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## Research Article

# Yield Optimization in a Cycled Trickle-Bed Reactor: Ethanol Catalytic Oxidation as a Case Study

The effect of slow ON-OFF liquid flow modulation on the yield of consecutive reactions is investigated for oxidation of aqueous ethanol solutions using a 0.5 % $Pd/Al_2O_3$ commercial catalyst in a laboratory trickle-bed reactor. Experiments with modulated liquid flow rate (MLFR) were performed under the same hydrodynamic conditions (degree of wetting, liquid holdup) as experiments with constant liquid flow rate (CLFR). Thus, the impact of the duration of wet and dry cycles as well as the period can be independently investigated. Depending on cycling conditions, acetaldehyde or acetic acid production is favored with MLFR compared to CLFR. Results suggest both the opportunity and challenge of finding a way to tune the cycling parameters for producing the most appropriate product.

## 1 Introduction

Trickle-bed reactors (TBRs) provide flexibility and simplicity of operation as well as high throughputs and low energy consumption. These reactors are widely used in chemical, petrochemical, and petroleum industries, in biochemical and electrochemical processing, and in waste water treatments [1]. In many applications, the gaseous reactant is slightly soluble and consequently the reaction is gas-limited. Liquid flow modulation (LFM) results in significant increase in production capacity and conversion compared to steady-state operation for gas-limiting reactions [2]. The effect of cycling on selectivity of complex reactions is a question that has been scarcely addressed although experimental studies have shown that ON-OFF LFM affect the product distribution of consecutive reactions [3–8]. Therefore, further investigation of the impact of LFM on product distribution of multiple reactions is still required.

Fraguío et al. [4] demonstrated that the product distribution during ethanol wet oxidation in a mini-pilot TBR was slightly affected by LFM. Longer dry periods have a positive effect on the selectivity toward the end product. Massa et al. [5] studied the oxidation of phenol solutions over $CuO/Al_2O_3$ catalysts.

Steady-state and slow-mode cycling experiments were performed. In the range of operating conditions investigated (low partial wetting of the bed), it was observed that LFM has a mild effect on phenol conversion but a positive effect on mineralization, especially at longer periods. Liu et al. [6] investigated the influence of periodic operation on hydrogenation of 2-ethylanthraquinones, over $Pd/Al_2O_3$ on a laboratory-scale TBR under isothermal conditions. The authors observed that the selectivity of the intermediate product can be improved by up to 12 % when working with ON-OFF cycling at periods between 20 and 80 s.

More recently, Liu et al. [7] studied the effect of unsteady-state operation on a TBR in which the exothermic hydrogenation of dicyclopentadiene (DCPD) over a $Pd/Al_2O_3$ catalyst takes place. For cycle periods from 60 to 400 s and splits from 0.25 to 0.75, the final product yield is enhanced compared to the one attained under steady-state operation. Skala and Hanika [8] also investigated DCPD hydrogenation on an egg-shell type palladium catalyst in a laboratory TBR for continuous and LFM conditions. For a split of 0.5 and a period length of 60 s, the reaction rate increased by 12 % compared with the steady-state regime. However, the selectivity of DCPD hydrogenation to the intermediate product was not favored.

All the above-mentioned contributions agree on the fact that LFM affects reaction rate and product distribution. It is well known that rate enhancement can be achieved by reduction of mass transfer resistance and/or an enhancement of the catalyst activity. Besides, for exothermic reactions and non-isothermal conditions, performance enhancements can also result from the arising thermal cycles [9–11]. Nevertheless, the impact of

LFM on product distribution of consecutive reactions still requires further investigation for establishing optimal operating conditions.

The objective of this contribution is to examine the influence of cycling variables on the yield of consecutive reactions, such as those involved in ethanol oxidation by noble metal catalysts. The liquid flow rate used during the ON portion of cycling was kept constant, regardless of the duration of dry and wet cycles. Therefore, cycling experiments would attain the same hydrodynamic conditions (degree of wetting, liquid holdup) during the ON period, provided it is sufficiently long. Using this strategy, the impact of duration of wet and dry cycles as well as the period effect on product distribution is independently studied.

## 2    Materials and Methods

Catalytic oxidation of aqueous ethanol solutions using molecular oxygen was studied in a liquid batch-recycled differential TBR operated at 1 atm and 70 °C. The experimental apparatus is schematized in Fig. 1. It basically consisted in a packed bed of a 0.5 % Pd/$\gamma$-Al$_2$O$_3$ egg-shell catalyst (120 g) through which the reactive solution flowed concurrently with the gas phase (pure oxygen, 200 mL min$^{-1}$). The mean particle diameter was 2.7 mm. At the reactor outlet the liquid was separated from the gas and returned to a reservoir, from which it was recycled to the reactor. The outlet gas was cooled in a vertical condenser kept at 273 K which finished in a distilled-water cold trap. The catalytic bed had 2.54 cm internal diameter and 40 cm height. For each experiment, 300 mL of a 0.25 M ethanol solution was introduced in the reservoir and subsequently fed to the reactor with a constant liquid velocity by a variable-speed peristaltic pump, commanded by a programmable logic controller (PLC). Experiments at constant liquid flow rate (CLFR) and modulated liquid flow rate (MLFR) were performed. Liquid flow rates ranged between 0.1 and 0.56 cm s$^{-1}$. Further details can be found in Ayude et al. [12].
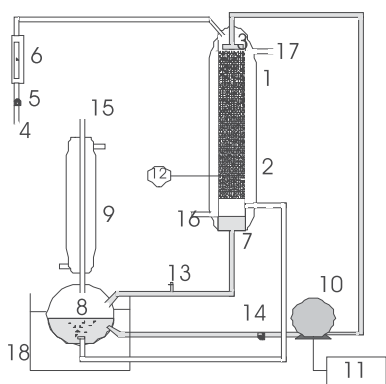


**Figure 1.** Schematic experimental setup. (1) Prepacking; (2) catalyst bed; (3) liquid distributor; (4) oxygen inlet; (5) needle valve; (6) rotameter; (7) gas liquid separator; (8) absorber; (9) refrigerant; (10) liquid pump; (11) programmable logic controller; (12) temperature thermocouple; (13) liquid sampler; (14) liquid sampler; (15) gaseous stream outlet; (16, 17) hot water; (18) thermostatic bath.

Constant gas and liquid flow rates were used in all the cycling experiments to analyze particularly the impact of duration of wet and dry cycles on reactor performance, carrying out LFM experiments under the same asymptotic hydrodynamic conditions (degree of wetting, liquid holdup) during the wet cycle. That is, the liquid flow rate used during the ON portion of cycling was kept constant, regardless of the duration of dry and wet cycles. This is known as constant bed irrigation condition. As follows, the impact of the duration of wet and dry cycles as well as the period effect on product distribution is independently studied. Wet and dry periods were varied in the range of 2–7 min and 1–7 min, respectively.

For all the experiments presented here, the catalyst bed was always flooded overnight with fresh ethanol solution. To start an experiment, the liquid was circulated through the bed for about 20 min in the absence of oxygen. An initial liquid sample was withdrawn and analyzed by GC to get the reference ethanol concentration. Then, the bed was flooded again and preheated up to the operating temperature. This reductive start-up procedure ensured complete internal wetting of the catalyst and a higher initial catalyst activity. Besides, it facilitates the reproducibility in experiments. Catalyst deactivation was regularly tested with conventional runs. Changes in measurements of CLFRs before and after a cycling experiment were taken as an evidence of variations in catalyst activity during periodic operation. Catalyst deactivation by over-oxidation, which is the most likely one under prolonged cycling experiments, is completely reversible in a reductive environment. This fact was already checked and reported in a previous work [12]. Hence, with the starting procedure of flooding the bed with ethanol solution, the reductive environment imposed by the alcohol ensures that the catalyst has always the same activity. The catalyst did not change its activity during the time in which all the experiments presented in this contribution were performed.

After the start-up procedure was completed, gas and liquid flows were introduced to the reactor. As the experiment progressed, small samples of liquid obtained from the absorber and the cool trap were withdrawn. With this procedure and taking into account that the variation of the liquid volume in the cool trap was negligible, the total liquid volume in the experimental setup changed by less than 1 %. The samples were properly refrigerated prior to analysis to minimize volatilization, and ethanol was detected and quantified by GC/FID. Under the operating conditions, acetic acid was identified as the final product. Ethanol, acetaldehyde, and acetic acid were effectively separated with a capillary column ECONO-CAP EC-WAX. A temperature program (30 °C for 3 min; 30 °C per minute ramp; 150 °C for 3 min) was used to improve separation.

For all the CLFR and MLFR tests performed, plots of the measured ethanol concentration versus time were linear, indicating a constant rate. As conversion per pass was very low, the reaction was allowed to proceed for a certain time meanwhile samples were taken. From these preliminary experiments, a reaction time of 180 min was fixed. The reaction rate was then evaluated from ethanol conversion at 180 min. After that time, the liquid solution was discharged and fresh ethanol solution was fed and allowed to stay overnight before starting a new experiment.

CLFR and ON-OFF cycling experiments were performed randomly. Reaction rates were evaluated considering the molar concentration in the liquid reservoir and the mass accumulated in the cold trap, as described in Ayude et al. [12]. Acetic acid yield was quantified as the ratio between the acetic acid reaction rate and ethanol reaction rate. All presented data indicate an average of at least three experiments. The relative error was within 12 %.

## 3    Results and Discussion

CLFR experiments at constant liquid flow rates were performed to provide a comparison basis for the LFM studies and to assess the importance of mass transport effects. Results are indicated in Fig. 2 as the rate of ethanol consumption and acetic acid production versus superficial liquid velocity ($u_L$).

Ethanol reaction rates increase at low liquid flow rates. This effect is observed when the limiting reactant is present in the gas phase. Low liquid flow rates result in partial wetting of the bed and regions of the catalyst directly exposed to the gas phase. In these regions, mass transfer of the gaseous reactant is enhanced and the ethanol oxidation rate increases. The acetic acid formation rate follows this trend (Fig. 2) as well as the acetic acid yield (Fig. 3). Since the acetic acid yield decreases with the liquid flow rate, it follows that a reduced wetting efficiency and/or an enhanced oxygen mass transport apparently favors oxidation toward acetic acid, the end product in the reaction scheme under the explored conditions. However, it should be mentioned that excessive exposure to oxygen may lead to catalyst deactivation by over-oxidation [12].

Ayude et al. [12] studied this system with LFM and found that reaction rates obtained during cycling are higher than rates obtained in CLFR experiments, provided neither over-oxidation nor liquid reactant depletion occurs. It was established that cycling performance is affected not only by the duration of wet and dry cycles but also by the magnitude of the liquid flow rate, which influence reactor hydrodynamics.
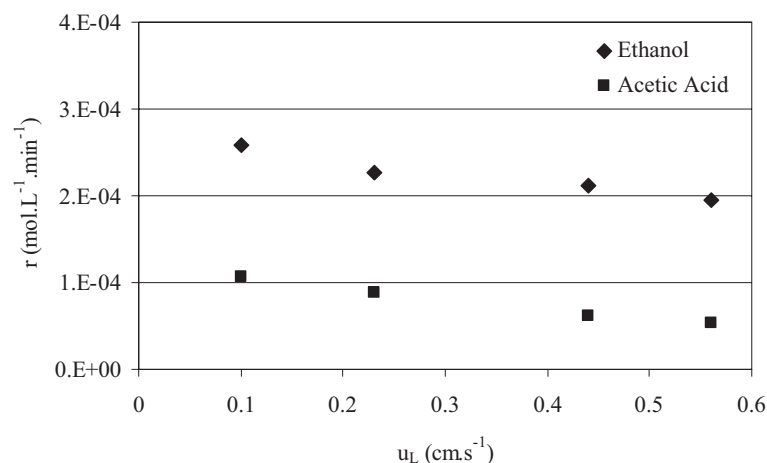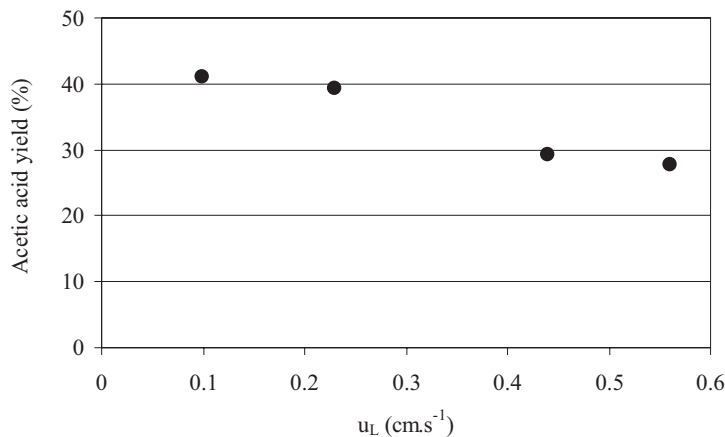


**Figure 3.** Acetic acid yield vs. superficial liquid velocity.

The duration of the optimal ON cycle is given by replenishment of the catalyst while the optimal OFF cycle length is given by the time necessary to avoid over-oxidation or liquid reactant depletion. Taking into account these findings, the present analysis was particularly oriented to determine the impact on reactor performance of wet and dry cycles' duration, carrying out LFM experiments under the same hydrodynamic conditions (degree of wetting, liquid holdup) during the wet cycle. Therefore, the liquid flow rate used during the ON portion of cycling was kept constant, regardless of the duration of dry and wet cycles (constant bed irrigation conditions).

Ethanol reaction rates and yields for typical MLFR experiments are presented in Figs. 4 and 5. Reference values of the attained rate and yield under CLFR at the same liquid flow rate used during the wet cycle are presented in the figures as dashed lines. Fig. 4 displays the reaction rates against the duration of the dry cycle for two different wet cycle times, long enough to ensure replenishment of liquid reactant but not so extended to achieve the same results as with CLFR. The impact of the duration of the dry cycle is evident. Both curves present a maximum. For small OFF cycle times (splits > 0.8), the complete draining of the bed is not accomplished during the dry cycle, therefore, bed conditions (wetting, holdup) change with time [13–15]. Liquid holdup and, consequently, catalyst wetting is not homogeneous along the bed and, in spite of decreasing as a whole, it does not lead to a substantial enhancement of the oxygen mass transport all over the reactor. As the OFF cycle time is increased, mass transport of oxygen during the dry cycle is enhanced and rates increase. Finally, when the dry cycle lasts more than 4 min, the rates decrease due to the prevalence of adverse effects [12]. For extended dry cycle duration, reaction rates are not favored with respect to values attained with CLFR since liquid reactant scarcity and particularly deactivation by over-oxidation may occur. It has been evidenced that aerobic liquid phase oxidation of alcohols over $Pd/Al_2O_3$ progress through alcohol dehydrogenation, and the role of oxygen in the re-



**Figure 2.** Ethanol consumption (◆) and acetic acid production rates (■) vs. superficial liquid velocity.
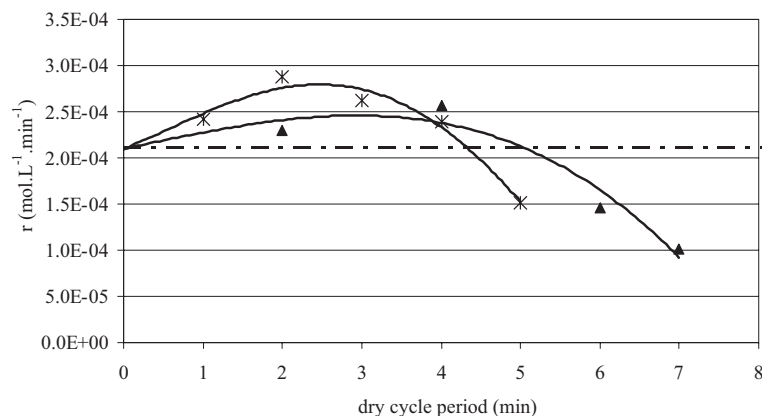
**Figure 4.** Ethanol reaction rate vs. dry cycle period for different wet cycle periods: (✳) 5 min, (▲) 7 min. Dashed line: outcomes of the reference CLFR run performed at the liquid flow rate used during the wet cycle (constant bed irrigation). Curved solid lines are used to guide the eyes.
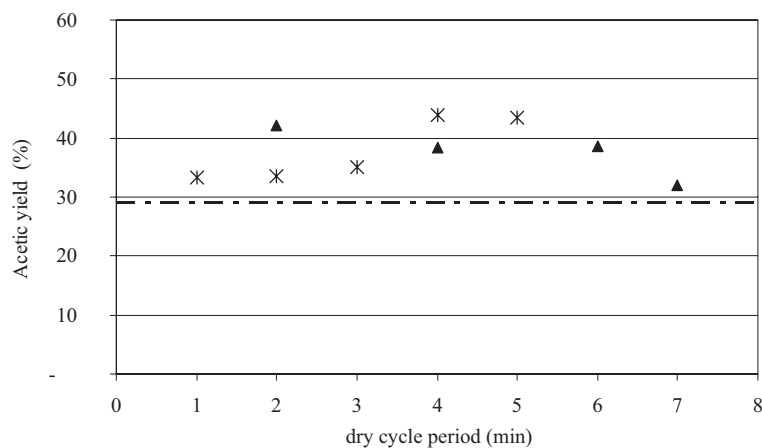


**Figure 5.** Acetic acid yield vs. dry cycle period for different wet cycle periods: (✳) 5 min, (▲) 7 min. Dashed line: outcomes of the reference CLFR run performed at the liquid flow rate used during the wet cycle (constant bed irrigation).

action can be illustrated by a bell-shaped curve [16, 17]. Below a certain oxygen coverage of the metal active sites, the rate decreases due to catalyst poisoning by the hydrocarbon chain residues, and the major role of oxygen is the oxidative removal of degradation products to remove the poisoning species and thus increase the number of active sites available for alcohol dehydrogenation. On the other side, when the amount of oxygen is too high, the oxidized metal is poorly active in alcohol oxidation (deactivation by over-oxidation). Hence, for maximizing the aerobic alcohol oxidation process, the reactor should be operated by fine-tuning the rate of oxygen supply. The extension of the dry cycle in an ON-OFF cycling strategy has to be optimized to avoid excess contact since it deactivates the catalyst.

Acetic acid yields versus duration of the dry cycle results are presented in Fig. 5. For the operating conditions studied, cycling always improves the production of acetic acid. When the liquid flow is halted, the intermediate products remain inside the catalyst and are further oxidized to final products.

Additionally, the residence time of the intermediates and the average oxygen concentrations inside the pellet during cycling are higher than those attained with CLFR.

In Figs. 6 and 7, LFM results are presented as a function of cycle period for cycling experiments carried out with split 0.5. Reference values of the attained rates and yields under CLFR condition at the same liquid velocity used during the wet cycle (constant irrigation) and at half of this liquid velocity (considering that the split of the experiments is 0.5) are indicated in the figures as dashed and solid straight lines, respectively. A progressive decrease of ethanol consumption rate versus cycle period profile is observed. For cycle periods < 6 min, the ethanol oxidation rate is larger than those attained with CLFR for both reference conditions. Extended cycle periods lead to a decrease in the ethanol reaction rate. The acetaldehyde formation rate also decreases with the cycle period, however, the reaction rate is significantly larger than the one attained for the reference states at the lowest cycle period examined, and decreases more pronouncedly for cycle periods < 10 min. Distinctly, the acetic acid formation rate remains almost unaltered as the cycle period is modified, presenting a flat maximum for a cycle period around 6 min.

Fig. 7 highlights that the acetic acid yield exhibits a maximum with the cycle period and that it is almost always larger than the yield attained for CLFR under constant irrigation conditions. Only for the lowest cycle period, the acetic acid yield is adversely affected by a cycling strategy. These outcomes indicate that when a TBR is operated with LFM during alcohol oxidation with molecular oxygen in aqueous media using Pd/Al$_2$O$_3$ as catalyst, short cycle periods favor selectively the aldehyde formation, while generally any other cycling strategy benefits the carboxylic acid yield, end product in the consecutive reactions for the explored conditions. For long cycle periods as well as for long dry periods, adverse effects related mainly to catalyst deactivation and liquid reactant scarcity govern the process, leading to the schemes generally found for consecutive reactions at very low conversion levels.

The comparison between CLFR and MLFR runs performed at a liquid flow rate times the split (when the split is 0.5) indicates that the ethanol reaction rate is enhanced at cycle periods lower than 6 min, a condition in which the acetaldehyde yield is promoted. This trend is in agreement with Boelhouwer et al. [3] who suggested that selectivity towards the intermediate product in consecutive reactions may require relatively high cycled liquid feed frequencies to reduce the residence time of the intermediate product inside the catalyst. It is interesting to remark that through frequency tuning product distribution can be significantly modified.
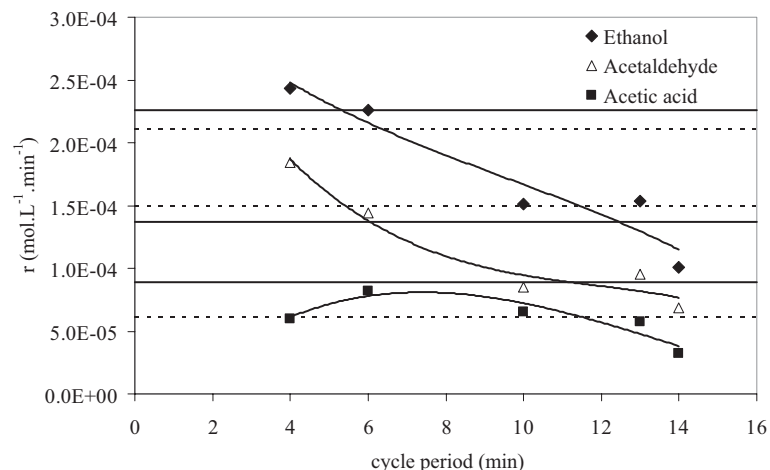
**Figure 6.** Reaction rates as a function of cycle period. Split = 0.5; (◆) ethanol, (△) acetaldehyde, (■) acetic acid. Reference CLFR experiment: dashed lines at the liquid velocity used during the wet cycle; solid lines at the liquid velocity used during the wet cycle multiplied by the split. Curved solid lines are used to guide the eyes.
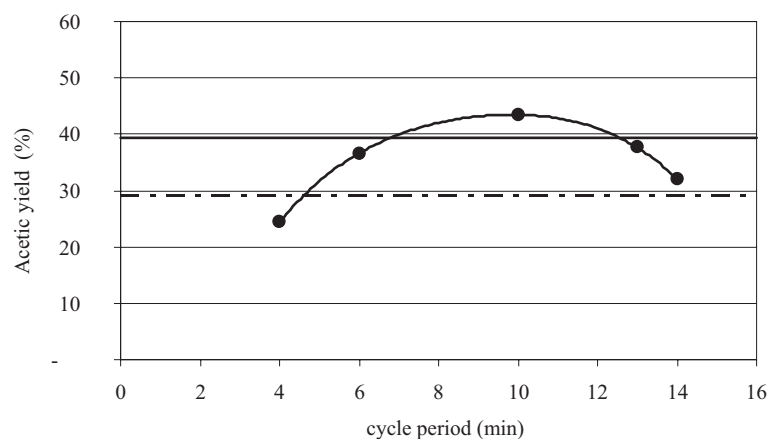


**Figure 7.** Acetic acid yield as a function of cycle period. Split = 0.5. Reference CLFR experiment: dashed lines at the liquid velocity used during the wet cycle; solid lines at the liquid velocity used during the wet cycle multiplied by the split. Curved solid line is used to guide the eyes.

## 4 Conclusions

The effect of LFM on product distribution attained for alcohol oxidation with molecular oxygen in aqueous media using Pd/Al$_2$O$_3$ as catalyst is investigated in a liquid batch-recycled differential TBR operated at 1 atm and 70 °C. Experiments were performed with a CLFR during the ON portion of cycling, regardless of the duration of dry and wet cycles. Outcomes were compared with the ones attained in experiments with CLFR.

For intermediate periods, the residence time of the intermediate product and average oxygen concentrations inside the catalytic pellet during LFM are higher than those attained in experiments with CLFR, leading to a significant increase of acetic acid yield. For short periods or high cycling frequencies,

LFM leads to an increase in selectivity towards the intermediate product. For long cycle periods, adverse effects related mainly to catalyst deactivation and liquid reactant scarcity govern the process, resulting in very low conversion levels. The results indicate that the product distribution can be significantly modified through frequency tuning.

*The authors have declared no conflict of interest.*

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