The Technology of Catalytic Oxidations 1

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Chemical, catalytic & engineering aspects

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1

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To our wives Anne, Elena and Meri for patience, love and support.

It is sincerely hoped that the second volume of this book will help to prevent chemical plant and laboratory accidents and will contribute to a much safer future. However, the reader assumes all liability for damage, injury or loss to persons or property arising out the application of any information provided by the authors in this volume. The authors cannot accept liability whatsoever for the consequences of its use or misuse by anyone.

FOREWORD

Having had dealings with oxidation with mixed degrees of success in my early days in the world of industry and with the hindsight I have after 40 years' work, I now see oxidation as one of the most complex and trickiest research sectors in petrochemistry. Indeed, it includes a combination of difficulties of all types but, because of this, it opens up for investigation a vast field that is still relatively unexplored and offers a potential for considerable improvements to be made.

Hydrocarbons have physical and thermodynamic properties that are now fairly well known and the reaction mechanisms in which they play a part to generate substances with the same atomic nature appear, at first sight, to be satisfactorily mastered. But, in fact, the situation proves to be completely different when one or more heteroatoms are involved. This is particularly true in the case of oxygen. In this case, the problems encountered, in terms of both their severity and their diversity, are such that we may sometimes even find them almost dissuasive. On the other hand, they may attract the brightest and most enterprising researchers to turn their attention to the study of a field that offers a great wealth of innovative opportunities.

Without pretending to be exhaustive but with the sole purpose of drawing attention to the degree of complexity characterizing the process of the oxidation of hydrocarbons, in which the constraints of tonnage production and extremely strict requirements in terms of quality and safety must constantly be reconciled, it would appear to be instructive to list, as far as possible, the main demands or difficulties we face in this field of work:

- Great diversity and multiplicity of chemical species involved
- Incomplete knowledge of the physicochemical and, above all, thermodynamic properties of constituents (consistency, reproducibility of information)
- Practically constant deviations from the ideal situation
- Complex kinetics with strong competition between consecutive and parallel reactions
- Wide variety of catalytic systems with regard to the nature and number of species concerned as well as their conditions of implementation
- Tricky management of operating parameters
- Diversity and complexity of reaction equipment:
  - control of exothermicity, procedures for heat removal and regulation of the temperature in the reaction medium

  - compromise between selectivity and conversion per pass
  - rigorous procedures for starting up and shutting down installations (avoiding the flammability domain, inerting, etc.).
- Elimination of used catalytic species and regeneration
- Numerous, varied and often difficult separation of products with frequent occurrence of azeotropes and eutectics, and risks of explosion or flame propagation
- Complex and tricky purifications requiring specific or sophisticated equipment
- High-quality of materials used: highly alloyed steels, refractory coatings, etc.
- Complex validation of procedures. especially on the basis of tests conducted on final products (coloring of fibers for example, stability, mechanical properties, etc.)
- and so on.

It would certainly be tedious to make this list any longer as it already includes a good many problems which. in spite of immense progress achieved over recent decades and full-scale experiments carried out on industrial sites, remain unsolved in many instances owing to the fact that the underlying fundamentals are still a long way from being mastered or even. in some cases, identified.

To illustrate these points and, at the same time, to demonstrate their practical reality, I will relate an especially revealing actual experience which ended in failure and shows how apparently small variations in operating conditions can sometimes lead to a series of practically insurmountable difficulties. This example concerns the production of pure terephthalic acid by oxidation of *p*-xylene in an acetic medium.

Without going into all the details or fully describing all the problems associated with this transformation, I will focus on only one of the main parameters governing the process: temperature, while emphasizing the necessity, in this case, of ensuring rigorous control by restricting its variations as far as possible. Even before we tackle the subject in hand, everyone knows how tricky it is to regulate a highly exothermic reaction. Furthermore, this explains from the outset why special protective measures are often taken in this context. In the circumstances, questions of industrial property become paramount as it is enough to simply patent a range of possible variations in order to secure a near-monopoly on production for several years. In the final analysis, as proved further on in this preface, failures encountered are often related to those considerations alone.

Indeed, in the case of direct oxidation of *p*-xylene in terephthalic acid, the optimal selectivity is obtained in the vicinity of 195°C, and acceptable deviations around this value are within a range of 50°C, between 175 and 225°C. Above that temperature, the hydrocarbon molecule is broken down into carbon dioxide and water. Below that temperature, the transformation is partly stopped at intermediate degrees of oxidation, which adversely affects the global efficiency of the operation and, above all, generates impurities which are difficult to eliminate. This is the case for *p*-toluic acid and 4-carboxybenzaldehyde, the production of which increases when the temperature is moderated. In fact, this is a crucial point if it is decided to operate below a temperature of 175°C in order to steer clear of patented operating conditions.

The above-mentioned aldehyde is known to be a sequestering agent acting on metals such as nickel, a property which has been harnessed in the color-based detection of the presence of the corresponding ions. The drawback is that steel in equipment used in industry, with a high alloy content to satisfy anticorrosion requirements, contains a lot of nickel. This nickel is complexed by the 4-carboxybenzaldehyde and produces substances with a high coloring power which then appear in the end product, i.e. the fiber, and which make the end product unsuitable for marketing even in minute quantities. This also explains why the acceptability of a procedure depends on extremely elaborate and laborious tests that can only be conducted on a full-scale basis by the polymerizing unit.

Consequently, commercial specifications generally limit the content of 4-carboxybenzaldehyde to 50 ppm in what is described as pure terephthalic acid whereas, on outlet from the reaction vessel, this content level is in the region of 2 000 ppm at best. We can already appreciate the degree of complexity of the purification operations to be implemented, in the light of the performances required to achieve a result of this type in a highly diluted medium. But, what is more, the problem becomes even more complicated when, in particular, we take the following two additional factors into account.

Firstly, *p*-toluic acid is an intermediate in the formation of 4-carboxybenzaldehyde which gives rise to the solution proposed to eliminate the aldehyde by carrying out a reverse transformation, which in this case is selective hydrogenation. Even so, *p*-toluic acid is a troublesome impurity as, over the course of time, it can be reoxidized. It must therefore be removed until only very small residual content levels remain.

The treatments are then mostly conducted in solid mediums. In this way, the *p*-toluic acid is removed by dilution in pressurized steam. This process of washing the crystals of terephthalic acid is all the more efficient when the contact area is restricted, i.e. when the mother liquor containing the *p*-toluic acid wets the solid particles less. In other words, the cooling and crystallization conditions must ensure that a sufficiently great average crystal size is reached (150 μ) in order to limit the overall wetting area.

Cases equivalent to this example are found in many other transformations involving oxidation and, even though even this brief description may make it appear tedious, it at least has the merit of showing that, in this field of chemistry, a situation can quickly become technically and economically insoluble as soon as we stray from what are considered to be the optimal operating conditions. It also shows how important it is, before undertaking to market a procedure, to be well informed of the main traps that may be lying in wait.

To complete this foreword, I cannot resist the temptation of relating an anecdote concerning the troubles besetting the industrial construction of an installation for the production of acetic acid by oxidation of a light hydrocarbon. Apart from the many coproducts produced by this process and which have the effect of increasing the number of distillation operations to be performed in order to separate them, I would just like to mention two points. Firstly, the problems raised by the effects of corrosion led to the choice of copper as the material to be used. Secondly, in spite of the number of high plates, the diameters of the columns had to be small owing to the quantities to be processed. The

consequence of these two constraints, which was unexpected at the time, was that it proved necessary to undertake the extremely laborious task of finding and training people small enough to perform the brazing operations required to fit the internal equipment.

I think I have placed enough emphasis on the extent and variety of difficulties that can arise when using oxygen and which make it hard to fully master industrial processes. Indeed, this situation is reflected in the levels of global efficiency achieved which often remain modest unless roundabout means are used (such as hydroperoxydes). Nevertheless, it would be wrong to conclude that this field is without interest. On the contrary, the current state of knowledge is still unsure enough to leave a great potential for improvements to be made on all levels: physical, chemical, technological, metallurgical, mechanical and so on. Indeed, this may be one of those rare fields in the production of major petrochemical intermediates in which creativity and innovation have a full part to play and in which progress in mathematics and information technology will provide the means of dealing fully with problems that were previously insurmountable because they were too complicated or were governed by too many parameters, and in which the need for relevant and consistent data is glaringly obvious.

With this in view, the book written by Professors Trifirò and Cavani, along with Mr. Arpentinier, is most timely and will be found to be invaluable. It clearly responds to a demand in a fast-developing sector where competency is hard to come by. With more than 700 pages divided into two volumes, it is complete enough to constitute a reference work reviewing the current state of the art on a good many important questions in the field of oxidation. Planned in the manner of an encyclopedia, it is likely to appeal to a very wide readership and to cater for the needs in universities as well as in industry, of general readers as well as specialists, and of researchers as well as technicians.

This very full summarized work covers, on the one hand, fundamental aspects, particularly in terms of reaction mechanisms, regarding both transformations that are actually desired and their conditions of implementation and parasitic degradation phenomena which often have disastrous consequences in the field of oxidation (secondary reactions, self-ignition, deflagration, explosions, etc.). It also deals with technological questions regarding equipment, its design, its performances, its installation and its integration into the industrial environment. Here, again, the subject is examined on a number of levels with, in particular, one part emphasizing production aspects and another dealing with questions of the prevention of the risks of divergence which are inherent in all installation operating modes. Indeed, these two facets of the problem are so essential that the authors have divided these subjects between two separate volumes. This overview would not be complete if I did not wind up by mentioning the authors' determination not to overlook various other less scientific or technological aspects of the subject, such as economic or logistic aspects.

On examining this work and in view of the comments I have already made, one feature seems to be especially positive with a view to practically satisfying readers of a wide variety of types where each one requires suitable answers to specific questions. This feature is the division of the work into two volumes, the first dealing more specifically with matters concerning the transformations themselves and the second focusing on questions of

prevention and safety. This makes the work easier to read or consult by allowing readers to turn straight to the sections they are interested in and, as I have already said, this increases the work's suitability as a reference book.

In short, although there is no doubt that the oxidation field is turning out to be one of the most promising for the future offering a wealth of potentials of all types owing to the diversity of related subjects, it also appears that there are practically no high-quality works in this field that are sufficiently summarized and yet complete enough to satisfy demanding readers. We can therefore quite justifiably be grateful to Professors Trifirò and Cavani, and to Mr. Arpentinier, for having tackled this difficult task and thank them sincerely for their hard work in seeing it through. All that remains is to wish them the success they deserve in bookshops. For my part, I feel it is a great honor to have been asked to write this foreword.

Rueil-Malmaison, in December 2000

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PREFACE

Nearly all the monomers, intermediates and solvents employed by the petrochemical industry are produced starting from raw materials obtained via the well-known processes of steam cracking, fluid catalytic cracking, catalytic reforming and dehydrogenation of paraffins. The majority of all high-volume organic chemical intermediates is manufactured by direct oxidation of a hydrocarbon substrate. The significance of oxidation technology is readily apparent in more than 50% of all chemicals produced world-wide involving selective oxidation processes and this situation is likely to persist for at least the next two decades. Many of these processes have been in commercial operation and improvements in processes and catalysts are always in progress. The cycle of development in the chemical industry, like in that for most technologies, is similar to an S-shape curve. In the relationship between performance and effort, there is an initial period where extensive effort leads only to modest improvements in performance; after this period comes a period of rapid development which is then followed by the achievement of a certain degree of technological maturity. It can be expected, however, that during this final period significant technological innovations will be possible when effort is applied in the following directions:

- Creation of a point of discontinuity in the S-curve, with the insertion of a second curve as a result of substantial modifications of the technology, such as the use of new raw materials or catalyst or the development of new process technology and/or new machinery and equipment.
- Advent of new requirements and demands: the need for processes with less environmental impacts (lower emissions of gaseous pollutants, less liquid waste and less risk related to possible accidents and injuries) or for products with less contamination necessary to produce higher quality polymers.

Particular methods of intervention within each of these innovative directions have been developed since the 1980s in the catalytic oxidation field:

- Use of paraffins rather than olefins: it appears that, in the future, the petrochemical industry will be based on the direct use of paraffins, an even more economical raw material which can be obtained both from petroleum and natural gas.

- Processes based on the use of oxygen together with recycling the unconverted reactants, rather than air without recycling.
- Oxidative dehydrogenation rather than simple dehydrogenation.
- Development of new catalytic systems.
- Use of heterogeneous catalysts rather than homogeneous catalysts.
- Lowering costs by new engineering of the process.

The purpose of this book is, firstly, to cover most important chemical, technological, engineering and safety aspects associated to the use of molecular oxygen for catalytic oxidation reactions and secondly, to report some examples of technological innovations which have been achieved in recent years, to describe efforts presently in progress by industries producing monomers and intermediates, and to point out the various incentives for these developments.

The book has been organised into two volumes concerning respectively the chemical, catalytic and process aspects and the safety aspects of catalytic oxidation technologies . The first volume covers most important technological aspects associated to the use of molecular oxygen for catalytic oxidation reactions. Particular attention is devoted to the following aspects:

- Chemical and chemical-physical aspects associated to the activation of molecular oxygen.
- Overview of the main oxygen production technologies and oxygen distribution ways.
- Engineering aspects associated to the design of reactors for monophasic and multiphasic catalytic reactions.
- Technical aspects associated to the choice of the best operative conditions in catalytic oxidation reactions.
- Comparison of advantages and disadvantages in the use of either air, enriched-air or pure oxygen as the oxidizing agent, or ballast components other than nitrogen.
- Overview of the main industrial processes of catalytic selective oxidation of hydrocarbons; focus is given to those aspects which address the choice to the use of either air or oxygen as the oxidizing agent.
- Review of some industrial oxidation processes in the gas and in the liquid phase, either with oxygen or with other oxidants. These processes well summarise the chemical, technical and engineering aspects related to the use of oxygen in catalytic processes, as well as to the choice of the oxidizing agent and reaction conditions.
- Analysis of most recent developments in the field of selective oxidation of light paraffins, for the production of either olefins or oxygenates, as new raw materials alternative to traditional feedstocks based on olefins and aromatics.

The second volume of the book is dedicated to the safety aspects associated to the use of oxygen in catalytic oxidation reactions. The imperatives regarding the safety of industrial processes require precise knowledge of the flammability limits or, even, the detonability limits of the reactant mixtures used in operating conditions, and full comprehension of certain theoretical notions regarding the ignition of gases and vapors by an external energy source, on the one hand, and spontaneous ignition, on the other. Unfortunately, there is generally a lack of data when dealing with mixtures in non-standard temperature and

pressure conditions and when those mixtures are located in specific geometric conditions imposed by the industrial system. It is for that reason that the aim of this volume is to state certain theoretical notions regarding chemical explosions in general, the flammability of gases and liquids and spontaneous ignition, in particular. Furthermore, the detailed analysis methods of the inherent factors and dangers which can upset the course of a chemical reaction which are the basis for defining operating instructions and preventive measures ensuring the safety of a chemical process are briefly presented.

This book has not been written with any particular audience in mind. Different readers may find different parts of it of interest. Thus, this book addresses itself to a wide range of readers. We expect that engineers engaged in development, conception, design, installation and operation of oxidation processes should appreciate the chemical, catalytic, process and safety aspects developed in the book. We hope it will be useful for chemists and chemical engineers of both industry and academy who work in the field of catalytic oxidation. Moreover, it can be a text of reference for students attending university courses of industrial chemistry, of chemical reaction engineering and of safety aspects in the chemical industry, since general problematic concerning oxidation reactions are here examined.

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Philippe Arpentinier

CONTRIBUTION OF THE AUTHORS

P. Arpentinier	Chapters 1, 3, 5, 9, 10, 11, 12, 13, 14, 15
F. Cavani	Chapters 1, 2, 4, 5, 6, 7, 8
F. Trifirò	Chapters 1, 2, 4, 5, 6, 7, 8