

Ethanol oxidation in a trickle-bed reactor using a hydrophobic catalyst Effect of dilution with hydrophilic particles

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Abstract

Ethanol oxidation at moderate temperature and atmospheric pressure is carried out in a trickle-bed reactor using a hydrophobic catalyst and pure oxygen as the oxidizing agent. The influence of diluting the hydrophobic catalyst with different proportions of the hydrophilic inert support is particularly studied by performing comparative experiments at different operating conditions. Reactor performance is not significantly modified when the hydrophobic catalyst is diluted with the hydrophilic support in a 50% mass proportion. For a larger dilution, 75% (w/w), significant differences in ethanol conversions are found for certain conditions, presumably due to the influence of the liquid holdup, gas–liquid interfacial areas and wetting efficiency characterizing a bed with a major proportion of hydrophilic particles. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Trickle-bed reactors (TBRs) have been traditionally employed in petrochemical industries, mainly for hydrotreating of gas–oils. Actual applications of these reactors have extended largely in various fields, including wastewater treatment, fine chemical, biochemical and electrochemical processes [1]. The suitability of TBRs for catalytic wet oxidation of organic compounds has been recently noticed [2–6]. These reactors are particularly adequate when the concentration of organic compounds is too high or toxic to microorganisms [7].

The advantages of using hydrophobic catalysts instead of the conventional hydrophilic ones for catalytic wet oxidation in humid air have been put in evidence in the last years [8–10]. However, the use of hydrophobic catalysts in TBRs has been scarcely examined for this purpose. Only few studies concerned with the effect of the hydrophobic character of the catalyst on the performance of TBRs for catalytic oxidation in aqueous solutions have been reported [2,4,11]. From these works, the use of hydrophobic catalysts in TBRs for wet oxidations proved to be advantageous. Moreover, even research works concerned with hydrodynamics and transport phenomena in TBRs packed with hydrophobic particles of small size are scarce [12–16].

In a recent contribution, Horowitz et al. [4] have compared the performance of a TBR packed either with a hydrophilic catalyst or the same catalyst cov-

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Nomenclature

| | |
|----------|---|
| C_f | ethanol concentration in the feed solution (kmol/m ³) |
| G | gas mass velocity (kg/m ² s) |
| L | liquid mass velocity (kg/m ² s) |
| N_{Ti} | total number of moles entering the system, including gas and liquid phases (kmol) |
| N_{To} | total number of moles leaving the system, including gas and liquid phases (kmol) |
| x | ethanol conversion, $(N_{Ti} - N_{To})/N_{Ti}$ |

ered with Teflon, to turn it hydrophobic. The oxidation of aqueous ethanol solutions was employed as a model reaction. A significant improvement in the reactor performance was found for the studied conditions while employing the hydrophobic catalyst, especially for relatively high concentrations of the organic compound since the access of O₂ to the catalyst surface is favored. Considering that catalytic wet oxidations are generally carried out at high pressure to increase O₂ solubility in water, this result suggests the possibility of employing milder conditions in TBRs by using a hydrophobically coated catalyst whenever the reaction is gas-limited.

Chen and Chuang [2] have carried out the catalytic oxidation of methanol in aqueous solutions using a hydrophobic catalyst diluted with different proportions of the hydrophilic inert support in a TBR. They found an increase in methanol conversions when the hydrophobic catalyst was diluted with hydrophilic particles. Since they considered that the reaction took place in the gaseous phase, the larger conversions found for higher proportions of hydrophilic particles were attributed to an increase in the gas–liquid interfacial area, which promoted methanol stripping.

Rangwala et al. [13] studied the hydrodynamic characteristics of fixed beds packed either with hydrophobic or hydrophilic particles and mixtures of these particles in different mass proportions. They found that the use of particles of different wettability in packed beds with trickling flow of the liquid phase induces significant modifications in the hydrodynamic characteristics of this type of gas–liquid contactors. In this context, the aim of the present study is to examine the influence of hydrophilic inert particles dilution on the performance of a TBR for a wet oxidation process carried out using a hydrophobically coated catalyst.

For this purpose, the catalytic ethanol oxidation, a well-documented model reaction often used to study TBRs behavior [17–19], was selected. For the experimental conditions explored in this work, the reaction behaves as gas-limited [20]. A conventional Pt/ γ -Al₂O₃ catalyst coated with Teflon, to turn it hydrophobic, and pure oxygen as the oxidizing agent were employed. The bed was diluted with the catalyst support, namely γ -Al₂O₃ hydrophilic particles. The reactor performance, while packed either with the hydrophobized catalyst particles or mixtures of the hydrophobic catalyst diluted with the hydrophilic inert support in different mass proportions, was determined in a bench scale installation. Results are analyzed taking into account modifications of liquid holdup, wetting efficiency and gas–liquid interfacial areas induced by the presence of particles of different wetting characteristics in gas–liquid contactors with trickling flow of the liquid phase.

2. Experimental

A schematic diagram of the experimental installation is presented in Fig. 1. A bench scale TBR made in acrylic, 0.04 m internal diameter and 1 m high, was employed to carry out the catalytic wet oxidation of ethanol aqueous solutions at atmospheric pressure, using pure oxygen (99.9%, v/v) as the gaseous reactant. It was externally heated with warm water in order to keep the temperature at 70°C.

The hydrophobic catalyst was prepared by coating with Teflon 30N, a conventional Pt/Al₂O₃ (1%, w/w) catalyst obtained following the procedure described by Barth et al. [21]. Spheres of γ -Al₂O₃, mean diameter of 3×10^{-3} m, were used as catalyst support. The same hydrophilic spheres of γ -Al₂O₃ were employed to dilute the bed. The technique applied to coat externally the catalyst particles was proposed by Rangwala et al. [22]. The coating procedure did not modify the specific surface area of the catalyst, as determined from N₂ adsorption isotherms at 77 K using the conventional BET procedure. Calculated surface area before and after coating is 250 m²/g.

The TBR was packed either with 100% hydrophobic catalyst or with the hydrophobic catalyst diluted with the hydrophilic support in different mass proportions (50, 75%, w/w). The amount of catalyst and

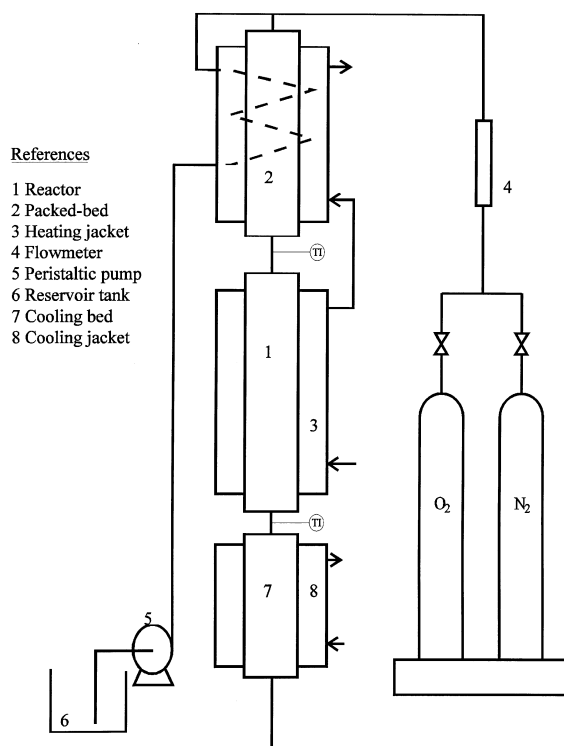


Fig. 1. Schematic diagram of the experimental installation.

diluent composing the trickle-bed in each case, and the resulting bed heights are given in Table 1. Experimental details of results obtained in a previous work [4] using the same catalyst before being coated are also included in the table, since they will be considered in the discussion with the purpose of comparison.

Aqueous ethanol solutions were contacted with O₂ in a packed bed of glass beads placed before the reactor inlet to achieve thermal and vapor pressure equilibrium between the solutions and the gaseous phase. At the reactor outlet, another column filled with glass

Table 2

Experimental conditions investigated

| | |
|--|----------------------|
| Gas mass velocity, G (kg/m ² s) | 0.002–0.055 |
| Liquid mass velocity, L (kg/m ² s) | 0.24–2.20 |
| Ethanol concentration in the feed solution, C_f (kmol/m ³) | 0.006–0.03–0.06–0.12 |

beads and provided with a cooling jacket allowed to absorb the non-reacted ethanol from the gas phase into the liquid. Temperature in the jacket was kept constant with flowing water. Gas–liquid equilibrium was tested by comparing the temperatures and liquid ethanol concentrations measured at the reactor inlet for several conditions with literature information [23]. Good agreement was found.

Before starting the experiments, the bed was flooded with the preheated liquid solution by closing the corresponding valves to ensure complete internal wetting of the catalyst and to heat the bed. Then, liquid and gas were circulated throughout the installation at high throughputs. Afterwards, the gas and liquid flow rates used for the experiments were fixed, starting from the highest ones, and the ethanol concentration at the reactor outlet was measured periodically (every 20 min) until steady state. The latter was identified by differences of less than 1% among ethanol concentrations for three consecutive samples.

Ethanol concentrations in the liquid feed and outlet streams were measured with a Perkin Elmer Autosystem gas chromatograph using an FID detector. These values were used to calculate ethanol conversions according to: $x = (N_{Ti} - N_{To})/N_{Ti}$, N_{Ti} and N_{To} indicate ethanol moles at the inlet and outlet streams, respectively. Experiments were carried out employing different ethanol concentrations in the feed solution and varying the gas and liquid flow rates. The experimental conditions studied are summarized in Table 2.

Table 1

Beds solid composition and height for the different dilution ratios examined

| Bed | Dilution ratio (%, w/w) | Bed height (m) | Hydrophobic catalyst weight (kg) | Hydrophilic catalyst weight (kg) | Weight of hydrophilic inert support (kg) |
|-----|----------------------------|-------------------|-------------------------------------|-------------------------------------|---|
| I | – | 0.33 | – | 0.4 | – |
| II | 0 | 0.33 | 0.4 | – | – |
| III | 50 | 0.67 | 0.4 | – | 0.4 |
| IV | 50 | 0.33 | 0.2 | – | 0.2 |
| V | 75 | 0.67 | 0.2 | – | 0.6 |

3. Results and discussion

Ethanol conversions achieved in the TBR packed with the coated catalyst at a given gas flow rate and various liquid flow rates are presented in Fig. 2 for different ethanol concentrations in the feed solution. Conversion diminishes as the liquid velocity increases due to a decrease in the space-time available for the reaction. For the sake of comparison, previous results [4] obtained for ethanol oxidation in the same reactor packed with 100% hydrophilic catalyst, namely using the same catalyst without the Teflon coating, are complementarily included in Fig. 2. Differences in ethanol conversions between the 100% hydrophobic catalyst bed and the 100% hydrophilic catalyst one attest the significant role of the catalyst wettability on the reactor behavior. According to the model reported in [4] to get insight on the behavior of a TBR for catalytic wet oxidation of ethanol when employing a hydrophobic catalyst, the reduction in the catalyst wetting efficiency improves ethanol conversions since reactants, specially oxygen that is scarcely soluble

in water, reaches the catalysts surface more readily through the “dry” zone of the particles. The hydrophobic character of the catalyst is particularly relevant for gas-limited reactions since it favors the access of the controlling reactant to the catalyst surface. Ethanol oxidation is gas-limited under all the experimental conditions examined in this work as confirmed by the criterion of Khadilkar et al. [20].

The effect of diluting the hydrophobic catalyst with 50% (w/w) hydrophilic support is also depicted in Fig. 2. A comparison between results obtained with 100% hydrophobic catalyst and with the 50% (w/w) dilution points to a negligible effect of this dilution ratio on reactor performance for the various experimental conditions examined. Fig. 3 shows that the influence of 50% (w/w) bed dilution on the TBR performance for the catalytic wet oxidation of ethanol does not change when the gas flow rate is modified. In addition, it can be inferred from the figure that the gas velocity has almost no effect on ethanol conversions within the studied range for given liquid flow rate and reactant concentration in the feed solution. The negligible effect of the gas flow rate may be attributed to an almost constant oxygen concentration along the

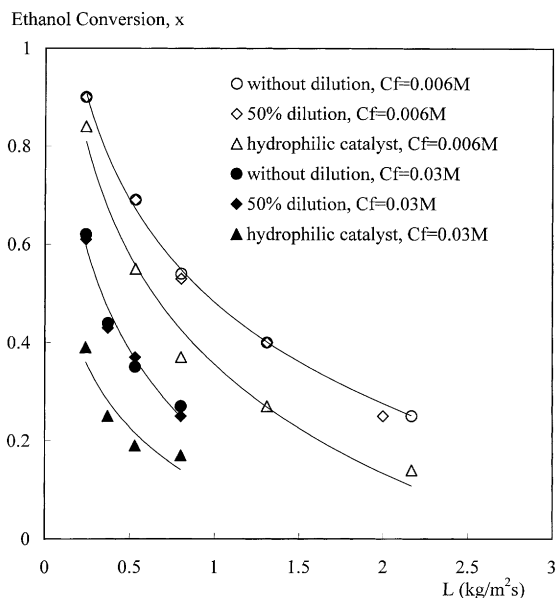


Fig. 2. Influence of bed dilution with 50% (w/w) hydrophilic support on the ethanol conversion for different liquid flow rates and ethanol concentrations in the feed solution, $G = 0.017 \text{ kg/m}^2 \text{ s}$. Comparison with ethanol conversions obtained with the catalyst before being coated [4]. Lines are only to guide the eyes.

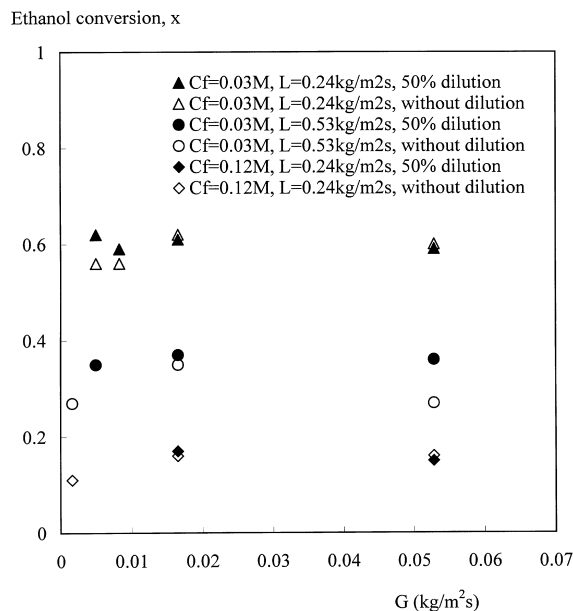


Fig. 3. Influence of bed dilution with 50% (w/w) hydrophilic support on the ethanol conversion for different gas and liquid flow rates and ethanol concentrations in the feed solution.

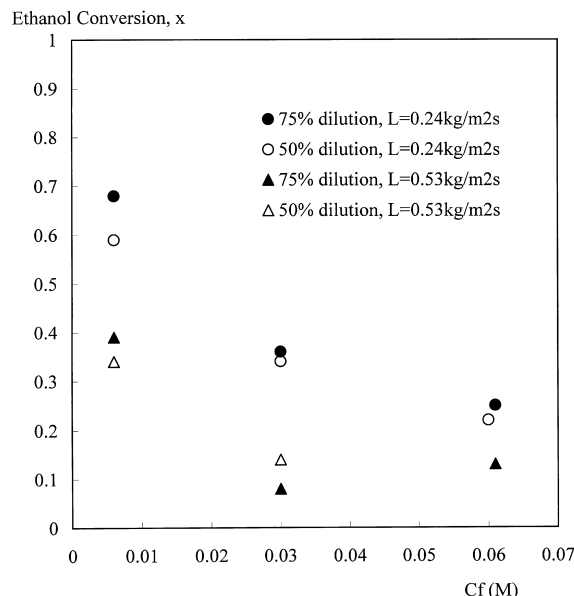


Fig. 4. Comparison of the TBR performance packed with the hydrophobic catalyst diluted either with 50 or 75% (w/w) hydrophilic support for different ethanol concentrations in the feed solution at two liquid mass velocities, $G = 0.017 \text{ kg/m}^2 \text{ s}$.

reactor, the high ethanol solubility in water and the weak influence of gas flow rate on the catalyst wetting efficiency.

Results obtained for the reactor packed with the hydrophobic catalyst and different mass proportions of hydrophilic inert particles (50, 75%, w/w) are illustrated in Fig. 4. Ethanol conversions are represented as a function of this reactant concentration in the feed solution. Differences in ethanol conversions between both dilution ratios are significant for large conversion levels attained at low liquid flow rates and the lower examined ethanol concentration in the feed solution.

To analyze present results, information on the influence of using particles of different wettability on the hydrodynamic characteristics of a fixed bed gas–liquid contactor with liquid in trickle flow, reported by Rangwala et al. [13], is used. These authors determined a progressive increase of the liquid holdup and the gas–liquid interfacial area as the mass proportion of hydrophilic particles in the bed was increased.

Thus, according to Rangwala et al. [13], increasing dilution leads to larger liquid holdups, which in turn

prolong the liquid residence time. The residence time (of both fluid phases) also increases due to the longer reactor lengths required for the diluted beds. Longer residence times allow a better mass transfer of both reactants between the gas and the liquid phases. Oxygen from the gas phase is likely to saturate the liquid phase and more in situ stripping of the dissolved ethanol is expected [2], which permits the access of this reactant into the catalyst via the “dry” surface when the wetting efficiency is less than 1. Hence, oxygen concentration in the liquid phase and ethanol concentration in the gas phase are larger, consequently modifying the reaction rate. This effect should be more pronounced for high conversion levels, since reactants are largely consumed.

In turn, although larger liquid holdups are known to induce larger mean wetting efficiencies in the bed [15,24,25], this trend has been only verified for trickle-beds formed either by 100% hydrophilic particles or by 100% hydrophobic particles. Unfortunately, the lack of information in the literature for trickle-beds packed with mixtures of particles of different wettability hinders a founded analysis in this direction. Nevertheless, it may be hypothesized that in the case of mixtures of hydrophobic and hydrophilic particles, the former would probably be less wetted by the liquid due to preferential channels for the liquid flow; consequently, the wetting efficiency of the hydrophobic particles might remain unchanged or be even lower. Then, at least, the more favorable access of reactants to the catalyst particles through the “dry” zone should hold.

Furthermore, the gas–liquid interfacial area increases as the amount of hydrophilic particles increases in the bed [2,13]. This trend leads to an effect similar to the one of the liquid holdup on the in situ stripping of the organic compound dissolved in water and the improvement in oxygen mass transfer to the liquid phase. The influence of diluting the hydrophobic catalyst bed on the ethanol conversion values, for low liquid velocities, is closely consistent with the trend reported by Rangwala et al. [13] for the gas–liquid interfacial area in a trickle-bed formed by 100% hydrophobic particles and mixtures of hydrophobic–hydrophilic particles of similar mass proportions as the ones used in the present study.

From the three analyzed parameters, holdup, gas–liquid interfacial area and wetting efficiency, the

last one appears to exert a decisive influence on the TBR performance for the ethanol oxidation behaving as a gas-limited reaction. This is clearly verified from the comparison between ethanol conversions achieved with the hydrophobic and the hydrophilic catalyst (see Fig. 2 and Ref. [4]). Since the wetting efficiency of the hydrophobic catalyst is probably not substantially modified by the dilution with the hydrophilic support, the TBR performance is similar for the beds composed by 100% hydrophobic catalyst and with the 50% (w/w) dilution (Figs. 2 and 3) and for several operating conditions at 75% (w/w) dilution (Fig. 4).

The larger ethanol conversions obtained for the reactor packed with 75% (w/w) hydrophilic particles (Fig. 4), mainly for high conversion levels and low ethanol concentrations, may be due to an additionally beneficial effect arising from the relative enhancement of both liquid holdup and gas–liquid interfacial area induced by the major proportion of hydrophilic particles constituting the bed. For 50% (w/w) dilution, this proportion may not be large enough to give rise to significant hydrodynamic modifications in order to be reflected in ethanol conversions, at least in an appreciable way.

4. Conclusions

The TBR performance, while packed either completely with a hydrophobic catalyst or diluted with different proportions of the hydrophilic particles used as the catalyst support, was comparatively examined in a bench scale installation. The improvement of reactor performance found, while using the coated hydrophobic catalyst instead of the hydrophilic one, holds for the bed composed by 100% hydrophobic catalyst and different dilution ratios with the hydrophilic support. Ethanol conversions attained in the TBR packed with 100 or 50% (w/w) hydrophobic catalyst are similar for all the experimental conditions examined. For a major proportion of hydrophilic particles in the bed, 75% (w/w) dilution, a further improvement is observed for high conversion levels and low ethanol concentrations. The influence of reactor dilution with hydrophilic particles is associated to the interrelated action of the liquid holdup, gas–liquid interfacial area and wetting efficiency that characterize the trickle-bed.

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