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The contribution of homogeneous reactions in catalytic oxidation processes: safety and selectivity aspects

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Abstract

After a brief summary of the main aspects concerning the formation and ignition of flammable mixtures, attention is given mainly to: (i) the identification of risk location in oxidation processes; (ii) how homogeneous phenomena may affect the products distribution in heterogeneously catalyzed gas-phase oxidations; (iii) how the flow regime in the oxidation reactor can affect the flammability limits of the process gas; (iv) the preventive measures for minimizing selectivity degradation and maximizing safety in oxidation processes.

Keywords: Catalytic oxidation; Oxygen; Inert gases

1. Introduction

In an industrial concept based on an ethic and a rational economy, safety is a basis that is essential to the control of any production in the industrial field, in general, and in the chemical sector, in particular. Any progress regarding production techniques automatically entails an improvement in safety. It is also true, however, that an improvement in the safety of an operation defined in the context of a production cycle will generally constitute an improvement in the cost-effectiveness of the production facility. Furthermore, it should never be forgotten that any accident, with the human, material and moral damage it entails, generates costs that are generally far higher than those entailed in rational safety and accident prevention.

Until the end of the 1960s, the traditional approach to safety was based essentially on experience and that experience was expressed in the form of legislation, regulations, recommendations and instructions. Another approach was based on the analysis of possible failures and their consequences, using lists of points to be checked and the imagination. By drawing comparisons with other known incidents, it was known that a given process could involve certain drawbacks. Two types of measure were adopted: (i) avoiding the occurrence of dangerous situations; (ii) limiting the effects of an accident and providing better protection for personnel and equipment. These methods proved their efficiency in both the chemical industry and the oil industry, the latter benefiting from a considerable decrease in accident statistics by implementing the same products and processes in many refineries.

In the chemical industry at the present time, the goal to be achieved will be to develop industrial manufacturing processes and build production facilities satisfying the following requirements:

- maximum safety (by means of prevention and protection);
- minimizing of capital investment and operating cost;
- maximum performances (yield);
- desired product quality with specifications defined according to product use downstream;
- adaptation to statutory environmental constraints (gaseous effluents, liquid discharges, toxicity).

In order to meet these requirements, the chemical industry has undergone gradual change in recent decades and its development has made a major contribution to increasing the complexity of installations and the range of products used in sometimes unusual operating conditions.

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Oxidation processes have developed in the same way, along with other processes. They represent a large proportion of chemical processes, since more than 50% of the chemical products manufactured in the world are produced by means of an oxidation process. New raw materials or reactants are used (such as alkanes, which are increasingly studied as alternative raw materials) and, moreover, although air was still the most commonly used oxidizing agent a few years ago, the use of pure oxygen or air with a highly enriched oxygen content as the reactant in the main manufacturing processes in the chemical industry has greatly increased since the 1970s.

All the concepts concerned with the properties relative to the formation of flammable mixtures (lower and upper flammability limits, maximum oxygen content) and with the properties relative to the ignition of flammable mixtures (autoignition temperature, temperature of cool flame formation, minimum ignition energy) are particularly useful in the chemical industry, in general, and for the study of catalytic oxidation processes, in particular. Indeed, knowledge of flammability properties for the mixtures involved in process flows (reactants, products, recycling, etc.), allows conclusions to be drawn regarding the following:

- Risk evaluation and means of prevention and protection to be implemented.
- The contribution of fuel oxidation and/or combustion in the gaseous phase to the degradation of desired product selectivity, i.e. the fraction of reactant and product consumed by homogeneous combustion in the gaseous phase. Indeed, of the total quantity of reactant converted, the greater part may be transformed into products by catalytic reaction, a second part is transformed into secondary products, water and carbon dioxide in the catalytic phase (solid or liquid), and a third part is transformed by the parallel homogeneous reaction into combustion products (water, hydrogen and carbon oxide) in the gaseous phase. This may occur in the gas overhead or in the gas bubbles in the case of a gas/liquid reactor and in areas free of catalyst in the case of a gas/solid catalytic reactor (in the gas bubbles of a fluidized bed or in areas of reactant distribution, and product release and recovery).

In this paper, after a brief summary of the definition of the properties relative to the formation of flammable mixtures and the properties relative to the ignition of flammable mixtures, attention is focused on the following: (i) identification of risk location in oxidation processes; (ii) how homogeneous phenomena may affect the products distribution in heterogeneously catalyzed gas-phase oxidations; (iii) how the flow regime in the oxidation reactor can affect the flammability limits of the process gas; (iv) preventive measures for minimizing selectivity degradation and maximizing safety in oxidation processes.

2. Flammability properties of gaseous mixtures

It is possible for a given gaseous mixture (fuels, oxygen and inert compounds) to plot a curve in the temperature–pressure plane that will separate the autoignition domain from the domain in which no explosion will occur (Fig. 1). During autoignition of hydrocarbon compounds, several types of macroscopic phenomena may occur [1–4]:

- *The domain of normal explosions* (Fig. 1c): normal explosions occur at high temperatures (in the order of 400 °C and higher), they produce a lot of energy and result in almost total combustion. In a confined environment, they bring about a pressure increase to between 6 and 10 times the initial pressure. They are easily visible and of blue or yellow colour, according to the concentrations and pressures involved.
- *The domain of multiple cool explosions(or flames)* (Fig. 1a) at low pressure and low temperature (250–350 °C), the autoignition domain is characterized by the presence of cool flames with a domain located between that of slow oxidation and that of explosions. This cool flame domain is located in the area of low pressures (from 0.5 to 5 bar abs depending on the equivalence ratio of the mixture), at temperatures that are several hundred degrees lower than those at which normal explosions occur, and at high fuel/oxidizer relative mixture strengths.
- *The domain of normal second-stage explosions* (Fig. 1b): normal second-stage explosions, or two-stage explosions, are produced in the temperature domain of cool explosions and begin in mixtures disturbed by the accumulation of products of the first cool flame and slow reaction; this type of explosion is caused by the first cool flame.
- *The domain of long ignition delay flames* (Fig. 1d): the low pressure and high temperature region shows three successive limit pressures because of the duration of the induction period, this domain is known as the long delay

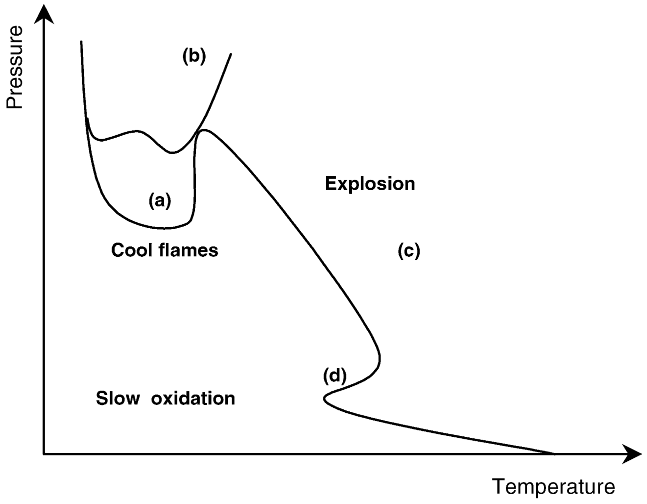

Fig. 1. Isochore diagram of autoignition of hydrocarbon/air mixtures.

autoignition peninsula. It is caused by the accumulation of hydrogen and carbon monoxide produced during the slow reaction and that are then at their ignition conditions; ignition occurs only after the initial fuel has been totally consumed.

A mixture that is too weak (equivalence ratio lower than the level corresponding to *Lower Flammability Level*) or a mixture that is too rich (equivalence ratio higher than the level corresponding to *Upper Flammability Level*), in other words, a mixture with a composition that is not within the flammability domain, can be locally ignited by the action of a sufficiently powerful energy source but the flame, which remains localized in the vicinity of the source of ignition, cannot maintain itself and will be quickly extinguished if there is no constant supply of energy.

The flammability limits are magnitudes that depend on the constituents of the mixture (oxidizer, fuel, inert gases), the dilution (oxygen/oxygen + inert gas ratio), the initial pressure and temperature, the acceleration to which the mixture is submitted (higher or lower than or equal to acceleration due to gravity) and the ignition criterion used to detect them experimentally. It is possible to draw a diagram indicating the ranges of composition for which the mixture is flammable. Generally, the diagram used to represent the flammability domain of a combustible mixture is a three-axis system (Fig. 2), with the axes representing the concentration expressed in terms of the percentage by volume of fuel, oxygen and inert gas, respectively. The maximum permissible oxygen concentration or content, which is also referred to as the nose of the flammability domain or maximum oxygen content (MOC) of a fuel/inert/oxygen mixture, is the maximum concentration of oxygen in the mixture below which no ignition will occur whatever the concentration of fuel. This is expressed as the concentration by volume of oxygen in the complete mixture or by the O_2/(O_2 + inert gas) ratio for the mixture.

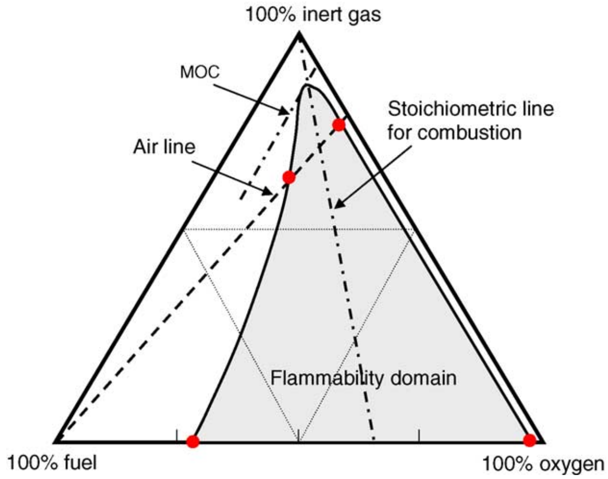

Fig. 2. Ternary diagram of flammability at constant temperature and pressure.

3. Risk location in oxidation processes

The different stages of a selective oxidation process can be briefly classified as indicated in Fig. 3:

- storage, provisioning and preparation of raw materials or reactants and catalysts;
- implementation of the oxidation reaction itself in the reactor;
- separation of the reaction mass into its components, main product, unconverted reactants and products to be recycled in the reaction, by-products and waste;
- purification of the main product;
- treatment of gaseous effluents and residual water, and destruction or recycling of organic liquid effluents.

Each of these operations raises specific safety problems and, while the control of the chemical reaction itself calls for very special attention with regard to operating safety and accident prevention measures, particular attention has to be done at locations A–D indicated in Fig. 3:

- Point A: mixing of recycle stream and reactants make-up (oxygen, fuels and inert compounds) at reactor inlet conditions.
- Point B: in empty spaces of reactor (reactant distribution area, product recovery area, bubbles, slugs, vapour overhead in G–L reactor).
- Point C: reactor outlet stream (mixture of inerts, unconverted reactants, product and by-products, catalyst).
- Point D: recycle stream (mixture of inerts, unconverted reactants and by-products, before and after compression).

At these four points, the main risks are related to the possibility of formation of flammable mixture, i.e. mixture in a state of false thermodynamic equilibrium. These are

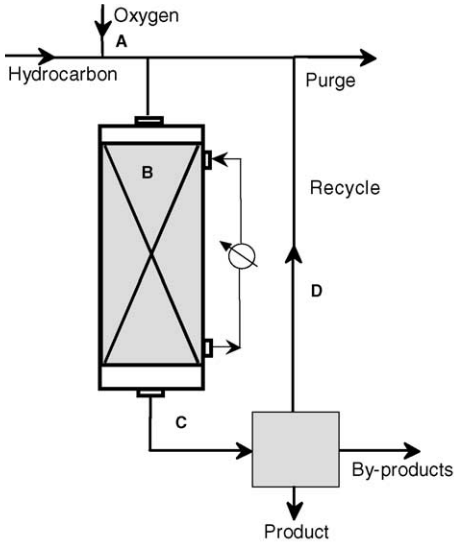

Fig. 3. The various stages of a typical oxidation process.

metastable mixtures as all that is required is an input of external energy, such as an electric spark, to trigger combustion reactions which can lead to a deflagration. Moreover, the operating temperature can be higher than the spontaneous ignition temperature or the temperature of formation of cool flame of the mixture in the relevant conditions (pressure, equivalence ratio, dilution, vessel volume and geometry). Finally, the possible formation of unstable compounds, such as ethylene oxide or peroxides, which, themselves, have explosive properties, has to be taken into account.

4. How homogeneous phenomena may affect the products distribution in heterogeneously catalyzed gas-phase reactions

Ensuring the safety of chemical processes operating under pressure and at high temperatures entails paying attention to the temperatures to which an explosive gaseous mixture can be raised or the temperature of the hot surfaces with which it may come into contact in a reactor, a heat exchanger or any other apparatus. In fact, these temperatures can cause autoignition of the reaction mixture. In the case of catalytic oxidation processes it is possible to choose suitable operating conditions so as to maximize selectivity with regard to the desired product, while avoiding temperatures that can lead to the autoignition of the explosive mixture.

The operating conditions (temperature, pressure and nature of reactants) of some large-scale catalytic oxidation processes are shown in Table 1. Generally it is always preferable to operate outside the flammability area at the reactor inlet (with an oxygen concentration below the maximum oxygen content of the mixture or with an hydrocarbon concentration below the lower flammability limit or above the upper flammability limit at inlet temperature and pressure conditions) and outside the autoignition pressure–temperature domain. But in some particular cases depending on the reactor technology implemented, gas–solid fluidized bed or gas–liquid reactors, and if the reactants are not premixed before the reactor but separately injected in it (for example, injection of the fuel directly inside the fuidized gas–solid bed), the operating conditions can be inside the flammability domain. Nevertheless, whatever the reactants are premixed or not, it should be kept in mind that (i) a small deviation of one of the operating parameters can lead to the formation of flammable conditions, (ii) during transient phases the system can be within the flammability domain and (iii) during normal operation, in some confined and generally well-controlled areas, the system can be flammable. That is the reasons why, phenomena such as cool flames, normal autoignitions or normal explosions are liable to occur on the reactor feed system, inside the catalytic oxidation reactor itself and at the product outlet, which contributes both to increasing the risk of explosion and to greatly degrading the desired product selectivity. In addition, it should be borne in mind that, apart from the reaction section, other sections of the process (separation, purification, recycling, and treatment of gaseous and liquid effluents, etc.) are concerned by gaseous mixture autoignition problems.

A second important aspect concerns the contribution of homogeneous reactions to products distribution in heterogeneously catalyzed reactions. The nature of products obtained in homogeneous oxidation of hydrocarbons is a function of temperature. Below say about 250 °C the reaction rate is practically nil, while at above 250 °C, after an induction period the reaction rapidly accelerates. When the temperature is increased above 250–300 °C, at atmospheric or higher total pressure, the conversion of the hydrocarbon is initially increased, but after a temperature level that is a function of the hydrocarbon type and of the pressure (approximately 250–350 °C) the overall reaction rate is decreased (negative temperature coefficient). Finally, after this intermediate temperature range (at above 400–450 °C), the rate of hydrocarbon depletion is again increased. At even higher temperatures (higher than 500 °C) (above the self-ignition temperature of the

Table 1
Operating conditions for various catalytic oxidation processes

Product	Reactants	Operating conditions	Technology implemented	Coproducts (other than CO_2 and H_2O)
Acrylic acid	Propylene, oxygen	300–400 °C, 1–3 bar	Gas/solid fixed bed	Acrolein, acetic acid, maleic acid, propionic acid, acetaldehyde, acetone
Acrylonitrile	Propylene and/or propane, oxygen, ammonia	400–500 °C, 1–4 bar	Gas/solid fluidized bed	Acetonitrile, hydrocyanic acid, carbon monoxide
Ethylene oxide	Ethylene, oxygen	230–290 °C, 10–30 bar	Gas/solid fixed bed	Acetaldehyde, formaldehyde
Formaldehyde	Methanol, oxygen	300–400 or 650–700 °C[a] 1–2 bar	Gas/solid fixed bed	Formic acid, carbon monoxide
Maleic anhydride	*n*-Butane, oxygen	350–500 °C, 1–3 bar	Gas/solid fixed bed	Carbon monoxide, acetic acid
1,2-Dichloro-ethane	Ethylene, hydrochloric acid, oxygen	220–300 °C, 2–6 bar	Gas/solid fixed bed and fluidized bed	Carbon monoxide, chloral, light chlorinated compounds
Terephthalic acid	*p*-Xylene, oxygen	175–230 °C, 15–30 bar	Gas/liquid CSTR (acetic acid solution)	Benzoic acid, *p*-toluic acid
Phthalic anhydride	*o*-Xylene, oxygen	350–450 °C, 1–3 bar	Gas/solid fixed bed and fluidized bed	Maleic anhydride, *o*-toluic acid, phthalide, benzoic acid, carbon monoxide

[a] Depending on the catalyst used.

hydrocarbon) hot flames are formed, provided there is yet oxygen available. The products distribution is correspondingly varied; in the low-temperature region, oxygenated products are the prevailing products (alcohols, aldehydes, ketones, acids and carbon oxides); in the intermediate temperature range, olefins predominate, while in the high-temperature range olefins of lower molecular weight are the prevailing products. When combustion and hot flames develop, the main products are carbon oxides and water.

The major difference between low and high temperature mechanisms is the relative importance of alkyl and peroxy radicals ($R^{\bullet}$ and $ROO^{\bullet}$). In the low temperature region, the variation of the rate of oxidation with temperature can be attributed to the fact that the reaction:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

is favoured at low temperature. Under these conditions, the alkylperoxy radical is the prevailing species, and chain propagation occurs by the reaction:

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

On increasing the temperature to the intermediate range, the reaction of alkylperoxide formation is less thermodynamically favoured, and the concentration of the $R^{\bullet}$ species increases. The negative temperature coefficient, that is the decreasing of the overall reaction rate with increasing temperature, is thus the result of the sudden reduction in peroxy radical concentration. Then, the rising importance of formation of olefin and $HOO^{\bullet}$ from alkyl radicals shifts the initiation process towards hydrogen peroxide which is a poor initiator compared with carbonyl- and alkyl-hydroperoxides. Thus, the rate of the irreversible reaction:

$$R_2CH{-}C^{\bullet}R_2 + O_2 \rightarrow R_2C{=}CR_2 + HOO^{\bullet}$$

increases, and the formation of the olefin becomes competitive with the formation of the alkylperoxy radical. Since H_2O_2 is more stable than the alkyl-hydroperoxide (the low-temperature chain-branching agent), it becomes the dominant branching agent and the generation of new radical species via the reaction:

$$HOOH \rightarrow 2OH^{\bullet}$$

is less efficient than the generation of radicals via the reaction:

$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet}$$

Therefore, the generation of new radicals is decreased with respect to the temperature range. A further increase in the temperature leads to the complete displacement of the reaction of $ROO^{\bullet}$ generation; the rate of decomposition of H_2O_2 (intermediate- and high-temperature chain-branching agent) is enhanced, with generation of new radical species. Decomposition reactions of alkyl radicals prevail on the direct oxidation and the high concentration of $R^{\bullet}$ species makes the reaction:

$$R_3C{-}CR_2^{\bullet} \rightarrow R^{\bullet} + R_2C{=}CR_2 \text{(alkyl radical cracking)}$$

becomes competitive for the formation of the olefin. Thus, at high temperature level, combustion process mainly proceeds through smaller olefins oxidation. It is worth noting that this mechanism for olefin generation does not require the presence of an H atom in the α position. When pressure is increased much above the atmospheric one, the region of decreased hydrocarbon conversion disappears, and the formation of olefins is suppressed; the formation of oxygenate compounds is preferred.

In recent years a significant interest has been directed towards the possibility of replacing the currently used raw materials, mostly olefins and aromatics, with cheaper and more environmentally friendly organic substrates like the alkanes [5–13]. But contrary to the case of olefins, homogeneous oxidation of alkanes with more than three carbon atoms proceed at temperatures similar to those of the heterogeneous catalytic reaction and these are relatively low. Fig. 4 (unpublished calculations based on [14]) represents the variation in the conversion of propane at 400 °C and 3.5 bar as a function of the relative mixture strength in air and in pure oxygen, for a residence time of 100 s. The greater the relative strength, the more the conversion is boosted, and it can reach values of more than 70 mol% for relative mixture strengths greater than 6 in pure oxygen whereas, in air, its variation is practically linear up to a value close to 37 mol% for a relative mixture strength of 10. Consequently, in the case of an oxidation reaction in which a catalyst is used, the main reaction will be in competition with the parallel homogeneous combustion reaction of the hydrocarbon reactant, especially if the latter is an alkane, which may contribute to severely degrading the desired product selectivity.

In general, the autoignition temperature of a mixture provides information on the temperature level as from which the mixture reacts and, consequently, the comparison of the limit temperatures of various mixtures can be used to classify them according to their reactivity. This classification is relatively unaffected by the operating conditions (volume, geometry, pressure, etc.) whereas the actual values of limit

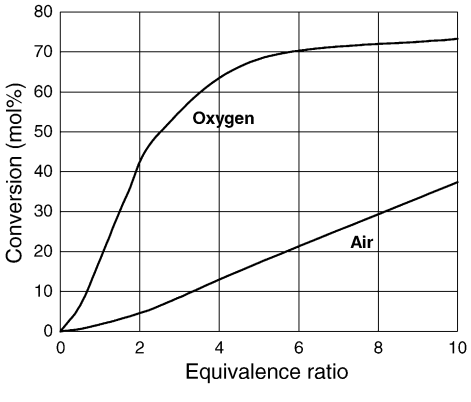

Fig. 4. Conversion of propane according to the equivalence ratio of the propane/air mixture or of the propane/oxygen mixture at 400 °C and 3.5 bar for a residence time of 100 s.

temperatures can show considerable variation according to these conditions. Knowledge of the autoignition temperature of a reactive mixture and of the products and coproducts liable to be formed in given operating conditions thus allow conclusions to be drawn regarding the oxygen consumption of homogeneous combustion reactions in the gaseous phase, and the possibilities of autoignition.

Homogeneous phenomena may remarkably affect the products distribution in heterogeneously catalyzed gas-phase reactions; indeed, often it is necessary to talk of heterogeneous–homogeneous reactions, which are initiated on the catalyst surface and may in part continue in the gas phase as free radicals chain reactions. These phenomena are known to be particularly important in the case of the oxidative coupling of methane on heterogeneous catalysts such as Li/Mg/O [15–17]. In these cases the homolythic dissociation of the C–H bond occurs as a consequence of the interaction with an heterogeneous oxidative center, with the generation of the $CH3^{\bullet}$ and of a surface OH group. The methyl radical is then transferred to the gas phase, where it continues the reaction homogeneously. The same phenomena affect the distribution of products in the oxidative dehydrogenation of light alkanes [9,18–20].

Fig. 5 (unpublished calculations based on [14]) gives a view of the significant influence that certain components can have, even in the state of impurities, on the homogeneous gaseous phase composition of propane in oxygen, at 3.5 bar and 400 °C, for a relative mixture strength of 2.5 and a residence time of 30 s. It is clear that the coproducts or by-products formed during the catalytic reaction, such as formaldehyde or acetaldehyde, are therefore liable to cause a non-negligible increase in the contribution of combustion in the gaseous phase to the degradation of the desired product selectivity. The addition of 2% of acetaldehyde or formaldehyde, respectively, to the propane/oxygen mixture increases the conversion of the combustion reaction in the homogeneous phase from 3.4 to 10 or to 26 mol%, respectively.

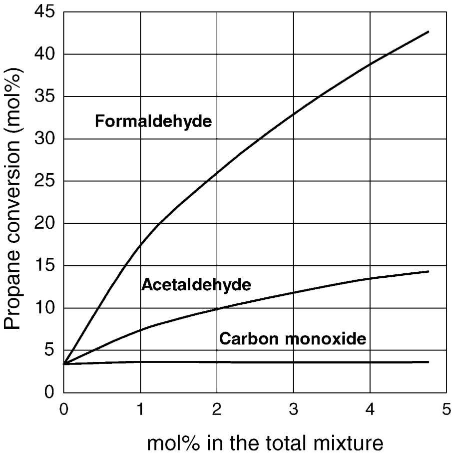

Fig. 5. Influence of acetaldehyde, formaldehyde and carbon monoxide on the conversion of propane in oxygen at 400 °C, 3.5 bar, an equivalence ratio of 2.5 and a residence time of 30 s.

In the case of gas/liquid reactors, it is preferable to have exact knowledge of the minimum temperature for the occurrence of cool flames and the autoignition temperature for each of the constituents that may appear in the gas overhead of the reactor and in gas bubbles, especially if the latter represent a large volume. For example, in the case of the process for the manufacture of terephthalic acid from *p*-xylene, the operating temperature and pressure are in the region of 200 °C and 20 bar, respectively; the solvent used is acetic acid and acetaldehyde can be present in the reaction environment. In these conditions, given that acetic acid has an autoignition temperature of 523 °C at 1 bar abs, of 378 °C at 6.8 bar and 299 °C at 34 bar, and knowing the influence that acetaldehyde has on the autoignition phenomenon, it is important to control the temperature and pressure in the reactor and avoid any degradation of the system ensuring injection, distribution and agitation of the gaseous mixture in the liquid phase that may cause a non-negligible increase in the size of the bubbles.

Finally, it can be concluded that in the study of heterogeneous oxidation reactions of the hydrocarbons in general and of the alkanes in particular, the interaction of both homogeneous and heterogeneous processes must be taken into account. The homogeneous oxidation contribution to the decay of the selectivity of the heterogeneous reactions can be minimized by:

- Operating at a temperature lower than the autoignition temperature or much better lower than the temperature of the occurrence of the first cool flame of the reaction mixture in the operating conditions (equivalence ratio, dilution, pressure, volume).
- Operating with a residence time lower than the ignition delay of spontaneous ignition or of the first cool flame.
- Correctly controlling the operating pressure to avoid a pressure increase which could drop the spontaneous ignition temperature of the reaction mixture.
- Using a catalyst selective enough in order to avoid the formation of homogeneous combustion promoters like acetaldehyde, formaldehyde and nitrogen oxides.
- Adding to the reaction mixture a substance with an established ability to suppress initiation of radicals to protect the hydrocarbon reactant against an oxygen attack in homogeneous phase.
- Operating with high flow rates to allow the increase of the mass transfer of reactants towards the catalytic surface by thinning the boundary layer. In such a way, also the diffusion of radicals formed in the gas phase towards the surface (which acts as a radical scavenger) is favoured, thus preventing chain propagation and undesired reactions in the gas phase, and hence lowering the gas-phase temperature. Moreover, high flow rates allow to minimise the residence time in the void volume of the reactor.

- Minimizing the volume of the empty space (areas free of catalyst) of the reactor and the residence time in it in the case of gas/solid catalytic reactors (fixed-bed and fluidised-bed): (i) in the gas bubbles moving through the dense phase of a fluidized bed, in areas of reactant distribution and product release and recovery; (ii) in the interparticle volume which defines the bed voidage in the fixed beds, because the autoignition temperature of a gaseous mixture decreases when the containing volume increases due to a smaller ‘‘wall’’ effect per unit of volume.
- Avoiding, in the case of gas/liquid reactors, any degradation of the system ensuring injection, distribution and agitation of the gaseous mixture in the liquid phase, that may cause a non-negligible increase in the size of the bubbles.

5. How the flow regime in the oxidation reactor can affect the flammability limits of the gaseous mixture

The presence of finely divided solid particles (e.g., catalyst particles) in the flame front can have a considerable influence on flame propagation and, in particular, can lead to a significant inhibiting action. Indeed, three different inhibiting effects can occur:

- Chemical inhibition: the presence of a finely divided solid increases the probability of heterogeneous recombination of radicals. As heterogeneous terminating reactions are favored, this contributes to decreasing the laminar burning velocity and, therefore, to narrowing the flammability domain of a given mixture of fuel and oxidizer. The effectiveness of inhibition depends on the nature of the surface of the solid particles, their shape and their porosity.
- Thermal inhibition: independently of any chemical inhibiting effect, solid particles can exert a significant influence by simply cooling the reaction zone. Indeed, heat is transferred from the gas to the solid and, because the specific heat of the solid is much higher than that of the gas, the mean temperature of the reaction zone is decreased and, on the basis of a preliminary approximation, this occurs without any significant change in the mean temperature of the solid particles.
- Inhibition by emission of inert volatile compounds.

Depending on the type of inhibitor, any one of these effects will be significant or all three may occur simultaneously [21]. The effect of inert particles on the laminar burning velocity and, thus, on the flammability limits of a gaseous mixture is especially great in the case of selective oxidation processes in the gaseous phase using a solid catalyst, as in fluidized-bed technology. Experimental studies concerning this subject have been published, dealing with mixtures of ethylene, oxygen and nitrogen in the presence of alumina particles [22] and mixtures of propylene, ammonia, oxygen and nitrogen in the presence of silica particles [23], and the various theoretical results mentioned above on the effects of inert solid particles on laminar burning velocity and flammability limits have been demonstrated. It should be noted that, according to the nature of the particles and the operating conditions implemented, the fluidization regime in the reactor used for these experimental measurements is homogeneous, or quiescent, fluidization: the superficial velocity of the gas is between the minimum fluidization velocity and the minimum bubbling velocity. In the range between these two velocity values, expansion of the bed is homogeneous and regular, and no gas bubbles are formed so that the mixture of particles and gas can be assumed to be perfectly stirred.

Different is the case for the bubbling fluidization regime and the slugging fluidization regime. For both these fluidization regimes, the bed is heterogeneous as it is made up of two separate parts: the phase described as dense, with a homogeneous mixture of particles and gas, and the bubbling phase (in the case of the bubbling fluidization regime) or the slugging phase (in the case of the slugging fluidization regime), which contains practically no particles and which carries the other part of the fluidizing gas. For a given type of particles, increasing the superficial velocity of the gas results in a switch from the bubbling fluidization regime to the slugging fluidization regime. This increase causes the coalescence of small bubbles resulting in the formation of bubbles with a diameter equal to that of the bed (slugs). It was demonstrated [22] that ignition is not possible in the dense phase whereas a flame can be effectively propagated in a slug and, moreover, the higher the gas superficial velocity is, the wider will be the flammability domain of the mixture. Indeed, the dense phase has a concentration of solid particles that is higher than the critical threshold that prevents flame propagation as it contains practically all the fluidized particles and only some of the gas while the initial particle concentration was already higher than the threshold value. On the other hand, slugs can be assimilated with a vessel containing a flammable gaseous mixture and it is for that reason that ignition is observed when a slug passes in front of the ignition system. When the fluidization regime was that of a bubbling flow, it appeared that the flammability domain was narrower in the bubbling flow regime than in the slug flow regime.

Since usually fluidised-bed reactors are operated in the bubbling or slug flow regime in many industrial applications, it is possible to be in the flammability domain in the bubbling phase or in the slugging phase whereas, in the dense phase, the particles exert an efficient quenching action. In the case of ignition in a bubble or in a slug of small size by an external energy source (hot spot, etc.), the pressure increase and temperature increase generated by propagation of the flame can generally be quickly damped by the dense phase so that the hazard involved is reduced but, in this case, the drawback is a degradation of the desired product selectivity.

6. Conclusions: preventive measures for minimizing selectivity degradation and maximizing safety in oxidation processes

Besides indications given above, other preventive measures for minimizing selectivity degradation and maximizing safety in oxidation processes have to be taken [24]:

- Avoiding adiabatic compression and shock wave which could lead to spontaneous ignition.
- Using properly design mixers at reactor inlet (mixing of fuels, inert compounds and oxygen) to minimize mixing duration and gaseous mixture inventory.
- Operate in such a way to reach as high as possible oxygen conversion to be outside the flammability range at reactor outlet conditions.
- Correctly controlling oxygen conversion inside the reactor.
- Choosing the best approach for reactor operation conditions in case of recycling of unconverted hydrocarbon and pure oxygen use: fuel-lean region: fuel content below the LFL in the recycle stream (adding fresh oxygen in the recycle is possible); oxygen-lean region: oxygen content below the MOC in the recycle stream (adding fresh hydrocarbon in the recycle is possible).
- Choosing the more inerting ballast according to purge to recycle ratio and recycle composition to reach one of the here above situation.
- Correctly control catalyst selectivity to avoid an increase in CO production and consequently an increase in CO content at reactor outlet and in the recycle stream (CO is a fuel which has a wide flammability domain).
- Correctly controlling the fluidization regime and bubbles or slugs size in fluidized bed reactors.
- Implementing control systems to check oxygen and fuel contents in areas and stream in which flammable mixture can be formed.
- Identification and control of ignition sources: flames and combustion products, hot surfaces and hot spots, electrical ignition sources (static electricity), physical sources of ignition (mechanical, shock waves), chemical sources (pyrophoric compounds, undesirable catalytic phenomena, unstable compounds).
- Preferring gas/solid fluidized bed reactor when reactor feed composition is near or inside the flammability range at reactor inlet conditions.
- Preferring CSTR and liquid loop reactors rather than batch reactor for liquid phase reaction.
- Using internal cooling system rather than external cooling systems.
- Using the best selective catalyst in the less severe operating conditions because, generally, the flammability bell is wider when the temperature and the pressure increase.

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