growth of micro-organism

7. CONCLUSIONS

Surprisingly few enthalpimetric on-line instruments are in use, and among the process-oriented calorimeters just one is available commercially.

In future, the following developments are to be expected:

- For on-line concentration analysis, specific methods like spectroscopy, flow-injection analysis and various kinds of chromatography will become more reliable and less expensive than they are now. Therefore, calorimetric analyzers will be advantageous only in exceptional cases.

- Reactor control based on heat-release monitoring will become a standard method of process control. Already now, the method seems to be more widely applied than one would assume based on references in the open literature.
- Laboratory reaction calorimeters will be widely used for process design and process optimization, when suitable instruments are available commercially.

In instrument design, the trend to more and more sophisticated mechanical constructions should be abandonned. Simple instruments can be conceived which are dependable and easy to operate. If their performance deficiencies are appropriately analyzed and quantified, systematic errors in the primary calorimetric response can be corrected easily by powerful and inexpensive micro-processors.

8. REFERENCES

1 I.I Saslawskij, J. and E. Kaplanskij, Dyes Industry (Moscow) 3 (1971); 69

2 B. Hultman, A. Dalborg, L. Uhlin and A. Berglund, Svensk papperstidning 78 (1975), 471/507/546 (the author is indebted to M. Manssen for this reference)

3 F. Becker, Chem. Ing. Techn. 41 (1969), 1060

4 Supplier: Kamstrup-Metro, Aabyhoj, Denmark

5 L. Hub, Ph.D.Thesis 5577, ETH, Zürich 1975

6 L. Hub, Chem. Ing. Techn. 54 (1982), MS 978,82

7 Supplier: Systag, Rüschlikon, Switzerland

8 H. Schuler, Fortschr. Ber. VDI-Z, Series 8, Nr. 52 (1982)

9 E.D. Gilles, Chem. Ing. Techn. 55 (1983), 437-446

10 H. Schuler, Regelungstechnik 32 (1984), 190-200, 234-237

11 L.W. Morgan, US Pat 2'974'017, filed Nov. 21, 1957

12 K. Bayer and F. Fuehrer, Proc. Biochemistry July/Aug. 1982, 42

13 F. Becker, Chem. Ing. Techn. 40 (1968), 933

14 W. Regenass, Chimia 37 (1983), 430

15 H. Martin, Ph. D. Thesis, Basel 1973

16 L.G. Karlsen, Ph. D. Thesis, DTH-Lyngby, Denmark, 1985 (in cooperation with Prof. J. Villadsen)

17 W. Regenass, Thermochim. Acta 20 (1977), 65

18 M. Tian, Bull. Soc. Chim. France 33 (1923), 427

19 E. Calvet and H. Prot, "Microcalorimetrie", Masson, Paris 1956

20 H.J. Borchard and F. Daniels, J.Am.Chem. Soc. 79 (1957), 41

21 P. Baumgartner and P. Duhaut, Bull.Soc.Chim.France 1960, 1187

22 E.S. Watson et al., Anal. Chem. 36 (1964), 1233

23 W. Walisch and F. Becker, Z.Phys. Chem. NF 36 (1963), 97; and 46 (1965), 268

24 H. Nilsson, C. Silvegren and B. Törnell, Chemica Scripta 19 (1982), 164

25 H. Nilsson, C. Silvegren and B. Törnell, Ang. Makromol. Chemie 112 (1983), 125

26 H.M. Andersen, J. Polymer Sci. A-1, 4 (1966), 783 and 7 (1969), 2889

27 W. Köhler, O. Riedel and H. Scherer, Chem. Ing. Techn. 45 (1973), 1289

28 W. Litz and D. Biehler, German Offenl. 2'355'952 (1973)

29 J. Schildknecht, Thermochim. Acta 49 (1981), 87

30 S. Igarashi and S. Katayama, Eur.Pol.Journ. 15 (1979), 805

31 W. Litz, J. Therm. Anal. 27 (1983), 215

32 H.U. Moritz and K.H. Reichert (TU Berlin), Achema lecture 1985

33 M.R. Meeks, Polym. Eng. Sci 9/2 (1969), 141

34 L. Hub, I.Ch.E.Symp.Ser. 49 (1977), 39

35 B. Hentschel, Chem. Ing. Techn. MS 725 (1979)

36 H. Nilsson, C. Silvegren and B. Törnell, Brit.Pol.Journ. Dez.1981, 164

37 W. Regenass and A. Mauerhofer, Swiss Patent 455 325 (filed 1966)

38 W. Regenass, W. Gautschi, H. Martin and M. Brenner, Therm. Anal. 3 (1975), 834 (4th ICTA, 1974)

39 G. Giger, A. Aichert and W. Regenass, Swiss Chem. 4/3a, (1982), 33

40 Supplier: Mettler Instruments, CH-8606 Greifensee

41 J. Beyrich, Ph.D.thesis Nr. 6578, ETH, Zürich, 1980

42 J. Beyrich, W. Regenass and W. Richarz, Chimia 34 (1980), 244

43 I. Marrison and U. von Stockar, Proc. Biotech. 83 (1983), 947