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Clean Oxidation of Alcohols in a Trickle-Bed Reactor with Liquid Flow Modulation

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This work reports an experimental investigation of the catalytic oxidation of alcohols, using molecular oxygen as the oxidant and Pt/ γ -Al₂O₃ (1%w/w) as catalyst, in a trickle-bed reactor with ON–OFF liquid flow modulation under mild operating conditions. An aliphatic alcohol (ethanol) and an aromatic one (benzyl alcohol) are used as model reactants. The influence on reactor performance of different variables and modulation parameters (split and cycle period) are examined. Positive and detrimental effects of the liquid flow modulation are found and depend on the reactant used. Long cycle periods generally have a negative influence on the enhancement in conversion attained by using liquid flow modulation. For certain conditions, the enhancement versus cycle period curve shows a maximum, pointing to the importance of a systematic strategy to establish the experimental conditions to be employed if liquid flow modulation will be used. Found experimental trends are interpreted through a recently proposed model at the particle scale.

Introduction

Oxidation of alcohols and carbohydrates with molecular oxygen in aqueous media, catalyzed with noble metals, is a process that can profitably be applied in fine chemistry for the synthesis of specialty and fine chemicals possessing carbonyl or carboxylic groups. It can also be applied for carbohydrate conversion. The technique is attractive from both an economic and an environmental point of view since oxygen is an inexpensive and easily available oxidant and the solvent is not hazardous.^{1,2} More stringent environmental regulations are inducing the shift from classical stoichiometric oxidants (dichromate, permanganate, manganese dioxide, and nitric acid), which produce large quantities of waste materials and employ toxic reagents to catalytic liquid-phase oxidation processes with minimal amount of undesired byproducts.³ Especially for carbohydrate chemistry, the mild reaction conditions and high selectivity that can be attained for certain compounds are very attractive. However, catalyst deactivation is often reported and constitutes the major bottleneck for commercialization of the processes.⁴

Even if, in principle, any type of three-phase reactor can be used,^{5,6} the vast majority of research available has been carried out in slurry reactors.¹ Only a few works have been performed in trickle-beds, particularly to study catalyst stability.⁴ In a relatively recent review, Kluytmans et al.¹ have discussed engineering aspects

of this reaction, emphasizing particularly reaction kinetics, oxygen mass transfer restrictions, catalyst deactivation and reactivation, and implications for reactor design and operation.

In slurry reactors, two different reaction regimes could be clearly distinguished: an oxygen mass transfer limited regime and the intrinsic kinetic regime. From works carried out in the mass transfer limited regime, adherence of catalyst particles to the gas–liquid interface was proposed as a major factor determining reaction rate. Oxygen transfer direct from the gas to the catalyst would be responsible for the improvement with respect to situations where only dissolved oxygen has access to the catalyst surface. Hence, a three-phase reactor operation that enhances the gas–catalyst contact to decrease the oxygen mass transfer limitations could be beneficial. However, the increase in oxygen contact with active sites may also cause deactivation by over-oxidation or oxygen poisoning.^{4,7–9} This detrimental effect was observed for the oxidation of primary alcohols, secondary alcohols, and also carbohydrates.¹ It is generally accepted that over-oxidation is caused by the strong adsorption of oxygen or oxygen-containing species at the platinum surface. The catalyst activity was found to be easily recovered by a mild in-situ reduction applying a redox-cycle operation (viz., alternating exposure of the active sites to oxidative and reductive environments).¹⁰

If a trickle-bed reactor (TBR) with ON–OFF liquid flow modulation is used, periods of high gas reactant access to the catalyst surface (during the dry cycle) alternate with periods of gas reactant scarcity (during the wet cycles) due to strong mass transfer limitations.

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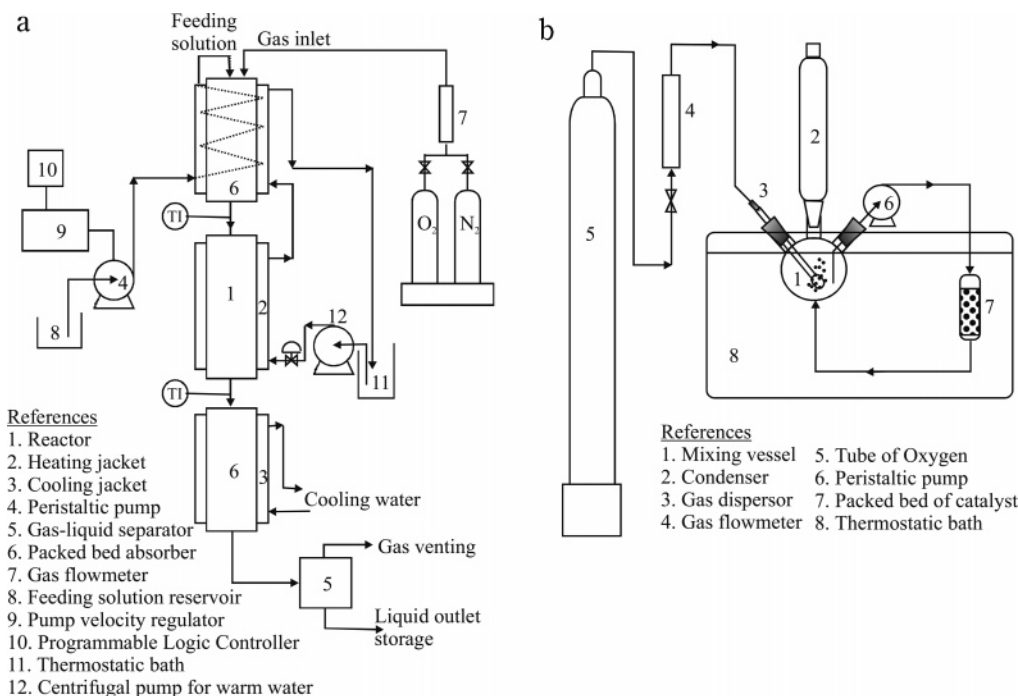


Figure 1. Schematic diagram of the experimental installations for (a) experiments in the integral trickle-bed reactor and (b) experiments to estimate a kinetic constant for the oxidation of benzyl alcohol.

In the latter, the surroundings become relatively richer in the liquid reactant concentration, which would provide a reductive environment. Therefore, this situation could be propitious for controlling over-oxidation deactivation in noble metal catalysts for the wet oxidation of alcohols with molecular oxygen and simultaneously enhance the oxygen contact with active sites after the self-reactivation.

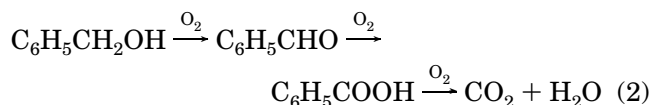
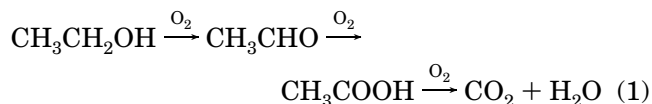
TBRs are widely used mainly in the petroleum and petrochemical industries.¹¹ Their application for wastewater treatment by catalytic oxidation of dissolved organic contaminants has received more attention in the past few years.^{12–16} This process, known as catalytic wet oxidation (CWO), is a suitable method for wastewater treatment when the organic compounds are toxic to microorganisms or their concentrations are too high.¹⁷ Due to the low solubility of oxygen in water, high pressure is required if an alternative way to increase the accessibility of oxygen to the active sites is not achieved. The possibility of having direct contact of the gaseous phase with the catalyst surface due to partial wetting of the catalysts exists in TBRs by using low liquid flow rates or hydrophobic catalysts.¹⁴ In addition, if flow modulation is imposed, the direct access of oxygen to the catalyst can also be achieved for certain operating conditions.^{18,19} Periodic operation of TRBs frequently results in higher reactants conversions at comparative liquid flow rates, especially for gas-limited reactions.^{20–25} Hence, it is likely that a CWO carried out in a TBR pursuing the clean oxidation of alcohols may be favored by interrupting periodically the liquid-phase feed to the reactor.

In the present work, the effect of modulating the liquid flow rate with an ON–OFF strategy, on the performance of an integral TBR used for carrying out the clean oxidation of ethyl and benzyl alcohols by CWO under mild operating conditions, is examined. The study is carried out at constant temperature to uncouple the hydrodynamic from the thermal effects. Averaged alcohol conversions obtained with periodic operation are

compared to the steady-state conversion at the same mean liquid flow rate for different cycle periods and splits (i.e., ratio of the time during which the liquid is ON over the total cycle period). In addition, the instantaneous ethyl alcohol concentration at reactor outlet is measured for different cycle periods. Finally, experimental results and qualitative trends obtained are analyzed with the aid of a recently proposed model aimed at the particle scale.²⁶ The model basically considers the influence of internal and external mass transfer on the reaction outcome for intermittently partially wetted particles.

Experimental Section

Integral Trickle-Bed Reactor Experiments. The catalytic wet oxidation of aqueous solutions of ethyl or benzyl alcohol is carried out in a mini-pilot-scale acrylic TBR. Reactions taking place can be stated concisely as:



The reactor has 0.04 m i.d. and 0.7 m height and is packed with 0.4 kg of a Pt/ γ -Al₂O₃ catalyst (1% w/w, mean particle diameter $d_p = 0.003$ m). A schematic diagram of the experimental equipment is presented in Figure 1a.

The TBR is externally heated with warm water in order to keep the temperature at 70 °C (± 2 °C) during the whole cycles. The liquid solutions fed to the reactor are previously contacted with O₂ in a packed bed of glass beads placed before the reactor inlet to achieve thermal and vapor pressure equilibrium. Liquid flow is regulated

Table 1. Solubility of Used Alcohols and Aldehydes²⁷

compound	average Henry's constant, k_H at 298 K (M/atm)	$d \ln(k_H)/d(1 - T)$ (K)
ethanol	200	6500
acetaldehyde	13	5700
benzyl alcohol	9000	not available
benzaldehyde	38	4800

with a peristaltic pump commanded by a programmable logic controller (PLC). Gaseous reactant stream is oxygen (99.9% v/v).

An absorption column, filled with glass beads and provided with a cooling jacket, is placed at the reactor outlet. Tap water was used as refrigerant. Temperature at the absorber outlet was always below 25 °C. When necessary, a cryostat was employed to reduce water temperature before entering the cooling jacket. The absorber has the purpose of absorbing the nonreacted alcohol and the soluble gaseous products. A chromatographic analysis of the gaseous stream at the absorption column outlet showed that the amount of alcohol remnant was negligible for both reactants used. Hence, alcohols could be determined quantitatively. Aldehyde concentrations were also determined to close the mass balance and for qualitatively analyzing the selectivity. For the case of acetaldehyde, which has very low boiling point, 10–20% of the generated amount remains in the gas phase. A longer absorber or a cooling section in the gas–liquid separator could have been beneficial to avoid acetaldehyde stripping from the liquid outlet stream. Henry's constants for both alcohols and aldehydes employed are listed in Table 1, together with the heat of solution.²⁷ Benzaldehyde has a Henry's constant three times larger than acetaldehyde and could be almost completely recovered in the liquid phase. Therefore, its concentration could be determined quantitatively from measurements in the liquid phase.

Alcohol concentrations in the feed solutions were maintained at 0.006 or 0.03 M for all the experiments. Their concentrations were determined with a Perkin-Elmer gas chromatograph using a FID detector with either a packed or capillary column. Ethanol and acetaldehyde were effectively separated for quantification with a packed column PORAPAC SuperQ, using an oven temperature of 180 °C. For benzyl alcohol and benzaldehyde, a capillary HP-Ultra 1 column was employed. A temperature program (40 °C: 2 min; 25 °C/min ramp; 220 °C: 5 min) was used to improve separation. Benzoic acid could also be determined with this column after quantitatively extracting it from the aqueous phase with methylene chloride to reduce tailing. However, for the conditions examined, selectivity to benzaldehyde was 100%.

Alcohol conversions were calculated as:

$$X = \frac{(N_{Ti} - N_{To})}{N_{Ti}} \quad (3)$$

where N_{Ti} and N_{To} indicate the moles of alcohol in the inlet and outlet streams, respectively. The catalyst bed was always flooded with the preheated liquid solution before starting. This preliminary procedure ensures complete internal wetting of the catalyst and also warms the bed. Steady state at high liquid throughputs and the selected gas mass velocity was imposed first. Then, the liquid flow rate was set to the one corresponding to the wet period, and liquid flow modulation was started.

After attaining an invariant cycling state, liquid samples were taken at regular intervals. In addition, for different cycle periods, the averaged final concentrations of nonreacted alcohol and products were determined by collecting the liquid outlet stream. The samples were properly refrigerated.

The mean liquid mass velocity (L_{SS}) was fixed at 0.36 or 0.76 kg/m²·s. Reactor performance at steady state with L_{SS} was evaluated repeatedly to get a reference for comparison. The cycle split, defined as the ratio of wet (t_w) over the total period ($t_w + t_{nw}$):

$$s = \frac{t_w}{t_w + t_{nw}} \quad (4)$$

was set to 1/3, 1/2, or 2/3. To establish the liquid mass velocity during the ON period of the cycle, the following relationship was used:

$$L_{ON} = \frac{L_{SS}}{s} \quad (5)$$

There was no liquid flow during the dry period (ON–OFF cycling strategy). Gas mass velocity was kept constant for all the experiments at 0.04 kg/m²·s. Cycle periods examined ranged from 10 to 1800 s.

Experimental Estimation of a Kinetic Constant for the CWO of Benzyl Alcohol. A set of experiments was carried out in order to estimate a kinetic constant for the catalytic wet oxidation of benzyl alcohol. This value was required to apply a model for interpreting the experimental results. Benzyl alcohol remains in the liquid phase and is easily quantified. Experiments were carried out in a 500-mL glass flask where the liquid was saturated with pure oxygen. A schematic diagram of the installation employed is illustrated in Figure 1b. The oxygen-saturated liquid contained in the flask was recirculated continuously, with the aid of a peristaltic pump, through a glass column where the reaction took place. The column was 0.02 m diameter and 0.10 m high and was packed with the same catalyst used in the mini-pilot-scale reactor. Temperature was fixed at 70 °C by placing the experimental vessel in a thermostatic bath. A condenser was located on top of the flask to prevent alcohol and aldehyde evaporation. Samples of 1 mL of the liquid in the flask were taken periodically to follow the reaction progress in time and to calculate the reaction rate. The alcohol and the aldehyde were determined by gas chromatography, as explained for the experiments in the integral reactor. The mass balance always closed to within 4%.

Different recirculation velocities and bubbling oxygen flow rates were used until no further improvement in reaction rate was attained for a given mass of catalyst. At this condition, negligible external mass transfer was assumed. Different catalyst mass were also employed to determine a kinetic constant assuming a first-order reaction with respect to oxygen and zero-order with respect to benzyl alcohol.²⁸

$$r = kC_{O_2} \quad (6)$$

The value obtained for the kinetic constant is $k = 0.008 \text{ s}^{-1}$

Results and Discussion

Time-Dependent Behavior. Instantaneous conversions attained for the catalytic wet oxidation of ethyl

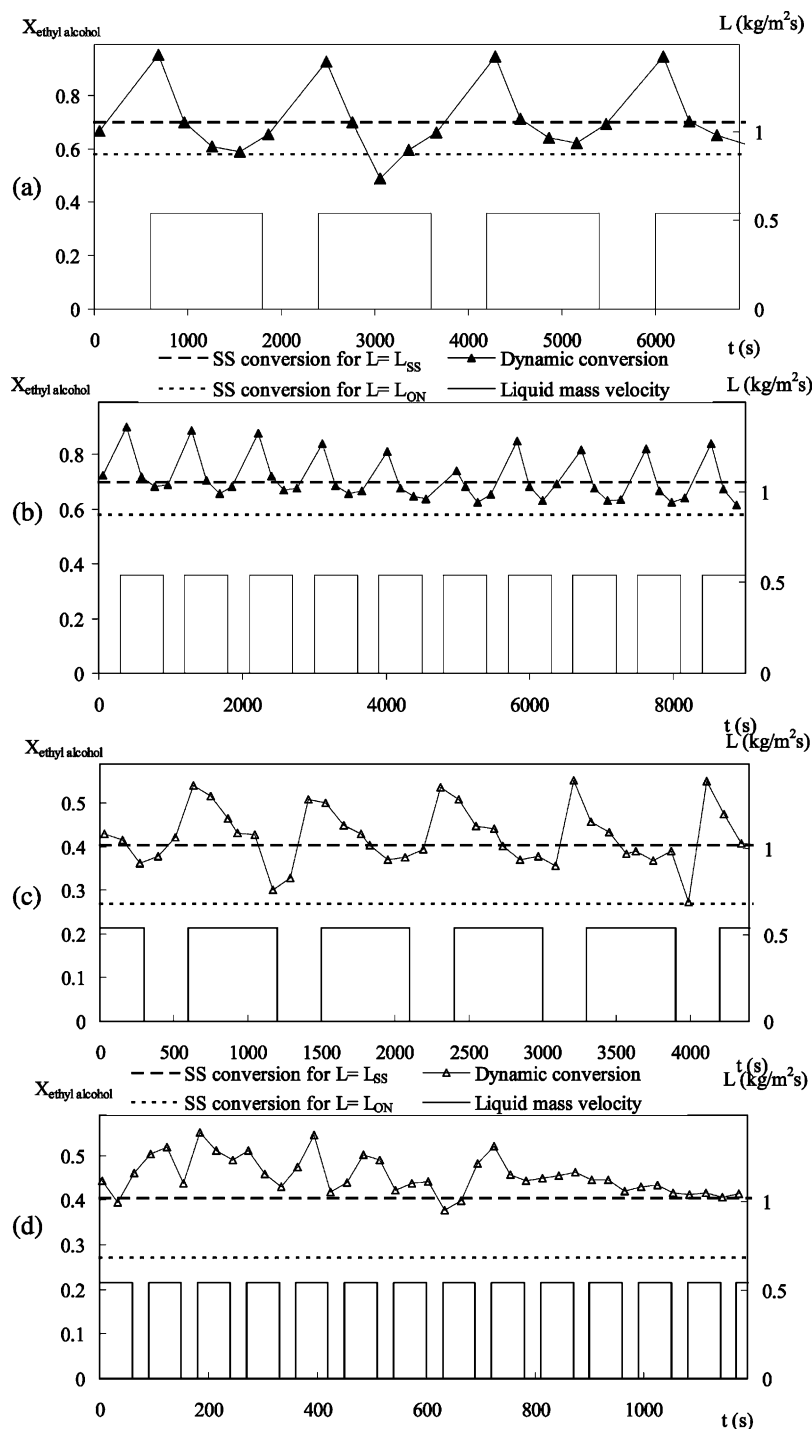


Figure 2. Time dependence of the instantaneous ethanol conversions for different cycle periods and initial reactant concentrations. Split = 2/3; $C_0 = 0.006$ M: (a) cycle period = 1800 s, (b) cycle period = 900 s. Split = 2/3; $C_0 = 0.03$ M: (c) cycle period = 900 s, (d) cycle period = 90 s.

alcohol in the periodically operated TBR are presented in Figure 2a–d. The conversions are calculated from the outlet reactant concentration after reaching an invariant cycle stage. Typical results obtained for a split of 2/3 with two initial reactant concentrations are illustrated for different cycle periods. Steady-state conversions achieved for the liquid mass velocity that corresponds to the ON period (L_{ON}) and for a liquid mass velocity that represents the same mean liquid residence time (L_{SS}) are also indicated in Figure 2. Instantaneous conversions oscillate around the steady-state value at L_{SS} and generally peak when the liquid starts to drain from the reactor after the dry period has ended. Once

the liquid flow stops, reaction proceeds between the liquid reactant retained in the reactor and the flowing gas reactant. The rate is higher because of decreased mass transport resistances. When the wet cycle starts, the product formed during the dry cycle is initially “washed out” by the flowing liquid and results in a conversion maximum. Then, conversions tend to the corresponding steady-state values at L_{ON} . This situation is more evident for slow flow modulation where very high conversions can be reached during the extended dry cycle (Figure 2a). Depending on period length, conversions obtained during the wet cycle are higher than those corresponding to steady-state operation at

L_{ON} . However, if the extent of the wet cycle is long, conversions will approach steady-state values at L_{ON} , as seen in Figure 2a for a cycle period of 1800 s, in which the wet period is 20 min.

For the higher initial reactant concentration, the conversions are lower (Figure 2c,d). This result was expected since a negative influence of ethanol concentration on reactor outcome was found for steady-state operation.¹⁴ However, the range of variation was similar to the one observed for the lower reactant concentration at the same cycle period (Figure 2b,c). When the cycle period is reduced, the range of variation of conversion clearly decreases. For the highest modulation frequency shown (Figure 2d), alternating conversions were not observed any more. On the contrary, the response became very irregular and in some cases tended to the steady-state value at L_{SS} . In the last case, the liquid drained from the reactor without interruption.

To interpret results shown in Figure 2, a model recently proposed at the particle scale was applied.²⁶ The model takes into account dynamic variations occasioned by intermittent external wetting of the particle and external and internal mass transfer resistances. Radial and angular variations in reactant concentrations are evaluated. Briefly, the model assumes a single first-order gas-limited reaction between a gaseous reactant (A) and a diluted nonvolatile liquid reactant (B) taking place within an isothermal porous solid catalyst particle with total internal wetting; the external surface of the particle is assumed to be partially wetted during the ON cycle and completely dry during the OFF cycle. A square-wave cycling of main parameters are considered to describe hydrodynamic behavior during ON–OFF operation, and negligible external mass transfer resistance is assumed during the dry cycle.

Actual experimental conditions employed for the oxidation of benzyl alcohol and a Thiele modulus of $\phi = 6.5$ have been used for solving the model. The Thiele modulus was determined using the kinetic constant calculated from the experiments (see the Experimental Section) and an estimated value for the effective diffusivity.²⁸ The model has been applied to the wet oxidation of benzyl alcohol since we had the kinetic information. Even if experimental instantaneous variations have been shown for the oxidation of ethanol (Figure 2) due to a more exhaustive experimental exploration, similar dynamic behavior was observed also for benzyl alcohol. The correlations of Goto and Smith²⁹ were employed to estimate overall volumetric gas–liquid and liquid–solid mass transfer coefficients. Biot numbers for $L_{SS} = 0.36$ kg/m²·s were as follows: $Bi_{gl,A} = 4.7$ and $Bi_{ls,B} = 36.5$. Their values during the ON period of the cycle were corrected considering the correlations dependences on the liquid velocity. The wetting efficiencies (f) were estimated with the correlation of Herskowitz.³⁰ It was $f = 0.7$ for $L_{SS} = 0.36$ kg/m²·s and, considering the variations in liquid mass velocity for split 2/3 and 1/3, were set to $f = 0.73$ and $f = 0.78$, respectively, during the ON cycle.

Figure 3 illustrates predicted instantaneous effectiveness factors, calculated by integrating the instantaneous reactant profiles,²⁶ for split 2/3 and different cycle periods. The effectiveness factor for L_{SS} is also shown for comparison. In addition, the instantaneous mean concentration of the liquid reactant inside the catalyst is shown.

According to the model, the effectiveness factor tends to a value close to the one attained at steady-state conditions during the wet period. This result arises from the combined effect of larger Biot numbers, which contribute positively to effectiveness factor during the wet period (η_w) counteracted by the negative influence of a slightly higher wetting efficiency, compared to the value for L_{SS} ; for example, $\eta_{ss} = 0.230$ and $\eta_w = 0.231$. The effectiveness factor during the dry cycle (η_{nw}) tends to the value characteristic of a completely dry particle and is responsible for the increase in the overall reaction rate. The mean liquid reactant concentration in the catalyst will finally determine the variations in the bulk concentrations in the integral reactor, which have been measured at the reactor outlet stream (Figure 2). The appearance of a sharp minimum in liquid reactant concentration at the end of the dry period anticipates a peak in conversion when the liquid starts to drain from the reactor after the dry cycle, as observed in the experiments. The shift in time naturally depends on the liquid flow rate and on the dynamics of the draining.

The shape of the mean liquid reactant concentration and effectiveness factor curves change as the cycle period is decreased (Figure 3b,c) in a similar way as observed for the experiments. The mean liquid reactant concentration varies within a smaller range due to a shorter dry period that prevents liquid reactant starvation. The effectiveness factor versus cycle period curve does not resemble any more a square-wave as for the longer cycle periods (Figure 3a). In contrast, it becomes saw-teeth-like, generally tending to an upper limit for higher frequencies and leading to larger improvements. When the cycle period is set to 90 s (Figure 3c), to compare with experimental results shown in Figure 2d, the effectiveness factor variations are reduced and the mean liquid reactant concentration tends to a constant value. The model predicts a pseudo-steady-state at a level different from the one at L_{SS} . The predicted effectiveness factor for the pseudo-steady-state increases as the frequency is increased, in agreement with other models found in the literature.^{21,31} This fact arises from the prompt response of the system to a sharp decrease in external mass transfer resistance during the dry period and a slower dynamic response to the increase in mass transfer resistance during the wet period.

The comparison between model²⁶ and experimental results leads to important conclusions. On one side, dynamics of mass transfer and reaction inside the particle clearly has a decisive effect on the system behavior for slow ON–OFF liquid flow modulation. For high modulation frequencies (short cycle periods), other factors not considered in the model will affect the system response. For instance, hydrodynamic effects will likely determine time variations of the governing parameters.

Time Averaged Behavior. The ratio of “averaged” cycling and steady-state alcohol conversions at a comparable liquid mass velocity will be called enhancement (ϵ) hereafter. This ratio is represented as a function of the total cycle period for different modulation parameters in Figure 4, for the clean oxidation of ethanol. For certain conditions, the enhancement is greater than one. This puts in evidenced that reactor performance can be improved by periodic operation at isothermal conditions. However, enhancements lower than one have also been obtained. Clearly, it is important to understand the underlying phenomenon to determine proper operating conditions for an ON–OFF cycling strategy.

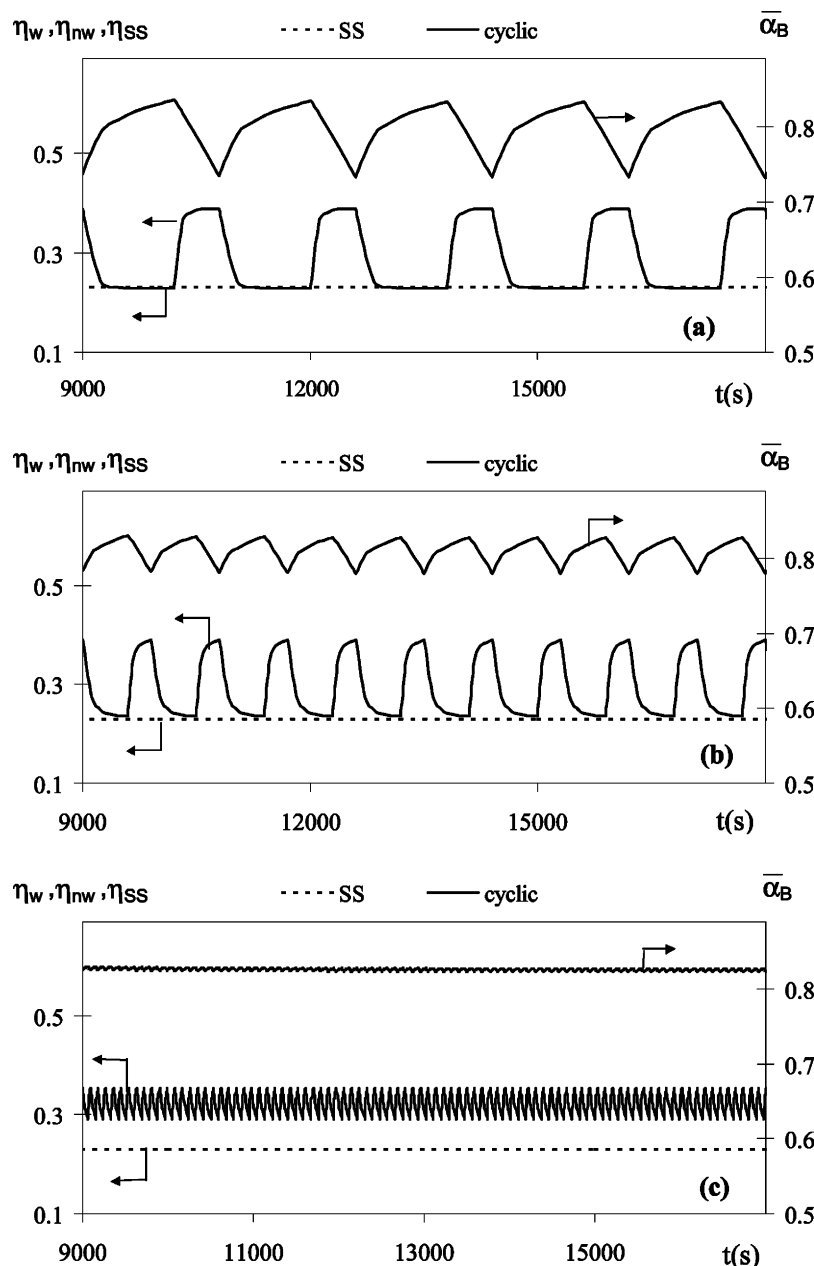


Figure 3. Influence of the cycling strategy on the predicted instantaneous effectiveness factor and mean liquid reactant concentration inside the particle for the CWO of benzyl alcohol. Comparison with steady-state behavior. Split = 2/3; $C_0 = 0.03$ M; $L_{SS} = 0.36$ kg/m²·s: (a) cycle period = 1800 s, (b) cycle period = 900 s, (c) cycle period = 90 s.

Enhancement improvement can be attributed to an increase in oxygen access to the catalyst surface. On one hand, this access is favored during the dry cycle due to reduction of liquid films, which imply lower external mass transfer resistances.^{21,26} The “dry” area depends on the cycling parameters and on the wetting efficiency; for longer cycle periods and lower splits, direct gas–solid contact is important and will probably be the predominant effect. In addition, oxygen access to the catalyst surface through the liquid phase that covers the wetted area of the catalyst can also be favored by larger mass transfer coefficients in the liquid. For high modulation frequencies, the system resembles a pseudo-pulsing flow regime, and mass transfer toward the wetted area of the catalyst is probably larger. However, high frequency liquid flow modulation may also prevent the appearance of “dry” catalyst surface, which adversely affects oxygen transfer, if the draining time is of the same order as the cycle period. A decrease in the

enhancement at low cycle periods has been experimentally observed for certain conditions in this contribution. This effect was also reported for other reaction systems.^{23,32}

On the other hand, at long cycle periods and low splits values, enhancements lower than one were found. This influence is more pronounced for low split values. Several factors can affect negatively the attained conversion for long cycle periods. A problem of the cyclic ON–OFF operation of a TBR is liquid reactant starvation during long dry periods. In addition, for low splits, there is less opportunity to reload the liquid during the wet period. Another factor, typical of alcohol oxidation with molecular oxygen on noble metals, is deactivation of the catalyst due to over-oxidation. It is well-documented that a prolonged contact of a Pt catalyst with high levels of oxygen can induce this effect.^{1,7,10,33,34} This phenomenon is a reversible deactivation, and the activity will be recovered during the wet cycle. The

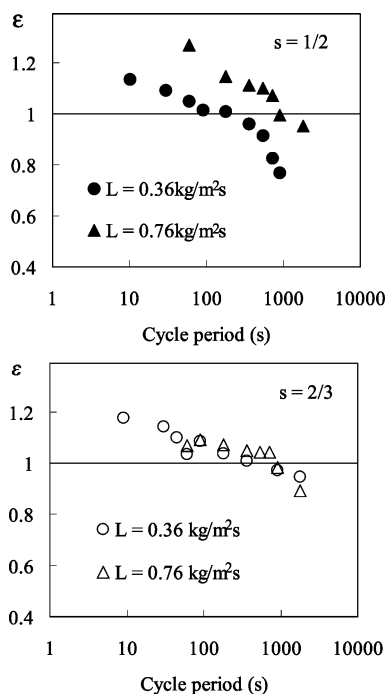


Figure 4. Effect of the liquid velocity on the enhancement due to liquid ON–OFF flow modulation in the catalytic wet oxidation of ethyl alcohol. $C_0 = 0.006 \text{ M}$ (a) split = 1/2, (b) split = 2/3.

volatility of the liquid reactant constitutes an additional effect. In this case, ethanol is relatively volatile (see Table 1), and its concentration in liquid-phase inside the reactor, at 70°C , would decrease by evaporation. Considering that the catalyst pores would probably be completely filled with liquid due to capillary forces, ethanol conversion would be affected, particularly for long periods and low splits. Indeed, the complex interaction of all these factors complicates the quantitative analysis of the experimental results.

The reactor performance improvement due to periodic operation depends on the liquid flow rate, particularly for the lower split (Figure 4a). In this case, the enhancement was larger for higher liquid flow rates. This could be related to the high steady state conversion reached at the lower liquid velocity due to a longer residence time and a lower wetting efficiency. Then, the differences in conversion attained with liquid flow modulation become relatively smaller for lower liquid velocities. No significant effect of the liquid velocity on the enhancement was observed for split 2/3 (Figure 4b).

The influence of ethanol concentration on enhancement is shown in Figure 5. Larger enhancements were obtained at higher reactant concentration. This is probably explained by the high conversion levels attained at low concentrations in steady-state operation. In addition, the decrease in enhancement for long cycle periods is more pronounced for the lower reactant concentration and lower split values and is likely related to liquid reactant starvation during the dry period.

The influence of the cycling parameters on the enhancement values obtained for wet oxidation of ethyl and benzyl alcohol while using the more concentrated solution, for which attained conversions are around 50%, can be observed in Figure 6. For many of the experimental conditions explored, the enhancement was larger than one. Detrimental effects were observed for long cycle periods, particularly in the case of benzyl alcohol (Figure 6a), and at the lowest split for ethyl alcohol

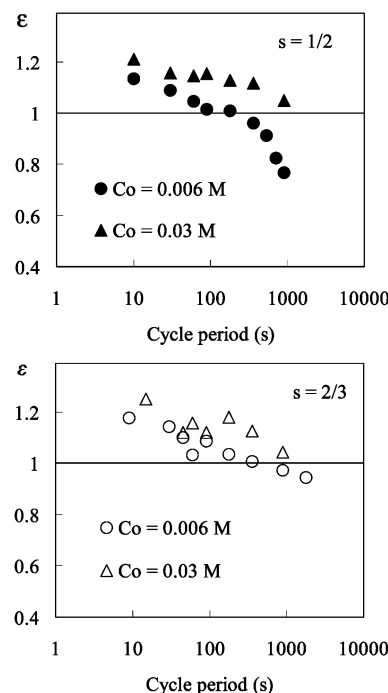


Figure 5. Effect of the liquid reactant initial concentration on the enhancement due to liquid ON–OFF flow modulation in the catalytic wet oxidation of ethyl alcohol. $L_{SS} = 0.36 \text{ kg/m}^2\text{s}$. (a) Split = 1/2; (b) split = 2/3.

(Figure 6c). In addition, for certain conditions, the enhancement versus cycle period curve shows a maximum. An a priori prediction of the behavior of each alcohol employed would require the quantification of the several factors already mentioned that can affect conversion. Figure 6 highlights the different influence of the split on the two reactants employed. Larger enhancements are found for ethanol oxidation than for benzyl alcohol oxidation at the higher split (Figure 6a), and the opposite trend is apparent for the lower split examined (Figure 6c). Considering the large difference in volatilities of both alcohols (see Table 1), it is likely that volatility explains this trend. For lower splits, ethanol concentration in the liquid phase would decrease sharply due to volatilization and may cause starvation. In contrast, benzyl alcohol would remain in the liquid phase. Hence, it seems that a lower split strategy would not be particularly beneficial to high volatile liquid reactants unless reaction could take place between vaporized and gaseous reactants. In this case, proper recovery of products from the gas effluent stream should be provided.

The model of Ayude et al.²⁶ was applied to get insights on the influence of cycling parameters on the attained enhancements for the wet oxidation of benzyl alcohol (Figure 7). Enhancements predicted by the model (ϵ_m) are evaluated by relating a time-integrated effectiveness factor for the cyclic operation to the one calculated for L_{SS} . As observed, a negative trend in the enhancement versus cycle period relation is found for the examined splits (1/3 and 2/3), but it is more pronounced for the larger one. Similar trends have been found in the experiments at moderate cycle periods (from 60 to 120 s, see Figure 5) for which other factors, not considered in the model, would have negligible influence. The model nicely illustrates the subtle influence of mass transfer dynamics on enhancement and how it is affected by different cycling parameters. However, it only describes

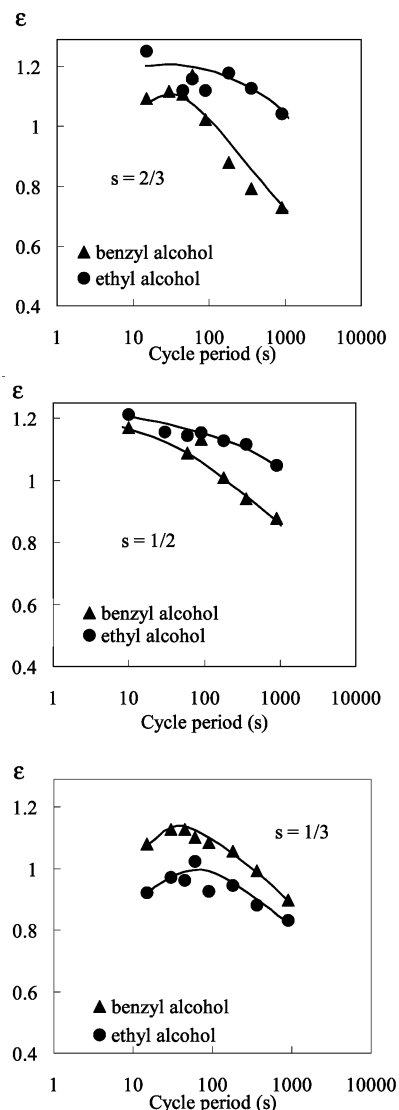


Figure 6. Comparison among the enhancement vs cycle period curves obtained for the catalytic wet oxidation of ethyl and benzyl alcohols due to liquid ON-OFF flow modulation. $C_0 = 0.03$ M; $L_{SS} = 0.36$ kg/m²·s. (a) Split = $2/3$, (b) split = $1/2$, (c) split = $1/3$.

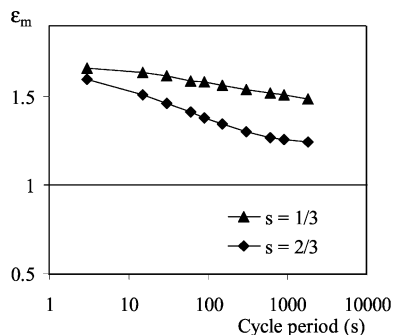


Figure 7. Estimated enhancement, predicted by the model, for the CWO of benzyl alcohol at the particle scale in a periodically operated TBR. $C_0 = 0.03$ M; $L_{SS} = 0.36$ kg/m²·s.

the situation while no effect of total depletion of liquid reactant exists, since it was applied for initial conditions with a large ratio of liquid to gas reactant and does not consider the possibility of over-oxidation of the catalyst. In addition, as discussed for Figure 3c, the square-wave assumption generally assumed for describing variations in parameters for the cyclic operation, would not be valid for short cycle periods. Hence, the model does not predict

the appearance of a maximum in the enhancement versus cycle period curve observed in the experiments.

Periodic variations in reactants supply to the catalytic particles can have a significant effect on the selectivity for consecutive or parallel reactions.³⁵ The wet oxidation of alcohols can lead to the corresponding aldehydes, carboxylic acids, and finally mineralization to carbon dioxide and water, as stated in eqs 1 and 2. Other intermediate products can appear for alcohols with more complex structures. For the wet oxidation of benzyl alcohol under the mild conditions employed in this study, only benzaldehyde was formed. For the wet oxidation of ethyl alcohol, acetaldehyde and acetic acid were found in the liquid samples leaving the absorber located after the reactor. Acetaldehyde was also found in the gas stream in nonnegligible amount. Acetaldehyde is a very volatile product, which probably leaves the liquid phase as soon as it is generated. Ethanol is also relatively volatile and likely evaporates inside the reactor. As the catalyst may remain completely filled due to capillary forces, evaporation of the liquid reactant and intermediate products will probably affect the product distribution. Another factor that can affect the product distribution for the oxidation of ethyl alcohol in an aqueous medium in contrast to the oxidation of benzyl alcohol is the possibility of acetaldehyde hydration to form a geminal diol, which can quickly dehydrogenate into the corresponding acid.^{2,36} Benzaldehyde presents steric hindrance so hydration does not occur, which prevents its further oxidation.² It is also likely that benzaldehyde evaporates inside the reactor, which would also prevent its contact with active sites for oxidation. To understand and be able to predict the effect of liquid flow modulation on selectivity of oxidation will be useful to establish appropriate operating conditions for taking advantage of periodic operation for this process.

Conclusions

The catalytic clean oxidation of alcohols with molecular oxygen on a noble metal catalyst is studied in a TBR operated with ON-OFF liquid flow modulation. Ethyl and benzyl alcohols are used as model reactants. The influence of cycle periods and split on the enhancement in conversion due to periodic operation is examined for different reactant concentrations and liquid mass velocities. Application of a model at the particle scale evidenced the influence of internal and external mass transfer dynamics on reactor performance at intermediate values of the cycle period.

Alcohol conversion is improved by the cycling strategy for many combinations of cycle period and split. Cycling parameters have different influence on reactor performance depending on the liquid reactant and operating variables employed. A maximum in the enhancement versus split curve is apparent for certain conditions, highlighting the significance of deeply understanding the underlying phenomenon to be able to establish a priori the proper operating conditions of a cycling strategy. The different behavior found for both reactants can be related mainly to their different volatilities. The wet oxidation of nonvolatile benzyl alcohol is improved by ON-OFF liquid flow modulation for lower splits. On the contrary, wet oxidation of the relatively volatile ethyl alcohol is favored especially at higher splits.

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Notation

Bi = Biot number
 C_0 = alcohol concentration in the feed solution (kmol/m³)
 C_{O_2} = oxygen concentration (kmol/m³)
 ϵ = wetting efficiency
 k = reaction rate constant (s⁻¹)
 k_H = Henry's law constant (M/atm)
 L = liquid mass velocity (kg/m²·s)
 N = number of moles
 r = reaction rate (mol/L·s)
 s = split
 t = time (s)
 T = temperature (K)
 X = conversion

Greek Letters

α = dimensionless reactant concentration
 ϵ = enhancement due to periodic operation, experimental value
 ϵ_m = enhancement due to periodic operation, estimated from the model
 ϕ = Thiele modulus
 η = overall effectiveness factor

Subscripts

0 = initial value
 A, B = gas and liquid reactant, respectively
 cyc = cycling
 i = inlet
 L = liquid
 nw = referred to the OFF period of the cycle
 o = outlet
 ON = referred to the wet period of the cycle
 T = total
 SS = steady state
 w = referred to the ON period of the cycle

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