



Liquid phase catalytic hydrodechlorination of 2,4-dichlorophenol over Pd/Al₂O₃: Batch vs. continuous operation

Santiago Gómez-Quero, Fernando Cárdenas-Lizana, Mark A. Keane*

Chemical Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, United Kingdom

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ABSTRACT

The three-phase (atmospheric pressure, $T=303$ K, bulk solution pH 12) catalytic hydrodechlorination (HDC) of 2,4-dichlorophenol (2,4-DCP) over Pd/Al₂O₃ has been studied in batch and continuous flow reactors. In both cases, 2,4-DCP yielded 2-chlorophenol and phenol as products of partial and complete HDC, respectively. Cyclohexanone, resulting from further ring hydrogenation, was also isolated but was formed with low selectivity ($\leq 4\%$). Conditions have been established in both reactors where HDC proceeds under catalytic control. A move from discontinuous to continuous operation resulted in a more efficient (five-fold) H₂ transfer, which can be attributed to an extended gas/liquid interface available for mass transport. Higher HDC rate and increased selectivity to phenol were obtained in the continuous flow reactor, which we attribute to a lower pH at the liquid/solid interface relative to batch operation. Furthermore, the productive catalyst lifetime was extended in the flow reactor due to the more effective removal of HCl from the catalyst surface. The results presented establish the feasibility of continuous, liquid phase HDC under mild conditions as a means of treating environmentally toxic 2,4-DCP.

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1. Introduction

2,4-Dichlorophenol (2,4-DCP) is a common feedstock used in the manufacture of herbicides, pharmaceuticals and dyes [1] with an estimated release into the environment of up to 2×10^4 lb year⁻¹ [2]. The low biodegradability of 2,4-DCP (recent biotreatment studies achieving maximum rates of $140 \text{ mg}_{2,4\text{-DCP}} \text{ g}_{\text{biomass}}^{-1} \text{ day}^{-1}$ [3]) and high associated toxicity [2,4] has placed this chemical on a list of high priority pollutants in terms of treatment [5]. A diversity of detoxification methodologies (e.g. photo-oxidation [6] and electrochemical degradation [7]) have been employed where catalytic hydrodechlorination (HDC), the H₂ scission of C–Cl bonds [8,9], has emerged as a progressive and viable approach that facilitates recovery and reuse of raw material [10]. 2,4-DCP HDC has been mainly studied in the liquid phase over carbon [11–18] and alumina [15–20] supported Pd catalysts, given the comparatively greater resistance of this metal to deactivation [21,22]. Structure sensitivity is a feature of HDC over Pd where catalytic performance has been demonstrated to be influenced by the size [23,24] and electronic structure [25,26] of the metal particles. The work to date has largely dealt with discontinuous operation to study reaction kinetics and provide a comparison of catalyst performance where cost and experimental effort has mitigated against the use of continuous reactors [27,28]. We can, however, flag

the work of Díaz et al. [29,30] who have reported kinetic data for the HDC of 4-chlorophenol in a CSTR. HDC operation in continuous mode is preferable from a practical point of view and represents a significant step towards industrial implementation, i.e. in waste abatement [31]. Indeed, Kalnes and James [32], in a pilot-scale study, clearly demonstrated the appreciable economic advantages of HDC over incineration while Brinkman et al. [33] have established the feasibility of a full scale hydrotreatment of PCB contaminated lubricating oils using a combined vacuum distillation/catalytic HDC.

Continuous operation in chlorophenol(s) HDC has focused on gas phase treatments, a trend which extends to the HDC of chlorobenzenes [34,35] and chloro-methanes [36,37]. Extensive gas phase chlorophenol(s) HDC research has been carried out by Marshall et al. [38,39], Halász et al. [40] and Keane and co-workers [41–47], who have demonstrated the feasibility of complete chlorine removal over unsupported Ag–Fe [38] and Mg–Pd [39], Pt and Co supported on ZSM-52 [40], Ni/SiO₂ [41–45], Au–Ni/SiO₂ [46] and Au–Ni/Al₂O₃ [47]. However, it should be noted that these studies are limited by the requirements of elevated temperatures ($T \geq 473$ K), pressures (up to 250 atm) and/or excess H₂ (400–1200 times), which represent significant energy consumption, a key factor in sustainable process design [48,49]. With regard to liquid phase chlorophenol(s) HDC, Calvo et al. [50,51] and Díaz et al. [29,30] have achieved near complete HDC of aqueous 4-chlorophenol over Pd/C in continuous (plug-flow (293–313 K, 1 bar) [50,51] and CSTR (298–373 K, 1–6 bar) [29,30]) reactors with an excess of H₂ (317–1333 times) relative to stoichiometric quanti-

* Corresponding author. Tel.: +44 0131 451 4719.
E-mail address: M.A.Keane@hw.ac.uk (M.A. Keane).

Nomenclature

a_g	gas/liquid interfacial area per unit volume of liquid ($\text{m}^2 \text{m}^{-3}$)
Ca	Carberry number (dimensionless)
$(C_{\text{H}_2})_{\text{bulk}}$	H_2 concentration in bulk liquid (mmol dm^{-3})
$(C_{\text{H}_2})_{\text{saturation}}$	H_2 saturation concentration (mmol dm^{-3})
C_{NaOH}	NaOH concentration in bulk liquid (mmol dm^{-3})
$C_{2,4\text{-DCP}}$	2,4-DCP concentration in bulk liquid (mmol dm^{-3})
$D_{\text{Eff},2,4\text{-DCP}}$	2,4-DCP bulk liquid effective diffusivity ($\text{m}^2 \text{s}^{-1}$)
$D_{2,4\text{-DCP}}$	2,4-DCP bulk liquid diffusivity ($\text{m}^2 \text{s}^{-1}$)
d	catalyst particle size (μm)
k_{Cl}	pseudo-first order hydrodechlorination rate constant (min^{-1})
k_j	pseudo-first order rate constant for step j (see Fig. 2) (min^{-1})
k_L	liquid film mass transfer coefficient (m min^{-1})
L	fitting parameter (dimensionless, see Eq. (14))
M	fitting parameter (dimensionless, see Eq. (14))
m_{Pd}	Pd catalyst loading ($\text{g}_{\text{Pd}} \text{g}^{-1}$)
N_{H_2}	H_2 mass transfer rate ($\text{mmol min}^{-1} \text{dm}^{-3}$)
n_{Cl}	mmoles organic chlorine
n_{HCl}	mmoles HCl
$\text{pH}_{\text{H}_2/\text{s}}$	pH at the liquid/solid interface (dimensionless)
pH_{pzc}	pH associated with the point of zero charge (dimensionless)
pK	acid–base equilibrium dissociation constant (dimensionless)
(R_{HDC})	hydrodechlorination rate ($\text{mmol}_{\text{Cl}} \text{g}_{\text{Pd}}^{-1} \text{min}^{-1}$)
T	temperature (K)
t	contact time (min)
$\bar{v}_{2,4\text{-DCP}}$	2,4-DCP molar volume ($\text{m}^3 \text{kmol}^{-1}$)
W	Pd mass (g_{Pd})
x_{Cl}	fractional dechlorination (dimensionless)
x_i	molar fraction of i (dimensionless)
<i>Greek letters</i>	
η	effectiveness factor (dimensionless)
η_{water}	water viscosity (Pa s)
ρ	catalyst bulk density (kg m^{-3})
ϕ	Thiele modulus (dimensionless)

ties. It should be noted that Calvo et al. [12] have also considered the HDC of 2,4-DCP in a fixed bed trickle reactor. Patel and Suresh [52] have recently quoted high efficiencies (*ca.* 80%) for (continuous) aqueous pentachlorophenol HDC over palladized cellulose discs at room temperature and atmospheric pressure.

In this study, we have established operational characteristics for the HDC of 2,4-DCP (in aqueous solution) over Pd/Al₂O₃ in a batch reactor and consider the feasibility/advantages of process scale up to continuous operation. We provide a comprehensive comparison of batch and continuous liquid phase catalytic HDC systems for treating toxic 2,4-DCP.

2. Experimental

2.1. Materials

The catalyst (1.2 wt.% Pd/Al₂O₃) was purchased from Sigma–Aldrich, sieved (ATM fine test sieves) into batches of 38 μm average particle diameter (d) and used as supplied. A full catalyst characterization can be found in earlier reports [18,53] where the presence of metallic Pd was established after room temperature

contact with H₂. The pertinent catalyst structural characteristics are: pH associated with the point of zero charge (pH_{pzc}) 7.7; bulk density (ρ) = 1154 kg m^{-3} ; BET surface area = 160 $\text{m}^2 \text{g}^{-1}$; total pore volume = 0.56 $\text{cm}^3 \text{g}^{-1}$ (porosity = 0.65, tortuosity = 1.54); Pd metal surface area = 208 $\text{m}_{\text{Pd}}^2 \text{g}_{\text{Pd}}^{-1}$; surface area-weighted mean Pd particle size = 2.4 nm. The 2,4-DCP reactant (Aldrich) and NaOH (Riedel-de Haën), both $\geq 99.0\%$, were used as received. An aqueous stock solution was prepared with distilled water using fixed concentrations of 2,4-DCP ($C_{2,4\text{-DCP}}$) = 30 $\text{mmol}_{2,4\text{-DCP}} \text{dm}^{-3}$ and NaOH (C_{NaOH}) = 100 $\text{mmol}_{\text{NaOH}} \text{dm}^{-3}$ (pH 12 at 303 K). The H₂ and He gases employed in this study were of ultra high purity (>99.99%, BOC).

2.2. Discontinuous reactor

Batch 2,4-DCP HDC reactions were carried out in a modified commercial glass reactor (Ken Kimble Reactors Ltd.); a schematic diagram is provided in Fig. 1a. The system is equipped with a constant H₂ supply (50–250 $\text{cm}^3 \text{min}^{-1}$, Brooks mass flow controlled) and a glass impeller provided effective agitation (300–1300 min^{-1}). A recirculator (Julabo HD-4) was used to stabilize the reaction temperature at $T = 303 \pm 1 \text{ K}$ with water as coolant (293 K); loss of the reactor liquid contents in the H₂ flow was negligible (<0.5%, v/v). At the beginning of each experiment, the catalyst (0.04 g) and 80 cm^3 of stock solution were charged and agitated in a He flow (50 $\text{cm}^3 \text{min}^{-1}$). The temperature was allowed to stabilize (15 min) and H₂ was then introduced ($t = 0$ for reaction). The pH of the reaction mixture was monitored continuously using a Dow–Corning pencil electrode coupled to a data logging and collection system (Pico Technology Ltd.). Blank tests conducted in He or over the support alone (*i.e.* in the absence of H₂ and/or Pd) did not result in any measurable conversion. A non-invasive liquid sampling system *via* syringe/in-line filters allowed a controlled removal of aliquots ($\leq 0.3 \text{ cm}^3$) of reactant/product(s). Upon completion of the reaction, the H₂ flow was replaced by a He purge. The reactant/product liquor was separated from the catalyst, which was retained in the reactor. The catalyst was then washed repeatedly with distilled water until the wash water exhibited near neutral pH.

2.3. Continuous reactor

Continuous HDC reactions were performed in a commercial COFLORE ACR[®] unit (AM Technology UK, see Fig. 1b). The reactor contains nine stages where the catalyst (0.04 g) was loaded, each containing the same catalyst mass and connected in series by channels fitted with 30 μm PTFE filters. The stock 2,4-DCP solution (80 cm^3) was fed using a Model 100 (kd Scientific) microprocessor-controlled infusion pump (0.4–7.6 $\text{cm}^3 \text{min}^{-1}$) and a constant volumetric H₂ flow (0–60 $\text{cm}^3 \text{min}^{-1}$) was provided using a (Brooks) mass flow controller. At steady state operation of constant gas + liquid flow, the available reaction volume (*i.e.* total liquid/solid slurry) was 80 cm^3 . The unit was equipped with a mechanical system providing an effective lateral shaking speed (29–53 min^{-1}) that served to maintain the catalyst in suspension. A water bath (Clifton) and a peristaltic pump (Watson-Marlow 502S) were used to stabilize the reaction temperature (303 K) to within $\pm 2 \text{ K}$, which was measured by an optical sensor (CALEX Electronics Ltd.) fitted to the stage(s) window(s). At the beginning of each run, distilled water was fed to the reactor with a co-current H₂ flow, a lateral shaking speed was fixed and the temperature was allowed to stabilize. The 2,4-DCP stock solution was then introduced and the catalyst/reactant contact time (t) was determined by the volumetric liquid flow rate. The effluent stream was collected for analysis and the pH was also monitored using a Dow–Corning pencil electrode as in the batch operation.

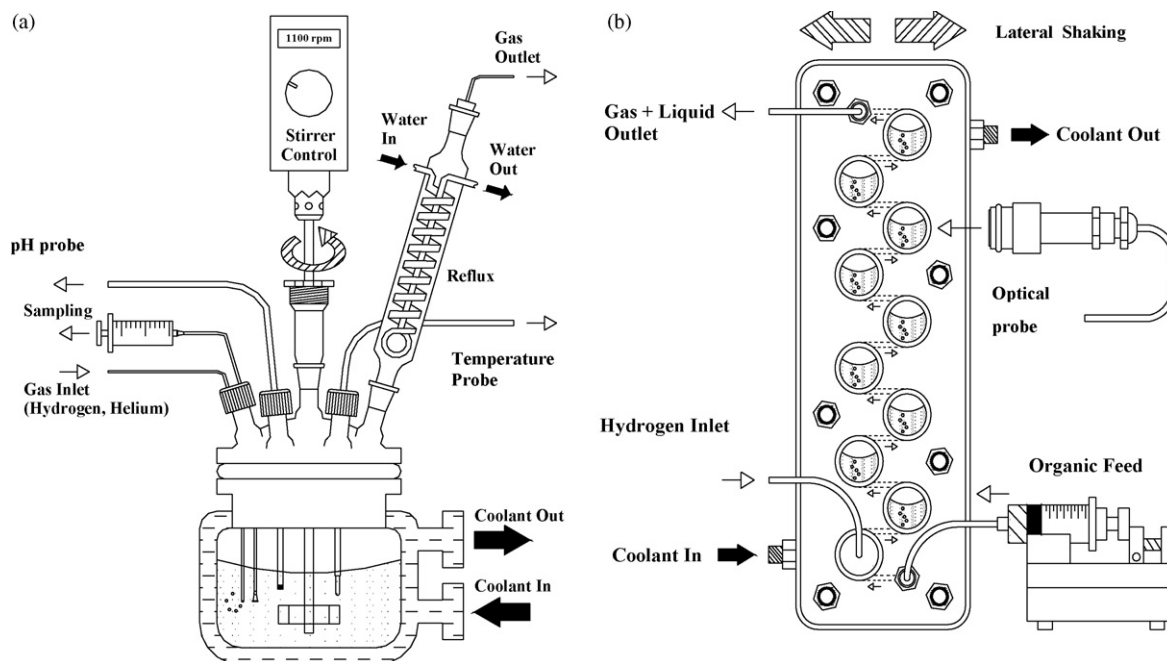


Fig. 1. Schematic diagram of the three-phase slurry (a) discontinuous and (b) continuous (COFLORE ACR®) reactors.

2.4. Product analysis and evaluation of HDC activity

Prior to analysis, the samples were neutralized with dilute acetic acid (200 mmol dm^{-3}). The composition of the reaction/product mixture was analyzed by gas chromatography (PerkinElmer Auto System XL), employing an FID and a DB-1 (J&W Scientific) capillary column (i.d. = 0.2 mm, length = 50 m, film thickness = $0.33 \mu\text{m}$) [14]. The concentrations of organic (and inorganic) species (2,4-DCP, 2-chlorophenol (2-CP), phenol, cyclohexanone and HCl) were determined from the total molar balance in the reaction mixture, where the effect of uptake on the support was negligible [54]. The efficiency of halogen removal is quantified in this study in terms of the fractional degree of HDC (x_{Cl}) as given by

$$x_{\text{Cl}} = \frac{n_{\text{HCl}}}{n_{\text{Cl}}} \quad (1)$$

where n_{Cl} and n_{HCl} are the mmoles of Cl associated with the organic reactant and inorganic product, respectively. Repeated reactions with different samples of catalyst delivered raw data reproducibility that was better than $\pm 6\%$.

3. Results and discussion

3.1. Product distribution: operation under catalytic control

The HDC of aqueous 2,4-DCP over $\text{Pd}/\text{Al}_2\text{O}_3$ under basic conditions (pH 12) in both batch and continuous operation generated 2-CP as the only partially chlorinated intermediate, and phenol as the principal product of complete HDC (see Fig. 2). This response is in accordance with reports in the literature [12,55] where dechlorination of *ortho*-substituted Cl was impeded due to steric hindrance effects. Further ring hydrogenation to yield cyclohexanone was detected at low selectivity levels ($\leq 4\%$, i.e. $(k_3 + k_5 + k_6) \ll (k_1 + k_2 + k_4)$). Liquid phase aromatic ring reduction over Pd catalysts is reported to be energetically demanding, requiring higher temperatures ($\geq 323 \text{ K}$ [50,56]) and/or pressures ($\geq 2 \text{ atm}$ [50,57]) than those used in this study.

In order to evaluate the true catalyst activity, reaction conditions must be first established wherein the reactor is operated

under kinetic/catalytic control. In a three-phase (gas/liquid/solid) system, the observed rate can be limited by H_2 diffusion through (i) the gas film and/or (ii) the liquid film at the gas/liquid interface. As undiluted H_2 gas has been used in this study, the gas film resistance can be neglected. Diffusion through the liquid film must be enhanced so that the bulk fluid is saturated in H_2 and its concentration ($(C_{\text{H}_2})_{\text{bulk}}$) approaches the limiting solubility in water: at 1 atm and 303 K, $(C_{\text{H}_2})_{\text{saturation}} \approx 0.8 \text{ mmol dm}^{-3}$ [53,54]. The H_2 mass transfer rate (N_{H_2} , $\text{mmol min}^{-1} \text{ dm}^{-3}$) is then proportional to the concentration gradient, as

$$N_{\text{H}_2} = (k_L a_g) [(C_{\text{H}_2})_{\text{saturation}} - (C_{\text{H}_2})_{\text{bulk}}] \quad (2)$$

where k_L (m min^{-1}) is the liquid film mass transfer coefficient and a_g ($\text{m}^2 \text{ m}^{-3}$) the gas/liquid interfacial area per unit volume of liquid; $(k_L a_g)$ represents the volumetric H_2 mass transfer coefficient. When operating at constant temperature and pressure, $(C_{\text{H}_2})_{\text{saturation}}$ is constant and N_{H_2} reaches a maximum value at an optimal $(k_L a_g)$. This can be obtained by adjusting the H_2 feed rate and/or the stirring/shaking speed, ensuring a gas/liquid interface equilibrium and facilitating a steady-state H_2 consumption in the bulk liquid [58,59]. The effect of increasing H_2 flow rate (I) and stirring/shaking speed (II) on fractional dechlorination (x_{Cl}) is presented in Fig. 3 for discontinuous (a) and continuous (b) operation. A constant catalyst loading (relative to the inlet chlorine content) was used (see Experimental section); optimal values are given in Table 1. In both

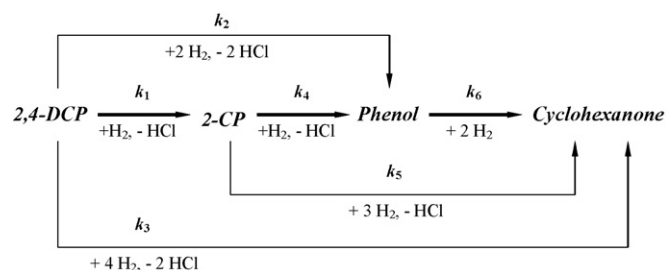


Fig. 2. Reaction network in the hydrotreatment of 2,4-DCP (bold arrows indicate stepwise mechanism).

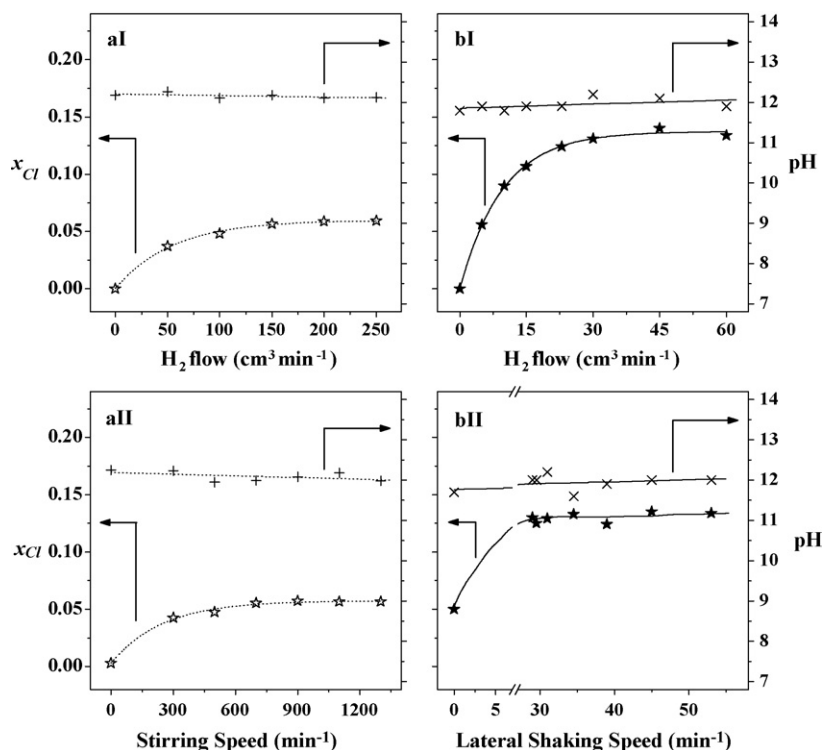


Fig. 3. Fractional dechlorination (x_{Cl} : ☆, ★) and associated pH response (+, ×) in establishing optimal conditions of (I) H_2 flow and (II) stirring/lateral shaking frequency for 2,4-DCP HDC in (a) discontinuous (☆, +) and (b) continuous (★, ×) operation; $t = 16$ min.

systems, x_{Cl} was enhanced at higher gas flows and/or agitation speed(s) where the (bulk) pH response was maintained at *ca.* 12 and was the same (within ± 0.1) for both systems. The minimum H_2 flow to achieve a constant x_{Cl} ($=0.13$) under continuous operation ($30 \text{ cm}^3 \text{ min}^{-1}$, see Fig. 3bI) was five times lower than that ($150 \text{ cm}^3 \text{ min}^{-1}$, see Fig. 3aI) required in the batch system to obtain a lower x_{Cl} ($=0.06$). Moreover, in the absence of any agitation there was no detectable HDC activity in the batch reactor while $x_{Cl} = 0.05$ was recorded in the continuous flow system (see Fig. 3aII and bII, respectively). These results suggest a more efficient H_2 diffusion in the continuous reactor and, since k_L is independent of the gas flow rate [58,60], this can be mainly attributed to a greater value of a_g , *i.e.* an extended gas/liquid interface for mass transfer. These results find support in the work of Takić et al. [61] who, calculating ($k_L a_g$) for O_3 transfer in aqueous solutions, obtained a higher value in continuous (0.266 min^{-1}) relative to semi-batch (0.198 min^{-1}) operation. Moreover, Machado et al. [62], studying liquid phase nitrobenzene hydrogenation in slurry (batch) and monolith (con-

tinuous) reactors, recorded a greater first order rate constant in the latter (0.2 vs. $1.4, \text{ s}^{-1}$) and ascribed this to a higher H_2 mass transfer rate when in continuous operation. The results presented in this section establish conditions under which both reactors are operated under catalytic control (see Table 1) and demonstrate that H_2 transfer is more effective in the continuous system.

3.2. 2,4-DCP HDC rate and selectivity

HDC activity was evaluated by monitoring x_{Cl} as a function of contact time (t) and the results are presented in Fig. 4. An increase in contact time served to enhance chlorine removal where the

Table 1

Operational and reaction parameters for the HDC of 2,4-DCP over $\text{Pd}/\text{Al}_2\text{O}_3$ in discontinuous (batch) and continuous reactors.

Regime	Discontinuous	Continuous
<i>Operational parameters^a</i>		
H_2 flow ($\text{cm}^3 \text{ min}^{-1}$)	150	30
Stirring/shaking speed (min^{-1})	1100	29
<i>Reaction parameters</i>		
$10^4 \times k_{Cl}$ (min^{-1})	2.8	5.2
(R_{HDC}) ($\text{mmol}_{\text{Cl}} \text{ g}_{\text{Pd}}^{-1} \text{ min}^{-1}$)	35	65
Ca	0.02	0.03
ϕ	0.03	0.04
η	0.99	0.99
L^b	0.99	0.66
M^b	1.00	1.44

^a Refers to optimum values in Fig. 3.

^b From data fit to Eq. (13), see Fig. 6.

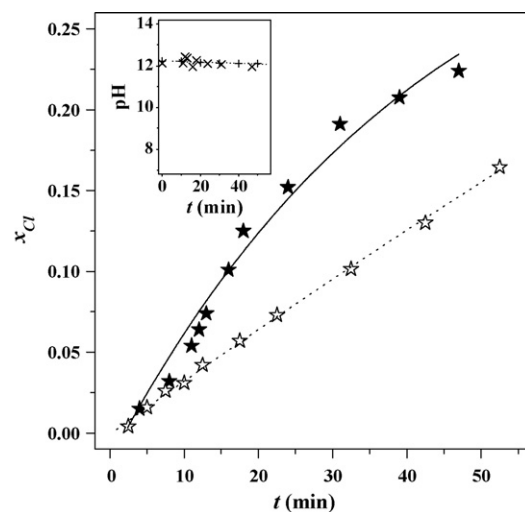


Fig. 4. Fractional dechlorination (x_{Cl}) and pH evolution (inset) as a function of $\text{Pd}/\text{Al}_2\text{O}_3/2,4\text{-DCP}$ contact time (t) in discontinuous (☆, +) and continuous (★, ×) operation. *Note:* Lines represent fit to Eq. (3).

(bulk) pH response was invariant (12 ± 0.1) and superimposable for both systems. Dehalogenation followed pseudo-first order kinetics according to

$$x_{Cl} = 1 - \exp(-k_{Cl} \cdot t) \quad (3)$$

where k_{Cl} , the dehalogenation rate constant, is a fitting parameter (see lines in Fig. 4). The HDC rate (R_{HDC}), units: $\text{mmol}_{Cl} \text{g}_{Pd}^{-1} \text{min}^{-1}$) was then calculated from

$$(R_{HDC}) = k_{Cl} \frac{n_{Cl}}{W} \quad (4)$$

where n_{Cl} represents the inlet chlorine moles (mmol_{Cl}) and W the mass of Pd in the reactor (g_{Pd}). The (R_{HDC}) values are given in Table 1 where a higher value was obtained for the continuous reactor. The Carberry number (Ca) approach was taken to estimate possible transport resistances in the liquid film at the liquid/catalyst interface which, for spheroidal catalyst particles, under isothermal conditions and constant $C_{2,4\text{-DCP}}$, i.e. absence of heat/mass gradients, takes the form [63]

$$Ca = \frac{\rho m_{Pd} d^2}{12 C_{2,4\text{-DCP}} D_{2,4\text{-DCP}}} \times (R_{HDC}) \quad (5)$$

where ρ and d are the bulk catalyst density and particle size (see Section 2.1), m_{Pd} represents Pd catalyst loading ($0.012 \text{g}_{Pd} \text{g}^{-1}$) and $D_{2,4\text{-DCP}}$ is the bulk liquid diffusivity ($\text{m}^2 \text{s}^{-1}$), as estimated from [64].

$$D_{2,4\text{-DCP}} = \frac{8.621 \times 10^{-14}}{(\eta_{water})^{1.14} (\bar{v}_{2,4\text{-DCP}})^{0.589}} \quad (6)$$

where η_{water} is the water viscosity ($7.97 \times 10^{-4} \text{Pa s}$ at $T = 303 \text{K}$ [65]) and $\bar{v}_{2,4\text{-DCP}}$ is the 2,4-DCP molar volume ($0.118 \text{m}^3 \text{kmol}^{-1}$, calculated following [64]); $D_{2,4\text{-DCP}} = 1.03 \times 10^{-9} \text{m}^2 \text{s}^{-1}$. Mass transfer limitations within the catalyst pores were estimated by the standard Thiele modulus (ϕ) and effectiveness factor (η) criteria, as given by:

$$\phi = \sqrt{\frac{(R_{HDC}) \rho m_{Pd} (d/6)^2}{C_{2,4\text{-DCP}} D_{Eff,2,4\text{-DCP}}} \quad (7)$$

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi} \right) \quad (8)$$

where $D_{Eff,2,4\text{-DCP}}$ is the effective 2,4-DCP diffusivity, i.e. within the catalyst pores: $D_{Eff,2,4\text{-DCP}} = D_{2,4\text{-DCP}} \times (0.65)^2$ [27]. The results of these calculations for both reactors (included in Table 1) are indicative of negligible resistance at the liquid/solid interface (Ca limiting value range = 0.1–0.15 [28]) with minimal reactant diffusional constraints in the pores ($\phi < 0.5$, $\eta \approx 1$ [58]).

Product composition is presented in Fig. 5 for batch (a) and continuous (b) operation, where a decrease in 2,4-DCP concentration with increasing contact time is in evidence with a different response in terms of the 2-CP and phenol concentration profiles for both reactors. As shown in Fig. 2, HDC can proceed *via* stepwise (k_1 , k_4) and/or concerted (k_2) routes so that, at a given fractional 2,4-DCP conversion, the simultaneous cleavage of both C–Cl bonds will lead to a higher phenol content in the product stream and a consequent higher (R_{HDC}) [53]. Reaction selectivity can be quantified on the basis of the mass balances that define the HDC steps (i.e. k_1 , k_2 and k_4 in Fig. 2) which, applying pseudo-first order kinetics, take the form:

$$\frac{1}{W} \frac{dx_{2,4\text{-DCP}}}{dt} = -(k_1 + k_2)x_{2,4\text{-DCP}} \quad (9)$$

$$\frac{1}{W} \frac{dx_{2\text{-CP}}}{dt} = k_1 x_{2,4\text{-DCP}} - k_4 x_{2\text{-CP}} \quad (10)$$

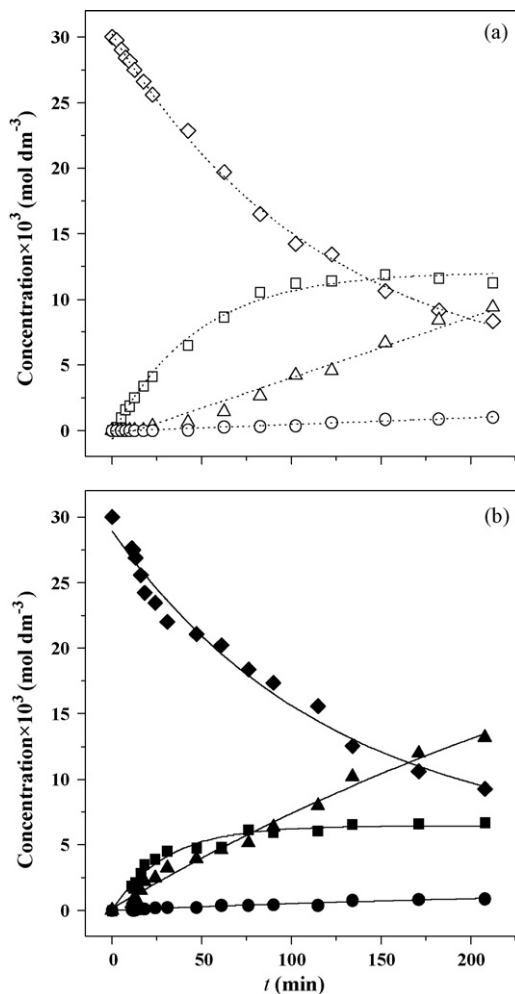


Fig. 5. Liquid phase composition (in terms of molar concentration of 2,4-DCP (\diamond , \blacklozenge), 2-CP (\square , \blacksquare), phenol (Δ , \blacktriangle) and cyclohexanone (\circ , \bullet)) as a function of Pd/Al₂O₃/2,4-DCP contact time (t) in (a) discontinuous (open symbols) and (b) continuous (solid symbols) operation.

$$\frac{1}{W} \frac{dx_{\text{PhOH}}}{dt} = k_2 x_{2,4\text{-DCP}} + k_4 x_{2\text{-CP}} \quad (11)$$

where x_i represent the molar fraction of compound i and k_j is the pseudo first order rate constant for step j . From a combination of Eqs. (9) and (10)

$$\frac{dx_{2\text{-CP}}}{dx_{2,4\text{-DCP}}} = \frac{k_1 x_{2,4\text{-DCP}} - k_4 x_{2\text{-CP}}}{-(k_1 + k_2)x_{2,4\text{-DCP}}} \quad (12)$$

which, when integrated gives

$$x_{2\text{-CP}} = \frac{L}{1-M} \times \left[(x_{2,4\text{-DCP}})^M - x_{2,4\text{-DCP}} \right] \quad (13)$$

where

$$L = \frac{k_1}{k_1 + k_2} \quad \therefore \quad M = \frac{k_4}{k_1 + k_2} \quad (14)$$

The significance of the L and M parameters, in terms of HDC mechanism, is summarized in Table 2. The results of data fitting to Eq. (13) are presented in Fig. 6 where a higher 2-CP content (at the same fractional 2,4-DCP conversion) characterizes discontinuous operation. The extracted values of L and M are given in Table 1. A strictly consecutive reaction network should yield a value of L close to unity, i.e. $k_2 = 0$, and the (significantly) lower L value generated for the continuous reactor is consistent with an enhanced concerted HDC to phenol. The M values (≥ 1) suggest an equivalent or higher

Table 2
Mechanistic significance of the parameters L and M (see Fig. 2 and Eq. (14)).

Case	L	M	Mechanistic considerations
1	$L=0$		$k_1=0$: no contribution due to stepwise HDC.
2	$L \neq 0$	–	$k_1 \neq 0$: involvement of stepwise HDC.
2a	$0 < L < 1$		$k_2 > 0$: both stepwise and concerted HDC routes possible, the concerted pathway is prevalent where $L \rightarrow 0$.
2b	$L=1$		$k_2=0$: no contribution due to concerted HDC.
3	–	$M=0$	$k_4=0$: no contribution due to sequential HDC, i.e. 2-CP HDC to phenol does not occur.
4	–	$M \neq 0$	$k_4 \neq 0$: involvement of sequential HDC, i.e. 2-CP HDC to phenol.

2-CP HDC relative to 2,4-DCP, i.e. the second Cl substituent serves to lower the HDC rate, as noted previously [9,34,66].

The experimental data establish that the hydrogen scission of both C–Cl bonds is promoted to a greater extent in the continuous reactor operated under catalytic control, which leads to higher (R_{HDC}). In order to account for this response, the reaction pH must be considered as this has been demonstrated [19,67] to be the critical factor that controls aqueous phase chlorophenol(s) HDC by influencing the nature of the species in solution and the catalyst surface charge. Under basic conditions (pH 12), the 2,4-DCP reactant and 2-CP intermediate are dissociated in solution as chlorophenolate species (pK_{a} 7.9 and 8.5, respectively [68]). The catalyst is characterized by pH_{pzc} 7.7, i.e. the pH at which the accessible wetted catalyst surface is electrically neutral. When $pH > pH_{\text{pzc}}$ the catalyst surface bears a negative charge, which does not favour interaction with (chlorophenolate) anions in solution [69]. A significant HCl component is released during HDC [70,71], with the result that the “local” pH, i.e. that associated with the liquid/solid interfacial layer ($pH_{\text{I/S}}$), can be quite different from that in the bulk liquid (pH) [72]. When $pH_{\text{pzc}} < pH_{\text{I/S}} \leq pH$ (i.e. low surface HCl concentration), catalyst interaction with chlorophenolate species is limited but at $pH_{\text{I/S}} < pH_{\text{pzc}} < pH$, the catalyst surface develops a positive charge where chlorophenolate interaction(s) are facilitated. Since the bulk pH response is equivalent for both reactors (see inset to Fig. 4), the difference in selectivity response must be associated with differences in $pH_{\text{I/S}}$. We have demonstrated previously [72] that, when $pH_{\text{pzc}} < pH_{\text{I/S}}$ (=13), the concerted 2,4-DCP HDC route (i.e. k_2 in Fig. 2) is inhibited leading to the selectivity response observed (in Fig. 6) for the batch reactor. It follows that the involvement of the concerted route in the continuous system must be linked to a lower “local” pH value so that $pH_{\text{I/S}} < pH_{\text{pzc}} < pH$. This response can be tentatively attributed to a reduced liquid/solid interfacial layer resulting from the continuous flow of liquid over the catalyst particles. It is known that the “thickness” of a fluid film on

a solid surface is inversely proportional to the relative velocity between them [73,74]. In the batch reactor (see Fig. 1a) the mechanical stirring keeps the slurry in suspension where, considering the fine (38 μm) catalyst size, the solution/particle relative velocity approaches unity [14,73]. On the contrary, in the continuous reactor (Fig. 1b) the catalyst is mainly fluidized by the upstream flow where the lateral shaking represents a secondary source of particle suspension. Therefore, the relative velocity between the liquid and the catalyst must be greater (to overcome deposition/sedimentation) and this results in a “thinner” liquid/solid interfacial layer [75,76]. With a decrease in the volume of this layer, the local HCl concentration is higher and $pH_{\text{I/S}} < pH_{\text{pzc}} < pH$. A direct comparison of these results with the available literature on aqueous phase chlorophenol(s) HDC is not feasible as the role of pH in determining reactant/catalyst interactions has not received any explicit treatment. Nevertheless, we can flag the work of David and Vannice [77] who, studying the semi-batch liquid phase hydrotreatment of 4-chloro-N,N-dibenzylaniline over Pd/C, quoted a shift in reaction selectivity (from exclusive debenylation to full HDC) when varying bulk solution pH (0.1 \rightarrow 12) and attributed this to the impact of pH on the catalyst/reactant surface interactions. Our results demonstrate that a shift from batch to continuous operation serves to enhance HDC efficiency, which we link to pH effects at the solid/liquid interface that are sensitive to the mode of operation.

3.3. Catalyst life in discontinuous vs. continuous operation

Batch HDC operation is compromised somewhat in terms of catalyst reuse. A temporal decline in activity is a general feature of HDC reactions and has been attributed to the action of the HCl by-product, which induces metal leaching [78,79], poisoning (via electronic modifications) [80–83], sintering [80] and/or coke formation [78,79]. This has been observed regardless of the support (oxide [78–81], carbon [82,83]) or metal (Ni [80,81], Pd [78,82,83],

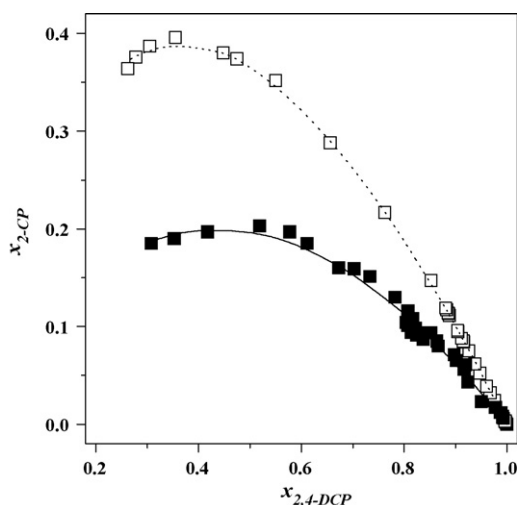


Fig. 6. Relationship between 2-CP ($x_{2\text{-CP}}$) and 2,4-DCP molar fractions ($x_{2,4\text{-DCP}}$) in discontinuous (\square) and continuous (\blacksquare) operation. Note: Lines represent fit to Eq. (13).

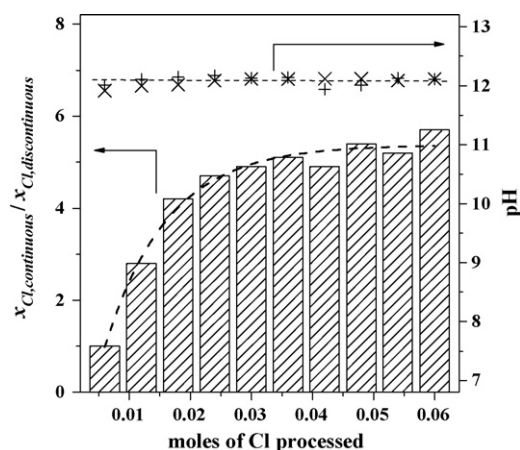


Fig. 7. Ratio of fractional dechlorination obtained in continuous ($x_{\text{Cl,continuous}}$) to discontinuous ($x_{\text{Cl,discontinuous}}$) operation as a function of moles of chlorine processed. Note: The associated pH for discontinuous (+) and continuous (x) operation is also given; $t = 24$ min.

Ru [79]) used. In the case of Pd/Al₂O₃, a decline in HDC activity with reuse in batch liquid operation has been ascribed [15,18] principally to HCl poisoning of small Pd clusters. HDC performance (in terms of x_{Cl}) in both reactors can be assessed in Fig. 7 in terms of the total number of moles of chlorine that had been processed. These results refer to repeated catalyst use in converting successive (up to 10) batches in discontinuous mode and extending continuous operation to arrive at a common total feed processed. It can be seen that the continuous reactor exhibited improved performance relative to discontinuous operation to deliver a five-fold higher x_{Cl} ; bulk solution pH was again invariant. Continuous flow operation serves to extend catalyst life and this can be linked to a more effective transport of HCl away from the catalyst surface. Urbano and Marinas [84] have also attributed a greater degree of (Pd) catalyst deactivation during HDC in batch (relative to continuous) systems to a prolonged HCl contact with the catalyst surface. The benefits of moving from batch to continuous operation then not only include more efficient H₂ usage (see Section 3.1) and enhanced HDC efficiency (see Section 3.2) but also prolonged catalyst life.

4. Conclusions

The three-phase HDC (H₂ gas, 1 atm) of 2,4-DCP (liquid, pH 12 ± 0.1) over Pd/Al₂O₃ (solid) has been studied at 303 K in batch and continuous flow reactors. Operation of both reactors generated 2-CP as the only partially dechlorinated product, phenol was the main product of complete HDC and cyclohexanone was isolated in trace quantities (selectivity <4%). Reaction conditions have been established for operation under catalytic control, where the continuous reactor delivered a five-fold higher efficiency with respect to H₂ transfer as a result of an enhanced gas/liquid interface. A switch from batch to continuous mode resulted in an increase in HDC rate (and lower 2-CP selectivity), which can be attributed to a lower pH at the liquid/solid interface. Moreover, catalytic activity was prolonged in continuous operation due to a more effective removal of HCl by-product. This report establishes the feasibility of operating chloroarene HDC in a continuous flow reactor and can serve as the basis for future process scale-up and/or industrial implementation.

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