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Photocatalytic process intensification by coupling with pervaporation

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ABSTRACT

The integration of photocatalysis with a membrane separation process, in particular pervaporation, permits the recovery of valuable intermediate compounds (aromatic aldehydes) while they are produced avoiding their further degradation in the reactive ambient. In this way the yield and the conversion are enhanced. The coupling of the two processes is straightforward and the integration is complete even maintaining pervaporation and photocatalysis in two separate apparatuses provided that the process stream is continuously recycled at a sufficiently high flow rate. Additional advantages are: higher degree of purification of the aldehyde in the powder-free product stream, semicontinuous production and possibility of operating in a continuous mode with high values of the yield.

1. Introduction

In the past the capability of photocatalysis to oxidize many organic compounds has been largely investigated for the degradation of recalcitrant pollutants [1–3], but in the latest years the proposals of utilizing photocatalysis also for the synthesis of fine chemicals [4,5] are notably increasing. The main reason for this interest is that most of the photocatalytic syntheses achieve the "green chemistry" goals [6]. Nonetheless the engineering of these processes is still at the beginning and enhancements of the rate of production, of the selectivity and of the yield are required to make photocatalysis effectively practicable in this field.

In many cases the photocatalytic reaction involved in the synthesis is a "partial" oxidation, so that the desired product is actually an intermediate compound, which is often prone to degrade by further oxidation. This problem can be surmounted by recovering the product while it is formed, but this task can be accomplished only if the separation takes place in the reactive ambient. A "membrane reactor" [7–9] can be the solution if it satisfies some requirements: the membrane should preferentially recover the product and reject the reagents to keep them in the reactor, the operative conditions of the separation process and of the reaction should be compatible, the coexistence of the two processes should not hinder their rates, but on the contrary their coupling should possibly enhance these rates. In summary, a process intensification [10–12] should be obtained from the process integration [13] of reaction and membrane separation, but not all the proposed applications of membrane reactors meet this objective.

Some works consider the peculiar case of photocatalytic membrane reactor (PMR) [14–20], in which the reaction is photocatalytic, while other studies regard the special case of pervaporation reactor (PVR) [21–24], in which the membrane separation is the pervaporation. Pervaporation is a membrane process which permeates selectively through a non-porous membrane the compounds from a liquid retentate to a vapor permeate thanks to a solution-diffusion mechanism [25]. Among several applications, it is worth observing that it can be used for the recovery of aroma compounds from process streams [26–29] and for the removal of volatile organic compounds (VOC) from aqueous effluents [30–32].

Only one paper deals with the integration of photocatalysis and pervaporation [33], but it is not in the field of chemical synthesis since the subject is water detoxification and the objectives and mechanisms are quite different. Despite the lack of studies on integration of photocatalysis and pervaporation, the coupling of these two processes can be straightforward, since the operative conditions are practically the same (relatively low temperature, atmospheric pressure, low concentration of the chemicals, low energy demand).

It could be therefore interesting to investigate the performance of a chemical synthesis obtained through an integrated photocatalysis-pervaporation process. For this reason the subject of the present paper is the continuous recovery by pervaporation of intermediate valuable chemicals which are produced by the photocatalytic oxidation of primary alcohols in aqueous solution.

It is known that aromatic aldehydes can be photocatalytically produced by partial oxidation of the corresponding alcohols

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[5,34–37], but no selective recovery of the aldheyde has yet been considered. To our knowledge there is only one attempt to recover the aldehyde during its production [38]. However in [38] the oxidation system is not photocatalytic and the oxidation reaction is carried out in anhydrous environment, whereas for green chemistry it should be preferable to work without organic compounds in addition to the reagents and the obtained products. Furthermore in the permeate stream high fractions of the reagent are lost.

Also in a photocatalytic reactor the aldehydes are successively further oxidized, so that they decompose and are eventually mineralized into carbon dioxide and water. This phenomenon obviously limits the yield of the process even if the system is driven at the best operative conditions. Other problems derive from the intrinsic difficulties of operating in a continuous mode and from the difficult post-process separation of the very fine photocatalytic powders, which are often used instead of immobilized photocatalyst for their higher photocatalytic activity. All these drawbacks could be overcome in an integrated process.

2. Material and methods

Benzyl alcohol (BA), 4-methoxybenzyl alcohol (MBA), benzaldehyde (BAD) and 4-methoxybenzaldehyde (MBAD) were laboratory grade (Sigma-Aldrich) and were used as received. Aqueous solutions were prepared by thoroughly mixing the organic compounds with water demineralized by ion-exchange and reverse osmosis. The concentrations were analyzed by HPLC (column Alltima C-18 10U by Alltech, UV detector working at 250 nm, elution at 25 °C with 1 mL/min of a 49:50:1 (v/v/v) mixture of methyl alcohol, water and acetic acid).

Different kinds of titania were used as photocatalyst: (i) commercial photocatalytic powders (Aeroxide P25, Merck TiO_2, Hombikat UV100); (ii) home prepared photocatalytic powders; (iii) home prepared immobilized films. The selectivities and activities obtained with these photocatalysts are intrinsically different. Since the aim of this preliminary study on the integrated process is not to optimize the system, but to analyze the mechanisms and the effects of some parameters, the results obtained with a commercial photocatalyst (Aeroxide P25) are here presented. Probably, this is not the catalysts that can show the highest performances (in particular the highest selectivity), but it is the most utilized catalyst in photocatalysis and it can be representative of the results that can be obtained in the integrated process. The slurries with the suspended photocatalytic powders were heated to the operative temperature and ultrasonicated for 15 min before any test.

Also several types of reactor were used. Only the results obtained with one of them are presented, since the qualitative behaviour does not change by varying the reactor.

The reaction is carried on in an annular flow reactor with complete recycle of the slurry at a flow rate of 80 L/h, with a length of the illuminated zone = 8 cm, internal diameter of the annulus = 2.4 cm and external diameter of the annulus = 4.2 cm, irradiated by a Philips TL/08 blacklight 8 W lamp on the axis. The internal glass tube is in borosilicate glass to minimize the absorption of the UVA radiation.

Since the permeate flux increases with the temperature, in presence of pervaporation the operating temperature has been varied between 40 and 60 °C, with a preference for 60 °C in most of the experiments, even if at this relatively high temperature the rate of photocatalysis slightly decreases principally as a consequence of the reduced concentration of dissolved oxygen.

The volume of the recirculating slurry and the concentration of the photocatalyst were changed in the experiments with the integrated process to adjust the rate of photocatalysis to the rate of pervaporation.

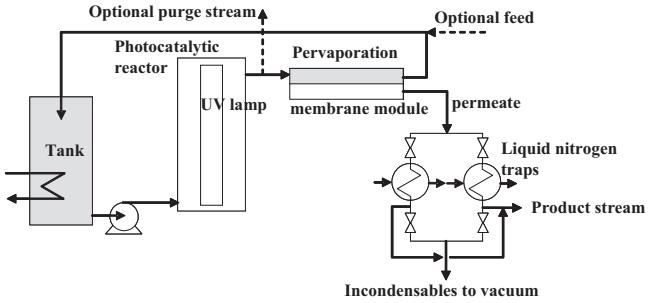

Fig. 1. Scheme of the experimental apparatus.

For the pervaporation experiments two stainless steel modules were utilized holding a flat sheet of an organophilic membranes (GKSS POMS/PEI) with an active surface of 160 cm^2 each sheet. The cross section for the passage of the fluid is 2 mm thick and 10 cm wide and the length of the active zone of the membrane is 16 cm, with a flow rate of 80 L/h. The permeate is maintained at 5–7 mbar and the vapors are collected by condensation in a liquid nitrogen trap. The POMS/PEI membranes have been chosen for this first approach to the coupling of photocatalysis and pervaporation since they have shown to be effective in the recovery of aroma compounds (see e.g. [28,29,39–41]).

The integration of photocatalysis and pervaporation has been tested in a laboratory plant where the coupling of the two processes has been achieved by the recirculation in a closed loop of the retentate from the pervaporation modules into the reactor and back to pervaporation, according to the scheme in Fig. 1. The permeate is collected by condensation of the "pervaporated" vapors and represents the product stream.

The fluid is maintained at an almost constant and uniform temperature in all the apparatus by thermostating the tank which is immersed into water kept at controlled temperature with a precision of ±0.1 °C. Furthermore a large part of the external surface of the membrane modules is thermally insulated by neoprene sheets and the residence time of the retentate in each of the two modules is very short (less than 1.5 s) to guarantee negligible variations of the temperature along the modules.

Before the starting of each run, that is before switching on the lamp and initiating the recovery of the permeate, the fluid is maintained in recirculation for one hour in the plant to reach the set temperature. Just before the starting the temperature is measured by a pyrometer in four different points of the external surface of the stainless steel modules to check that the temperature is anywhere at the desired value. The tubes from the pervaporation modules to the liquid nitrogen traps are heated by an electrical resistance to avoid undesired condensation of the vapors.

If the flow rate is sufficiently high to get a residence time in the reactor and in the pervaporation modules much shorter than the (characteristic) time of disappearance of the alcohol from the system, the coupling is almost complete and the system behaves as a batch. In the case that a feed is introduced into the system with a flow rate equal to the sum of the flow rates of the permeate and of the purge stream, after a transient time, the system can work in a continuous mode approaching the behaviour of a CSTR reactor (Continuous Stirred Tank Reactor).

3. Results and discussion

The consecutive reaction of degradation of the aldehydes in presence of the activated photocatalyst is confirmed by the occurrence of the characteristic maximum of the concentration at a certain reaction time, as it is apparent in Fig. 2, where the concentration profiles of alcohol (BA) and aldehyde (BAD) are plotted

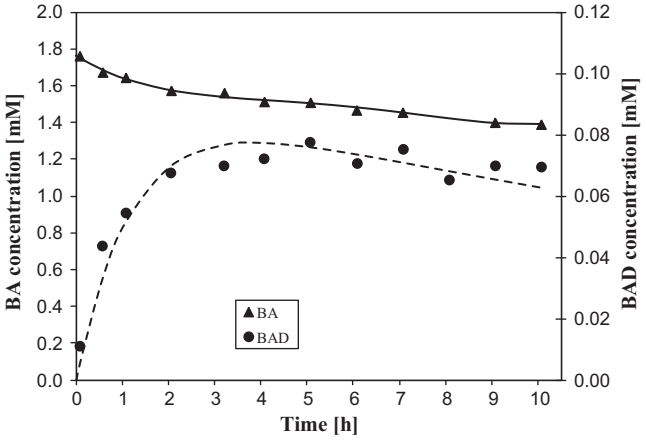

Fig. 2. Concentration profiles vs. time in a typical experiment of photocatalytic oxidation of an aromatic alcohol. Volume of the recirculating slurry = 600 mL, catalyst concentration = 0.27 g/L, temperature = 60 °C.

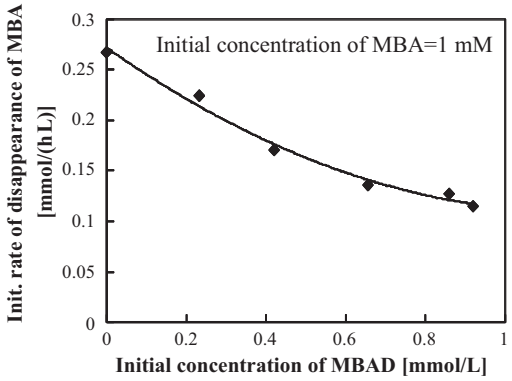

Fig. 4. The initial rate of disappearance of the original mother compound (MBA) as a function of the initial concentration of the aldehyde (MBDA). Volume of the recirculating slurry = 1300 mL, catalyst concentration = 0.5 g/L, temperature = 40 °C.

vs. time in a typical photocatalytic experiment. These results are in accordance with the reaction mechanisms analyzed in previous works [34–37].

The yield begins to decline when the conversion is still relatively low (usually between 15 and 40%, according to the type of photocatalyst and reactant) due to the decrease of the rate of oxidation of the alcohol and to the concurrent decrease of the selectivity caused by the consecutive reaction which degrades the aldehyde.

On the other hand, the destruction of the aldehyde is clearly observed also in photocatalytic experiments with the presence of only the aldehyde in the initial mixture. In Fig. 3 the time evolution of the concentration of the aldehyde is compared with the one of the alcohol in two different experiments with only the alcohol or only the aldehyde in the initial mixture. The evident decrease of the aldheyde concentration shows that also the aldehyde is degraded by photocatalysis.

The presence of the aldehyde in the mixture in contact with the photocatalyst can be detrimental also because the aldehyde is competitive with the mother compound (the alcohol) for the active sites and the photogenerated oxidizing agents, so that it slows down the rate of oxidation of the alcohol. A clear confirmation of this phenomenon can be obtained by varying the concentration of the aldehyde in the initial mixture, but keeping constant the concentration of the alcohol. The results are plotted in Fig. 4, where it is apparent that the aldehyde (MBAD) can significantly hinder the rate of oxidation of the alcohol (MBA).

Based on the previous observations, it is advisable to recover the aldehyde while it is produced. The separation from the reactive solution can be obtained by a membrane separation process. Pervaporation presents the advantage that the operative conditions are highly compatible with those of photocatalysis and the coupling is therefore straightforward.

In order to characterize the membranes and to determine the separation properties, the flux and the separation factor of the organophilic pervaporation membranes have been measured in normal pervaporation tests.

In Table 1, the separation factors, $\alpha_{i,j}$, of compound i in comparison with compound j, and the fluxes at different conditions are reported.

The data in Table 1 show that the aldehydes selectively permeate in comparison with the alcohols and the water. In particular MBAD can be separated effectively from MBA, which besides shows a lower concentration in the permeate than in the retentate ($\alpha_{MBA,water}$ is less than 1). On the other hand, BAD can be concentrated at much higher values in the permeate ($\alpha_{BAD,water} > 200$). The relatively high separation factors of aldehydes in comparison with those of the alcohol s show that the membranes are potentially suitable to recover the aldehydes in the permeate and, at the same time, to avoid significant losses of the alcohols. The results obtained for the binary or ternary mixtures considered in these experiments are the basis for the choice of the membrane, but they have been also verified in the real reacting system with complex and varying compositions, since it is known that interactions between the different compounds can modify the permeation properties.

The integration of photocatalysis and pervaporation has been studied in the laboratory plant described in Section 2.

The results which can be obtained in an experiment with the integrated process are illustrated in Fig. 5.

It can be observed that the concentration of BAD is highly enriched in the permeate (see Fig. 5b), in fact at any time the separation factor, $\alpha_{BAD,water}$, is about 120. The separation

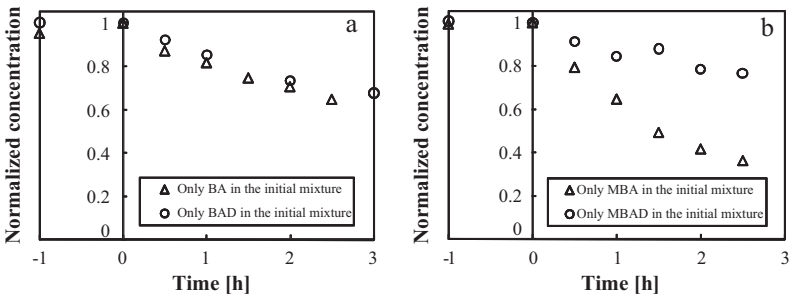

Fig. 3. The disappearance of BA and BAD (a) and MBA and MBAD (b) in runs with only the alcohol or only the aldehyde in the initial mixture. Volume of the recirculating slurry = 1300 mL, catalyst concentration = 0.5 g/L, temperature = 40 °C. Note that the light is switched on at time 0.

Table 1
Pervaporation performances of GKSS POMS/PEI membrane for aqueous solutions of alcohols and aldehydes.

Feed composition (values of concentration in mM)		$\alpha_{alcohol,\ water}$	$\alpha_{aldehyde,\ water}$	$\alpha_{aldehyde,\ alcohol}$	Flux (kg/(h m^2))	Temperature (°C)
[BA] = 1.5	[BAD] = 0.1	17	224	13	0.14	60
[MBAD] = 0.28		–	18	–	0.09	40
[MBA] = 1.35		0.11	–	–	0.11	40
[MBA] = 1.3	[MBAD] = 0.21	0.12	16	130	0.11	40

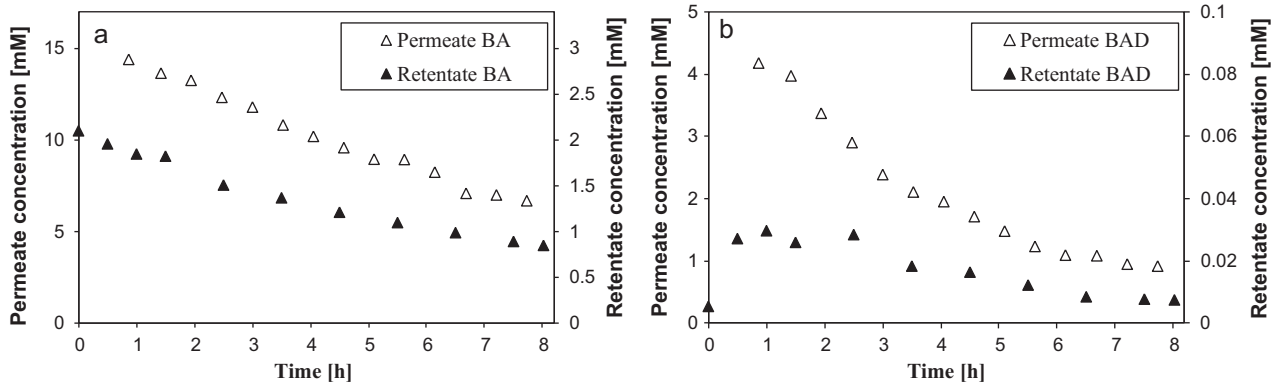

Fig. 5. The time profiles in the retentate and in the permeate of the alcohol (a) and of the aldehyde (b) during a representative experiment with the integrated process. Volume of the recirculating slurry = 600 mL, catalyst concentration = 0.27 g/L, temperature = 60 °C.

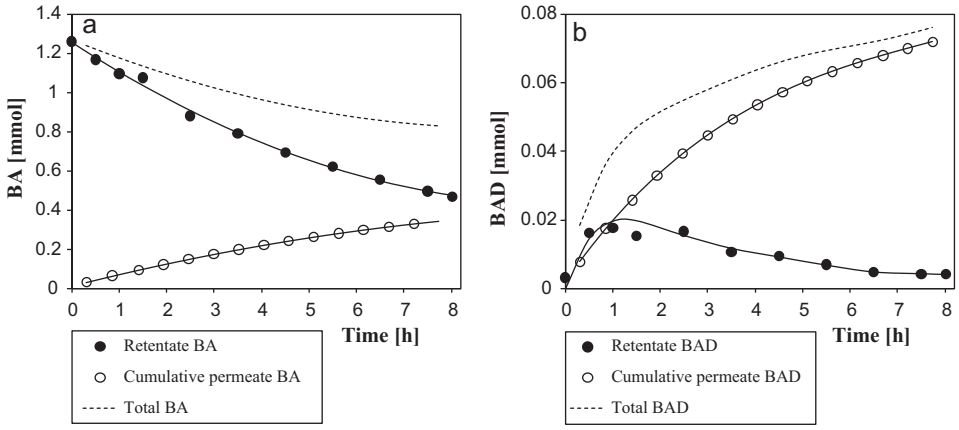

Fig. 6. Amounts of alcohol (a) in the retentate and (b) cumulatively collected in the permeate. Same experiment Fig. 5 refers to.

factor of the alcohol, $\alpha_{BA,water}$, remains almost constant at a much lower value (about 7.5), so that the aldehyde is selectively recovered in the permeate in comparison with the alcohol ($\alpha_{BAD,BA} \approx 16$).

Furthermore, in the case that the photocatalyst is present in the recirculation loop as suspended nano or micro powders, the powders do not pass the membrane and the product stream is always powder-free. In the long series of experiments it has been observed

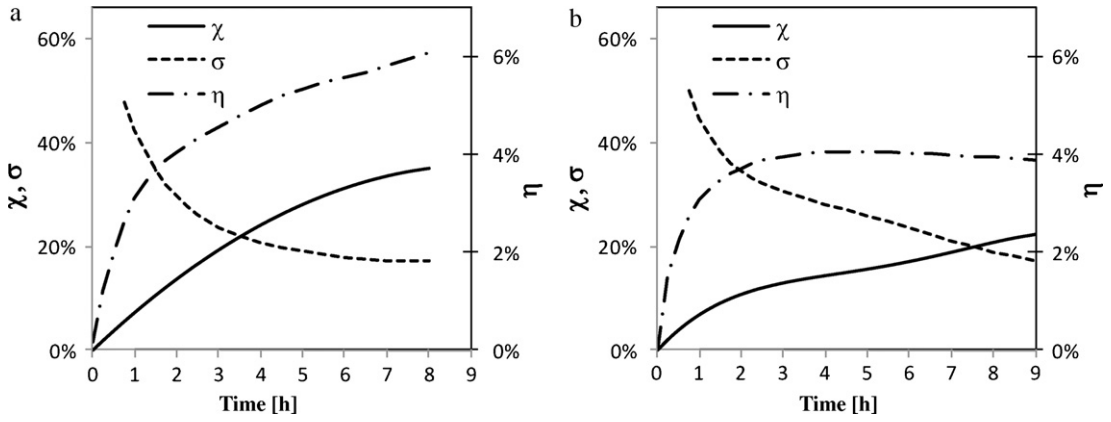

Fig. 7. Conversion, χ, selectivity, σ, and yield, η, (a) with pervaporation in the same experiment Fig. 5 refers to, and (b) without pervaporation in the same experiment Fig. 2 refers to.

also that the presence of the powders does not affect the performance of the membrane and both the transmembrane flux and the separation factor do not change for fouling even at very long times. Till now the same membranes have been used in pervaporation coupled with photocatalysis for more than 400 h without any appreciable decay of the performances. It is likely that the possible deposition of photocatalyst powders onto the membrane surface contributes only at a negligible extent to the overall resistance to the permeation, which in a dense membrane is intrinsically rather high even in absence of fouling.

Of course the values of the concentration in Fig. 5 depend on the operating conditions and in particular on the ratio, R, between the characteristic rate of permeation and the characteristic rate of the photocatalytic oxidation.

In Fig. 6 the quantities of BA and BAD in the retentate and cumulatively collected in the permeate are plotted vs. time for the same experiment Fig. 5 refers to.

Fig. 6 shows that the membrane cumulatively recovers in the permeate a significant fraction of the produced aldehyde, whereas a smaller fraction of the alcohol in the reacting solution is lost in the permeate. Note also that the curve of the total amount of produced aldehyde is continuously increasing, while, as it was observed previously, without the separation process a maximum is reached at a given time and after then, at longer times, the amount of aldehyde in the system decreases. Operating at higher values of R, which can be obtained by increasing the area of the membrane, the recovery of the aldehyde can be even more effective, particularly at the beginning of the process. For a continuous process higher values of R permit to obtain high recovery rate of the aldehyde and to limit the steady state value of the aldehyde in the recycle.

The following definitions are here adopted for the conversion, the selectivity and the yield:

conversion, χ: ratio between the moles of reactant (the alcohol) consumed by the reaction and the moles of reactant initially present in the system;
selectivity, σ: ratio between the moles of product (the aldehyde) present in the system (in the retentate and cumulatively recovered in the permeate) and the moles of reactant consumed by the reaction;
yield, η: ratio between the moles of product present in the system and the moles of reactant initially present in the system.

An examination of the values of the conversion, of the selectivity and of the yield, reported in Fig. 7a, reveals that the yield increases with the time and the selectivity decreases during the first hours, but after five hours it remains almost constant. The stage with a decreasing selectivity could be reduced by augmenting the area of the membrane. At any time the conversion is higher than the conversion obtained for the process without pervaporation (see Fig. 7b). Actually, as mentioned previously, the aldehyde is competitive with the alcohol and its recovery in the permeate is beneficial for the rate of the process. In spite of the possible decrease of the selectivity, the yield, which is the product of the selectivity by the conversion, increases with time. On the contrary, in the photocatalytic process without pervaporation the selectivity is continuously decreasing due to the reaction of degradation which acts as soon as the aldheyde is produced and the yield is always lower than in the integrated process, in particular after having reached the maximum.

4. Conclusions

The coupling of a membrane separation, namely pervaporation, with the photocatalytic partial oxidation of a primary aromatic alcohol to produce the corresponding aldehyde enhances the rate and the yield of the process. The improvement is a consequence of the continuous recovery of the aldehyde from the reactive ambient before it can be degraded by further oxidation. Even if the optimization has not yet been accomplished these effects are clear and allow to obtain a significant process intensification.

The related mechanisms are identified and discussed, together with the criteria which establish the correctness of the coupling, even maintaining the pervaporation module and the reactor in separate apparatus.

Other advantages obtained with this integrated process are: straightforward implementation, semicontinuous or continuous production, complete removal of the photocatalytic powders from the product stream, higher degree of purification of the valuable aldheydes and possibility to maintain mild operative conditions in both the processes.

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