PROCESS ENGINEERING VERSUS PRODUCT ENGINEERING
A Case Study on Volatile Organic Compounds Removal

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Three solutions for removing the dangerous volatile organic compound (VOC) xylene from an industrial coating process are presented and compared. Two of them are based on classical process engineering principles, i.e., development of separation-cleaning methods such as incineration and adsorption. The last approach is somewhat different and is based on the so-called product engineering concept, i.e., in this case, a change of the formulation so that xylene is entirely eliminated from the process. It is shown that both the process and the product engineering approaches yield viable solutions to the problem-need specified in the beginning of the project, but producing a novel formulation (chemical product design) represents a method that results to a completely xylene-free process which is environmentally and economically more interesting than those generated via the more traditional process engineering approaches.

Keywords: product design; formulation; emulsion; adsorption; environment; economics.

INTRODUCTION—THE CHEMICAL PRODUCT DESIGN APPROACH

This article will present and compare traditional process engineering and a product design approach towards solving of a specific problem of a coating process. The need is imposed by new environmental legislations. While chemical product design has been always, in one way or the other, used in certain industrial sectors e.g., paints, pharmaceuticals, catalysts, and food, an increased attention in the recent years has led to a systematic rationalization and increased interest in this approach as well as its transformation from 'art' to 'science' (Favre *et al.*, 2002; Wesselingh, 2001; Wintermantel, 1999; Wesselingh and Jansen, 1999; Favre and Kind, 1999; Villadsen, 1997; Charpentier, 1997). By 'chemical product design or engineering' is meant the whole process from the generation of ideas up to manufacture of complex chemical products, typically comprising of many individual components. Microstructred products, devices that effect chemical change and specialty chemical fall in this category (Cussler and Moggridge, 2001). Many of these products are emulsions, suspensions, foams/gels and other types of colloidal dispersions with one or more components in the categories of polymers, solid particles and surface-active compounds.

In this context, chemical product design is a highly multidisciplinary area and it involves a number of steps, of which the crucial ones are the clear identification of the actual need, the generation of a variety of ideas and the selection of the one to two more promising that will be selected for manufacture. Much more emphasis is thus given on the product itself rather than the manufacturing process, and it has been stated that much of the product design is often completed before manufacturing is even an issue (Cussler and Moggridge, 2001). Economic considerations and property rights, especially patents, are also of great relevance in chemical product design.

While certain nontraditional, in the chemical engineering viewpoint, manufacturing processes are often of much relevance (e.g., emulsification, granulation, and so on), the actual generation and especially the selection of ideas often requires enhanced understanding of the physical chemistry of complex materials, especially colloids and interfaces as well as transport phenomena especially diffusion and rheology.

Much of the effort towards putting some structure to the 'chemical product design' area is due to the recent textbook by Cussler and Moggridge (2001), which is based on the four-step procedure stated above: *Needs, Ideas, Selection, Manufacture.* Following this approach, we proceed in the next section in identifying the Need of interest to this particular project. Since the Need is related to a process, at first the ideas selected towards addressing this need are based on improvements/separation methods, which are rather

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conventional. These processes/ideas—solution to the need—are presented and compared in subsection *The Traditional Process Engineering Approach*. We then proceed, in subsection *The Product Engineering Approach*, towards testing and eventually selecting for manufacture, in *The Selection* section based on an economical analysis, an idea that meets the same need in a more satisfactory way, since it yields at the same time an improved product. This is accomplished by, instead of focusing on the process, looking back at the product and designing an improved formulation. This product design point of view approach requires knowledge of the physical chemistry/thermo-dynamics of a rather complex system, in accordance to the general lines stated above.

THE NEED: CONTROL OF EMISSIONS OF VOLATILE ORGANIC COMPOUNDS (VOCs)

There has for long been an increasing awareness with environmental protection. The scientific demonstration of the inter-relationship between sulphur emissions in continental Europe and the acidification in Scandinavian lakes, and several studies confirming the hypothesis that air pollutants could travel several thousands of kilometres before deposition and damage occurrence implied that cooperation at the international level was necessary to solve problems such as acidification. This awareness led to the signature of the Convention on Long-range Transboundary Air Pollution at Geneva in 1979. From this convention a number of protocols on the control and reduction of sulphur, nitrogen oxides, heavy metals, persistent organic pollutants and volatile organic compounds (VOCs) were issued. In 1991, a protocol concerning the control of emissions of volatile organic compounds was signed at Geneva. The countries that signed the protocol agreed on a 30% reduction on their VOCs emissions by 1999. The Gothenborg Protocol in 1999 for abating acidification, eutrophication and ground-level ozone, set new emission ceilings for 2010 for four types of pollutants: sulphur, NO_x, VOCs and ammonia. These ceilings were negotiated on the basis of scientific assessments of pollution effects. Once the protocol is fully implemented, Europe's sulphur emissions should be reduced compared to 1990 by at least 63%, its NO_x emissions by 41%, its VOC emissions by 40% and its ammonia emissions by 17%. These concerns were assumed by the European Union Council that issued the directive 1999/13/CE on the reduction of emissions of VOCs due to the use of organic solvents. According to this directive, there are limitations to all industrial activities on the release of VOCs. The implementation of this directive to the national legislations has had a strong impact on a number of industries e.g., paints and coatings that have to adapt to these new strict rules on solvent emissions. For example, large paint companies in Denmark such as HEMPEL Marine Paints A/S, which has productions in urban areas, are obliged to measure and report to the authorities the level of VOCs emitted during the production of the paints. This has led these companies over the recent years to a substantial (research and development) activity towards developing expert tools (both experimental and theoretical/modelling) for monitoring the VOCs emissions.

The industry under study in this work used xylene while applying a coating formulation based on zinc stearate on a fabric surface. The fabric was immersed in a dispersion of the zinc stearate. The xylene was then evaporated under a flow of ambient air at $30°C$ at a flow rate of $1 \text{ m}^3/\text{s}$ in an oven. The concentration of xylene on the gaseous effluent from the oven was about 7500 mg C/m^3 N, i.e., about 50 times above the limits introduced by the new legislation. The xylene used in this activity had an annual cost of about €100 000. (These operational parameters are obviously fictitious but they provide nonetheless a fair picture of the typical operational parameters for such a coating process.) The goal of the company was to reduce the VOCs on the effluent to within the legal limits in a way that is both technically feasible and economically viable, reusing if possible the solvent.

THE IDEAS

The Traditional Process Engineering Approach

According to Devinny *et al.* (1999), considering the conditions of the effluent under study two processes seem adequate and will be further discussed: regenerative adsorption and incineration. Although this latter process wouldn't allow for a recover of the solvent, it could be of economical interest since it would provide the hot air needed in the numerous drying ovens used in the plant. Other approaches such as cryocondensation and membrane recycling were also considered in a first stage of the investigation but although technically possible they were discarded at an early stage as they show to be economically nonattractive.

The incineration process

Incineration is a process that results, via combustion, in the oxidation of the organic compounds in the effluent to CO_2 and H_2O. It is a simple and reliable process allowing for a removal of up to 99.99% of VOCs from the effluent. The incineration process can be thermal or catalytic. Thermal incineration uses larger quantities of auxiliary fuel to sustain the combustion and requires higher temperatures ($600–1000°C$) to operate. Catalytic incinerators use a catalyst bed to promote the oxidation at lower temperatures ($300–450°C$) using less auxiliary fuel. They allow for lower levels of CO and NO_x emissions but require substantial maintenance and their operation is rather difficult. The design of incinerators was based on an operating temperature of $870°C$ for a 99% VOC removal and of $480°C$ for a 98% VOC removal. For the catalytic incinerator, a temperature slightly higher than the recommended was required to reduce the VOCs to within the legal limits. A higher temperature would damage the catalyst. The cost evaluation of the incinerators was performed using the *EPA Air Pollution Control Costs Manual* (Mussatti, 2002). The results are reported in Table 1 as UA (University of Aveiro) and compared to the data by two vendors. A fair agreement was obtained between the estimates produced and the vendors' quotations.

The adsorption process

During the adsorption process the gas molecules pass through a bed of solid particles, commonly activated carbon, and they are selectively removed from the gas

Table 1. Comparison of the costs for thermal and catalytic incineration estimated in this work (UA) with the values provided by two vendors.

	Catalytic incinerator *UA*	Thermal incinerator *UA*	Thermal incinerator *Vendor A*	Thermal incinerator *Vendor B*
Total capital investment	222,000	221,000	165,000[a]	172,000[a]
Annual costs	11,500	43,240	—	—

[a]Equipment cost. Total costs are 1.6* equipment cost according to Mussatti (2002).

stream. In a fixed bed unit the VOCs can be reduced to levels as low as several ppbv's. The adsorbed compounds can be removed from the adsorbent by heating, usually using steam, or by reducing the pressure allowing for the recovery of the solvent in the process as required. A continuous process is used that employs two carbon beds. One of the two beds is adsorbing at all times, while the second is regenerating. As the adsorbing bed is saturated, the flow is changed between the beds and the first bed starts the desorption process using steam. The steam-xylene mixture is condensed and the liquid decanted to recover the hydrocarbon while the water is treated. The main drawback of this process was the requirement of steam and cooling water that were not available in the process. As previously, the *EPA Control Costs Manual* (Mussatti, 2002) was used for equipment dimension and cost estimation.

The Freundlich isotherm has been used to describe the absorption of xylene on activated carbon:

$$w_e = 0.527\, P^{0.0703} \qquad (1)$$

The column dimensions, which are reported on Table 2, were calculated based on a saturation time of eight hours estimated from alone the equilibrium capacity of the activated carbon.

The kinetic effects due to the mass transfer were introduced in the project by estimation of the mass transfer zone (MTZ) using the Klikenberg equation (Seader and Henley, 1998). A column with the characteristics reported in Table 3 is required for the adsorption. A comparison with the project data obtained from several vendors is also reported. A general agreement was obtained. Using the correlations proposed by Mussatti (2002), the costs of the equipment and process operation can be estimated. A comparison between the costs estimated in this work (UA) and the budgets obtained from different vendors are shown in Figure 1. The estimations agree within 10%. The annual operation costs for the adsorption process are of about €20 000.

The Product Engineering Approach

The consideration and evaluation of the processes presented above represent the classical chemical engineering approach, a process engineering/design project. This approach is by no means the sole way of achieving the removal of xylene from the effluent. A product engineering approach (Cussler and Moggridge, 2001) may provide an alternative solution to the problem: the design of an improved coating formulation to completely remove the solvent from the process instead of cleaning the solvent from the effluent.

The solutions envisaged based on this approach aim at replace the xylene used in the initial formulation by a harmless and cheap solvent such as water. The problem is then to find an efficient and environmental acceptable dispersant for zinc stearate in water that would not affect the coating process or change the final product specifications.

Zinc stearate is a compound that is essentially insoluble in water. It is widely used for coatings or as additive in polymers and concrete. It is typically available as a thin free flowing white powder, hardly wettable. Nevertheless, aqueous dispersions of zinc stearate using various formulations are reported, especially in the patent literature (Hill and Flynn, 1987a, b; Hou and Hui, 1991; Kosal, 1993; Malloy, 1993; Flynn *et al.*, 1996). These aqueous dispersions are produced using different dispersion agents or complex formulations.

Most of the dispersing formulations previously proposed are based on PEG and PEG esters that are liquid at ambient temperature. Attempts to reproduce and test PEG based dispersant formulations reported in the literature were undertaken but they were not very successful. It was found that due to the low HLB value of these dispersants the dispersions were difficult to prepare requiring large amounts of dispersant and had high viscosities. As shown in Figure 2, this approach presents problems also on the coating behaviour of the dispersion. The large amounts and the characteristics of the dispersant used to prepare the dispersion change the coating characteristics. The dispersant did not allow for a homogeneous fusion of the zinc stearate preventing the formation of a good coating.

Following these initial efforts based on formulations previously proposed in the literature, a number of nonionic and ionic dispersants of high HLB values were studied with different degrees of success. The dispersants and dispersant blends were selected on two steps. A first step was based on their HLB values and the dispersants were screened using as parameters the stability of the dispersion, its viscosity and rheological characteristics, the quantity of dispersant required for a stable dispersion, the foaming, the commercial availability of the dispersants and their costs. The dispersant blends selected after this initial screening were further studied concerning their coating ability. From the successful dispersant blends studied one, hereby named DFA, based on a dispersant provided by Univar Iberia S.A. was adopted. This formulation, using low price commercially available dispersants, allows the preparation of

Table 2. Adsorption column dimensions based on the equilibrium conditions.

Activated carbon, kg	550
Column volume, m^3	1.14
Column diameter, m	1.83
Column height, m	0.41

Table 3. Comparison of the dimensions of the adsorption column designed in this work (UA) with values provided by three vendors.

	UA	Vendor A	Vendor B	Vendor C
Column diameter, m	1.9	2	2	1.9
Column height, m	2.3	2.2	2.5	3.2[a]
Activated carbon, kg	980	1000	1200	750

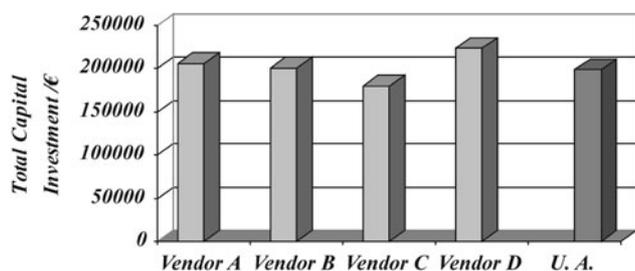[a]This value is for the total column height including connections.

Figure 1. Comparison of the total capital investment estimates for an adsorption equipment for xylene recovery from the gaseous effluent.

an aqueous dispersion of zinc stearate with only a minor quantity of dispersant. A 20 wt% dispersion of zinc stearate could be achieved at ambient temperature with less than 0.1% of the DFA blend. Its viscosity was within the coating equipment specification and the coating tests conducted produced excellent results, the final product being shown in Figure 3. The DFA formulation allows a uniform distribution of the stearate on the surface of the fabric and a perfect fusion of the zinc stearate producing an excellent coating. The coating capabilities of the new formulation were indistinguishable from the original. Moreover, industrial tests on the final product showed that its behaviour was fully acceptable and within the mechanical specifications for the product.

THE SELECTION: COMPARISON OF THE SOLUTIONS THROUGH AN ECONOMICAL ANALYSIS

The total capital investment for both equipments studied, incineration and regenerative adsorption, was similar and
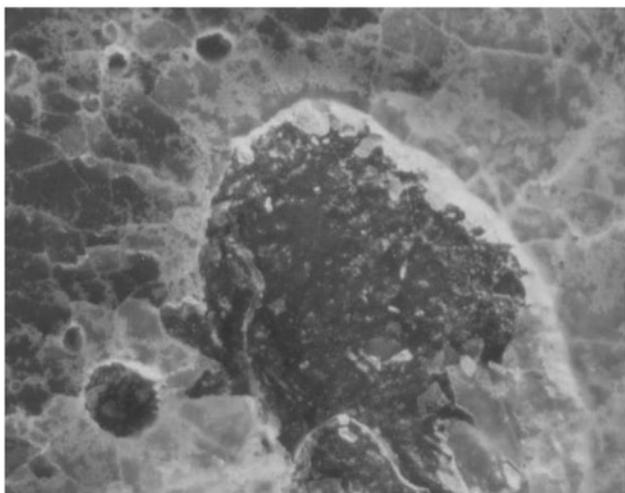

Figure 2. Zinc stearate coating using a dispersion based on a PEG dispersant. The dispersant remains at the surface producing a poor coating.
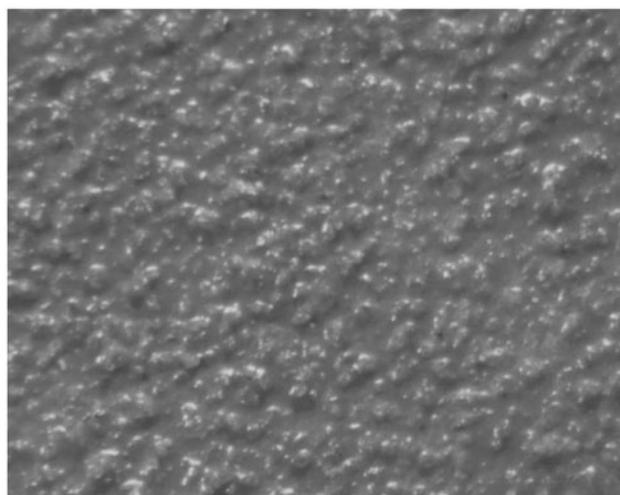

Figure 3. Zinc stearate coating using a dispersion based on the DFA formulation.

the annual operation costs for the adsorption process are only slightly higher than for the catalytic incineration. However, adsorption provides a more reliable and efficient removal of the VOCs from the effluent, and additionally allows for a recovery of the solvent. Thus, incineration was not considered further. Table 4 provides an economical analysis (Peters and Timmerhaus, 1991) for the adsorption process. This analysis demonstrates excellent indices that would allow for a return-of-investment of 35% and a payout period inferior to three years.

An economical analysis (Peter and Timmerhaus, 1991) for the new formulation using the dispersants blend developed is reported in Table 5. It shows that this new water-based formulation allows for a reduction of the annual and capitalised costs to half of its previous value with the complete elimination of the use of xylene on the process and VOCs on the gaseous effluents.

CONCLUSION

Chemical product design/engineering concepts provided, in this particular case, a solution that meets the

Table 4. Economical analysis for the installation of an adsorption process for xylene recovery from a gaseous effluent.

Total capital investment, €	200 000
Net present worth, €	150 000
Rate of return on investment, %	35
Payout period, y	2.8

Table 5. Comparison between annual and capitalized annual costs for the original xylene-based formulation and the new water-based formulation.

	Original formulation/€	DFA formulation/€
Annual costs	150 000	70 000
Capitalized annual costs	90 000	40 000

needs of a coating process imposed by new environmental legislation. The whole concept relies on looking back to the product rather than try to separate/remove the VOCs from the process. In this way, by changing the formulation used the same objectives are achieved at lower cost and without changes in the process. The chemical product design approach provides, in this case, a viable alternative to traditional process engineering approaches and it is not only economically advantageous but also very much environmentally friendly.

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