

NOVEL PROCESS DESIGN METHODS TO ACCESS SAFER PROCESSING OPTIONS

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The low tonnage organic chemicals sectors are distinct in having particular hazards that derive from the nature of the chemistries and the plant they use. The widespread use of inefficient batch technologies and relatively large inventories of materials are contributors to risk. While in principle, intensive processing techniques can be used to address these problems, adoption is slow. There are many reasons for this, but a central one is the failure of current design methodologies to identify early enough opportunities for more appropriate (and inherently safe) process technologies. The BRITEST™ project has developed a suite of tools that can be used in the early stages of process design to identify opportunities for more intensive and efficient processing. These involve the use of simple qualitative models to deduce favourable operating regimes and conditions. The cost and time requirements are consistent with the short duration and low cost development projects typical of the low tonnage sectors. Further, the qualitative models provide a useful framework to exploit the experimental data frequently collected for hazard assessment (typically calorimetric data). The methods are outlined and illustrated using a case study from a real industrial process.

KEYWORDS: Intensification; Process design; Safety

INTRODUCTION

It has long been recognised that inherent plant safety is improved by reducing the inventory of hazardous materials. This is particularly important in the low tonnage chemicals sectors (intermediates, agrochemicals, pharmaceuticals etc.), where batch processing is widely used. It is typical for batch process designers to slow down chemistry to match the poor processing capabilities of the stirred tank. The result is large volumes of process material that spend extended times (often days) in process, when an equivalent continuous process might need only seconds or minutes for the same transformation.

As well as the inefficiency of batch processes, the complex chemistry they typically involve tends to give rise to a greater scope for unintended reactions. Runaway reaction hazards are a major safety issue¹.

All other things being equal, lower inventories reduce the size of the worst-case incident. Inventory reduction can be achieved through logistical improvements and reductions in the amount of material in storage. It can also be reduced through the “intensification” of the processing operations. This may involve using higher reaction rates (by higher temperature, catalysis, increased concentration) accompanied by higher heat and mass transfer rates. By doing this, Process Intensification (PI) may bring additional benefits beyond inventory reduction:

- Reduced possibility of accumulation of materials in process;
- More rapid response to control actions;
- Better process performance;
- Cheaper plant.

PI is attracting increasing attention worldwide from industry, regulators and academe. However, the uptake of intensive technologies has generally been slow. There are several reasons for this. Firstly, much of the interest has been driven by “technology push” from equipment suppliers and designers. Intensive equipment has been a solution looking for a problem, often applied on a trial basis to look for improvements (rather than as a result of rational argument). Secondly, there is some perception of risk among potential users, who prefer to stick with familiar, tested technologies. Thirdly, intensification has focussed on the more glamorous areas, particularly reaction, rather than the feed preparation and product separation areas. These unglamorous areas often constitute the bulk of capital expenditure and materials inventory in a chemical process, making the potential benefits from intensification of the reaction section alone look rather small.

There have been some attempts at methodological approaches to PI. However, these have in general failed to attract widespread use. Problems with such methods may be:

- That they are not realistic within the resource limitations and business models of the target industry sectors;
- That they do not recognise the importance of aligning methods with existing practices in industrial process design;
- That they assume that the solution will be intensive and don't consider the possibility that the existing approaches may be better against several key criteria;
- That they are not credible to industry.

In the low tonnage chemicals sectors, time to market is a key driver, and all process development activities are organised to reduce it. By assuming that a batch stirred tank is to be used, companies can work with standard process development methods and safety screening tools. There is little opportunity to evaluate other processing technologies, and in general laboratories are not set up to do this. Process development is primarily empirical, thus avoiding the time-consuming and expensive activities needed to obtain data for detailed physico-chemical modelling¹.

Under the current low tonnage design paradigm, the assumption that a batch stirred tank will be used immediately focuses attention on the (limited) range of process features that are of importance in the implementation of a batch process – mixing and agitation, heat transfer requirements, phase dispersion etc. Laboratory protocols are designed to deliver representations of batch tank performance in those duties. Many degrees of freedom that in principle exist (contacting pattern, residence times, phases present among others) are not accessible in traditional batch processes. For example, in a two liquid phase system, batch processes cannot deliver counter-current contacting of the liquids. However, it is often those degrees of freedom (rapid mixing, intense heat transfer and so on) that are the key elements of intensive options.

A new set of tools has been developed as part of the BRITEST™ project^{2,3,4,5} to support the identification and adoption of innovative (including intensive) processes. The tools attempt to address the problems identified above by adopting a different philosophy - the methods start at the beginning of the problem rather than the end. The methods set out to identify the most appropriate process technology on the basis of the business need and the features of the chemical process. This is self-evidently sensible, and is broadly the practice

in large tonnage chemical process design. It is, however, the antithesis of current practice in the batch sectors. The tools have been designed to work with minimal data, yet can identify potentially valuable intensive options very early in design. This maximises the chance that these options can be adopted.

The framework of tools addresses four issues, as illustrated in Figure 1. The order of activities is important. Under the BRITEST™ method, the process concept is developed independently of and before the plant concept. The process concept is developed first to identify the best outcomes that can be delivered, independent of plant constraints. In doing this, the essential processing capabilities (eg the ability to deliver intensive heat transfer or counter-current phase contacting) are identified. This in turn allows the selection of equipment based on its processing capability.

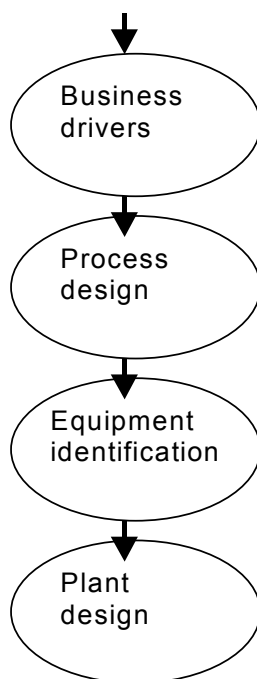


Figure 1. Overall framework for process and plant design

Of course, this is exactly the type of approach that would be taken in the development of a new continuous, large-scale process. However, the development of such a process would require substantially more time and effort than is available for a low tonnage process. The novel feature of the new methods is the capability to develop process and plant concepts without the need for the detailed quantitative information typically used in continuous process design. This distinguishes the method from other published methods. The latter generally amount to little more than exhortations to think about intensification opportunities early in process development. In this sense, the methods go beyond the rather restrictive philosophy of intensification.

METHODOLOGY

This paper concentrates on the core aspects of process design and plant concept development. The collection and presentation of business drivers will not be discussed here. All that needs to be noted is that the key desired business outcomes of a project are collected and presented in a form that makes them useful to the design technologist. This is important because the method generates a range of options (rather than the very restricted options that arise from the batch paradigm). The process developers need to be able to screen options during design without reference back to the business manager. In what follows, the design of the reaction system will be emphasised in order to illustrate the safety benefits in what is essentially a reaction hazard case study.

The following underlying axioms are used in deriving the approach to reaction conceptual design.

- To obtain the best outcome from a process we need to deliver conditions that in broad terms maximise the rates of the desired processes and minimise the rates of undesired processes.
- Lack of detailed knowledge of the rate behaviour requires the law of mass action to be applied (unless other prior knowledge is available).
- The phases (gas, liquid solid) present in a process represent central degrees of freedom in setting out distinct process options. For a given chemistry (i.e. intended stoichiometric reaction set) there may be several possible phase combinations.

We consider a process to be the provision of an ordered and structured set of conditions applied to the processed materials. This sidesteps the “Unit Operation” concept, and thus the need to assume the type of processing device. We initially seek conditions that should deliver the best process performance, rather than accepting the limitations that are inherent in selection from existing process equipment.

The method involves the collection of two sets of data:

- reaction stoichiometry and associated information about the reactions and other rate processes; and
- information relating to phase transitions.

The first set allows the identification of strategies to improve the outcome of the process in terms of yield and volume efficiency. The second set allows the identification of a set of “phase strategies”, or the phases present during the reaction.

The reaction information is presented in the form of a “Driving Force Table”, as illustrated in Table 1. Here, each column represents a rate process. Rows represent either factors that influence the rate or key reaction parameters. The symbols “+” and “-” represent a positive or negative influence on rate. Thus, a “+” opposite a species indicates that a higher concentration of the species would be expected to increase the rate of that rate process. It is rare (contrary to popular academic opinion) that designers have detailed and accurate models of reaction kinetics, and frequently the set of reaction pathways will be incompletely understood. Further, the time and cost of detailed kinetic analysis is seldom justified under the pressure of rapid time to market. In contrast, the level of information required to complete the driving force table is realistic in the early stages of process

development, and is typically assembled from prior knowledge, the literature and (minimal) experimentation.

The data required to suggest the range of possible phase behaviours are also quite limited – melting and boiling points (estimated if experimental data are unavailable) as well as solubility behaviour (based on molecular polarity for example). Typical data for a set of relevant materials are illustrated in Table 2. Of course, the detailed behaviour would need to be confirmed experimentally; but what is important at the early stages is the identification of possible, distinct strategies that may be broadly favourable to the process outcome.

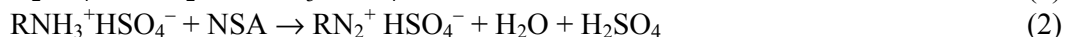
CASE STUDY

The illustrative case study presented centres on a runaway reaction incident⁶. The process involved the diazotisation of an aromatic amine, followed by decomposition of the diazonium compound in the presence of water to produce a phenol. The case attracted attention from the HSE. Ultimately, the company was allowed to restart the process in a significantly modified batch facility at a cost of £1 million, with further costs associated with the incident reaching £1.7 million.

A set of reactions which represent the chemistry (relying on information from Sykes)⁷ is given in Equations 1 to 6 below. Reaction 4 represents the reaction of ion R^+ with a range of other organic species, resulting in higher molecular weight species lumped under the name “tars”. Note that this is not a chemically complete or proven representation of the reaction set, but is typical of the state of knowledge that technologists could bring to bear at the early stages of development. The validity of the set of equations would be tested through the experiments during the process development activity. While the BRITESTTM methods assist in the definition of appropriate experiments, this aspect is outside the scope of this paper. It is also important to note that the published information is restricted to avoid revealing confidential details of the process – compositions, detailed conditions etc.

The data used to represent reaction rates was based on some of the calorimetric data presented in the original paper⁶. Such data would be readily accessible at reasonable cost to a competent development team, and the data needs are much less than would be required to elucidate the detailed kinetic behaviour of each reaction.

The driving force diagram that corresponds to the reactions is in Table 1.



Data concerning the phase behaviour of the system are given in Table 2. The identity of the aromatic amine is not given in the paper, so for the purposes of this study it will be assumed to be solid at room temperature, with a melting point of 120°C. On the basis of these data, a range of “phase strategies” can be developed for the key synthetic reactions. This is done by simple enumeration of the possible combinations of phases for the

components present as a function of the relevant variables (such as temperature). Some credible options for the case study are shown in Table 3.

While the paper refers to a process that had been carried out in batch plant, the information in the paper will be used as if it was part of a development process aimed to design a new plant, making no assumptions about the technology to be used.

Given the information in the tables, it is possible to develop processing options and plant concepts for the system. Option selection would rely on the fit with the previously identified business drivers. In the case study, the drivers would include cost issues, but also safety considerations for a reaction type that is known to pose significant hazard.

At least three distinct modes of operation for reaction 1 can be suggested. Any of them could be operated either batchwise or in continuous mode. The identification of “phase options” related directly to some requirements on the processing capabilities of the equipment. For example, the presence of a dissolving solid implies the needs to suspend and disperse the solid. For reaction 1, the main options that arise are as follows.

- Direct mixing of acid and solid amine. This would involve mixing, dispersion of the solid and the removal of heat (the temperature needing to be controlled as the next reaction cannot be allowed to run at too high a temperature). While continuous operation would be possible, the addition of solids into a liquid continuously is a difficult processing step.
- Melting the amine and dispersing it as a liquid in the acid. The amine and acid are mixed and reacted with simultaneous heat removal. Batch operation of this option would have no obvious advantage over the solid amine option, and would raise additional difficulties in heat transfer, but continuous operation in a heat-exchanger reactor is attractive.
- Dissolving the amine in an inert carrier solvent, toluene for example, and the two-liquid phase contacting of the acid and amine solution. The reaction product would dissolve in the acid, leaving the inert solvent to be recycled.

For reaction 1, there are no known side reactions, no and so long as the reaction is completed before the NSA is added, loss of yield issues are not relevant. It would be possible to produce the amine salt solution for storage before use, or equally continuously as needed.

The initiation of reaction 2 by mixing NSA with the amine salt solution has the potential to generate all of the subsequent reactions 3–5. It would be possible to consider suppressing those reactions by running the reaction at low temperature. The practicability of this would depend on the balance of reaction rates and the temperature dependency, but could readily be tested experimentally. Reaction 2 could be carried out batchwise or continuously. Its moderate rate would suggest that continuous operation would be suitable – for example the manufacture of 100 tonnes of diazonium salt per year can crudely be estimated using the published calorimetry data⁶ to require a reactor volume of a few tens of litres. Given the need to remove heat, the ideal equipment would seem to be another heat-exchanger reactor.

Table 1. Driving force table for the diazotisation synthetic reaction set. Question marks indicate uncertain or missing information

Driving force	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5	Reaction 6
H ₂ SO ₄	+
RNH ₂	+	+
RNH ₃ ⁺ HSO ₄ ⁻	-	+
NSA	.	+
RN ₂ ⁺ HSO ₄ ⁻	.	.	+	.	.	.
H ₂ O	+	.
R ⁺	.	.	.	+	+	+
N ₂
ROH`
organic pecies	.	.	.	+	.	.
Azo
Temperature	+	+	++	+	+	+
PH	.	?	?	?	?	++
Heat of reaction	Moderate exotherm	Moderate exotherm	Strong overall exotherm			Exotherm ?
	For these reactions taken together					
Representative reaction time	Very fast (order of ms?)	Few Minutes	Minutes (?)	Fast – Less than seconds	Fast – Less than seconds	Probably fast(?)

Table 2. Typical initial information on phase behaviour

Species	Melting point/°C	Boiling point/°C	Polarity
H ₂ SO ₄	Low	>>100	High
RNH ₂	120	High	Low-moderate
RNH ₃ ⁺ HSO ₄ ⁻	High	Decomposes	High
NSA	Low	?	High
RN ₂ ⁺ HSO ₄ ⁻	Decomposes	-	High
H ₂ O	0	100	Moderate-high
R ⁺	n/a	n/a	High
N ₂	n/a	permanent gas	Low
ROH	c120	high	Low-moderate
organic species	>100	high	Low-moderate
Azo	high	Decomposes?	Moderate

Table 3. Selection of suggested phase strategies for the reactions

Reaction	Phase options
1	Solid amine, liquid acid or Molten amine (>120°C), liquid acid or Solution of amine, liquid acid or Others...
2	Homogeneous liquid phase or Gas/liquid (water as vapour >c100°C)
3–6*	Homogeneous liquid phase + gas N ₂ or Gas water as vapour + gas N ₂ /liquid or Gas water as vapour + gas N ₂ /liquid/liquid (second immiscible phase with ROH)

*Given the reactivity of R⁺ it is not likely that its generation and reaction can be separated.

It is likely that the conditions required to drive high selectivity for reaction 5 would be a high concentration of water. This would suggest quenching of the diazonium compound from reaction 2 into water, ideally with a low concentration of the diazonium to minimise the concentration of organic species available for coupling with R⁺. This would generate aqueous waste and the cost of waste disposal would be balanced against any yield benefits. It is also obvious from Table 1 that slow mixing may increase the yield of crud.

Experimental work would be needed to identify the best conditions (water concentration) and to define the intensity of mixing required.

The equipment for reactions 3–6 needs to mix intensely, remove heat and to decant the phenol phase. Heat removal and mixing may need to be carried out simultaneously, but there appears to be no reason to carry out phase separation in the same equipment. As reaction 6 is suppressed under acid conditions it would not be significant in the conditions envisaged.

PLANT OPTIONS

The process could clearly be carried out in a batch system, as was done by Hollidays both before and after the incident. However, it is evident that a continuous plant using intensive mixers, heat exchanger reactors and continuous phase separation could deliver all of the primary functions identified. The largest volume may be associated with the diazotisation reaction, and even with a residence time of, say, 10 minutes, this would only have a volume of tens to hundreds of litres to give a production rate of hundreds of tonnes per year. One potentially viable continuous configuration is given in Figure 2.

The existing process prior to the incident was in standard batch equipment. As a result of investigations after the incident, a new configuration was developed, the changes centred on the instrumentation to avoid the accumulation of unreacted materials. It is interesting to note that even in the face of serious safety issues, and the possibility of operating the process continuously at low inventory, that the traditional style of process analysis did not result in a continuous process being developed.

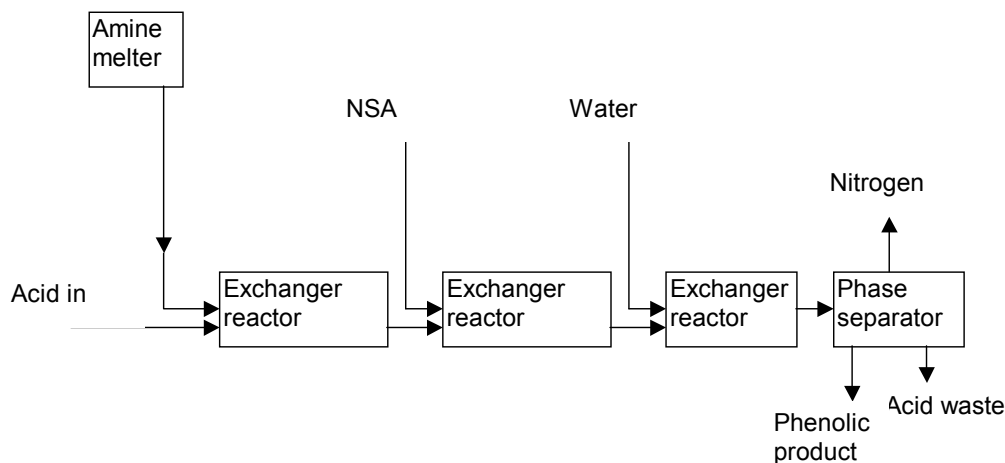


Figure 2. Block diagram representing a continuous process option

DISCUSSION

The analysis above demonstrates that relatively little information, and information of only moderate cost can be used to deduce innovative plant options. The option presented above is one of many that might be suggested, and is chosen to illustrate how easily a radically different approach can be identified. Of course, the identification of a potential processing

option would require experimental work to support its development and assessment. However, the early identification of possible options allows timely and appropriate experimentation to be defined. This is a shift away from the prevalent approach in low tonnage process design – that a stirred tank will be used and that experimentation is all carried out to support that decision.

The operation of an approach to design like that in Figure 1 would quickly identify the safety benefits associated with an intensive continuous design. The potential reaction hazards of the process are evident, and would easily have been picked out as important selection criteria. The clear and timely identification of process options that meet such safety criteria inevitably increases the chances of their adoption, as well as potentially reducing the cost and time requirements for implementation of a safe process.

It is important to recognise that while methodologies such as this can improve the outcomes of process and plant design, they do present companies with significant problems in their implementation. Difficulties are not only technology related but also include culture change, risk perception and the need to have a well designed implementation strategy. Nevertheless, the high costs that arise when processes go wrong, as well as the potential benefits in process efficiency, reduced effluent and reduced capital cost provide a strong argument to change.

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REFERENCES

1. Sharratt PN (Ed), 1997, "Handbook of batch process design", Blackie A&P, London, ISBN 0-7514-0369-5
2. BRITEST Limited, 2002, <http://www.britest.co.uk/>
3. Wall K, Sharratt PN, Sadr-Kazemi N and Borland JN, 2000, "Plant-independent Process Representation", Computer Aided Chemical Engineering 8: European Symposium on Computer Aided Process Engineering-10, Pierucci S., (Ed.), Elsevier Science BV., ISBN 0-444-50520-2
4. Wall K, Sharratt PN, Sadr-Kazemi N and Borland JN, 2001, "Plant-independent Process Representation", Org Proc Res & Dev, 5 (4): 43–437 Jul–Aug 2001
5. Sharratt PN, Wall K and Borland JN, 2001, "Crossing the border - chemistry and chemical engineering in process design", Proc 6th World Congress of Chemical Engineering, Sept 22nd–27th, Melbourne, Australia
6. Partington S and Waldram S, 2001, Runaway reaction during production of an azo dye intermediate, *IChemE Symposium Series* **148**:81–93
7. Sykes P, 1970, A guidebook to mechanism in organic chemistry, 3rd Edn. Longman