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# Sustainable process for adipic acid production from cyclohexene in microemulsion

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## ABSTRACT

Adipic acid appears as an intermediate compound for the synthesis of polyamides and preferentially for the production of nylon-6,6 polyamide. It can be synthesized by the oxidation of cyclohexene by hydrogen peroxide in microemulsion media which has the main advantage to lead a better contact between the two phases thus increasing the yield of the reaction. The microemulsion is generated by stearyl dimethyl benzyl ammonium chloride (C18) as a surfactant avoiding the use of harmful organic solvents and phase-transfer catalysts. The reaction is performed under mild conditions (85 °C, 8 h) with sodium tungstate, - a no heavy metal catalyst - leading to the production of adipic acid in high yield (> 80%). By recycling the catalyst and the surfactant, the process becomes truly green.

## 1. Introduction

Industrial production of adipic acid is obtained predominantly from cyclohexane, followed by an oxidation of cyclohexanol-cyclohexanone mixture and requires the use of nitric acid [1,2], a known hazardous chemical. Furthermore, nitrous oxide (N<sub>2</sub>O) is generated as a by-product during the production of adipic acid and nitric acid (0.3 t emitted by ton of adipic acid produced) which makes this process one of the largest sources of N<sub>2</sub>O industrial emissions and contributes to the ozone layer depletion [3]. Many processes based on the use of cyclohexane exist including the followings:

Concerning the Stamicarbon process, the first step consists in the air oxidation of cyclohexane to a cyclohexanol-cyclohexanone (ol-one mixture) mixture [4] which is a very exothermic reaction ( $\Delta H_{0,298} = -295 \text{ kJ mol}^{-1}$ ) carried out in the liquid phase between 145 and 175 °C and under a pressure of 0.8–1.0 MPa. It employs a soluble cobalt salt (octanoate or naphthenate) as catalyst. In the second step, ol-one mixture is oxidized by 40–60% nitric acid with copper and vanadium catalysts for obtaining adipic acid. In order to limit the formation of by-products, it is necessary to limit the conversion between 4 and 6% by mass for each pass in the first step; this requires considerable recycling. With these characteristics, an equimolar ol-one mixture is obtained and the overall yield of ol-one, adipic acid and ester mixture of the latter is about 80% by weight.

The Halcon process is an improvement of the Stamicarbon process, proposed by Scientific Design [5]. Boric acid is added to the reaction media, which makes it possible to block the cyclohexanol formed by the reaction in the form of borate and thus to protect it from any subsequent oxidation. Once isolated, boric esters are readily hydrolyzable and boric acid is recyclable. In order to prevent this hydrolysis, it is necessary to remove the water formed during the reaction. This method results in an ol-one mixture in the molar ratio of 9 to 10:1, the conversion rate by pass can be increased to 10% and the yield is 90%. Despite the disadvantage of working with a solid (H<sub>3</sub>BO<sub>4</sub>) this process exhibits a much better yield than the previous one. This ol-one mixture is then oxidized in the second step, either by nitric acid or by air.

- Nitric acid: the mixture is treated in excess of nitric acid in the presence of ammonium methavanadate and copper turnings. The reaction is very exothermic and the molecular yield of adipic acid reaches 92–96%. The process requires a separation step of formed gases and the recrystallization of adipic acid.
- Oxidation by air: the reaction is carried out at 70–80 °C under 0.7 MPa with copper acetate and manganese as catalysts. The crystallization of adipic acid is also necessary. This process reduces safety and corrosion problems and the acid yield is lower.

The Asahi process [6–9] consists in the direct oxidation by air of

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cyclohexane in solution in acetic acid. This technique uses the cobalt acetate as oxidation catalyst and operates between 90 and 100 °C. The molar selectivity to adipic acid reaches 70–75% for conversion rates by pass between 50 and 75%. Even if the yield of adipic acid is comparable to that of the previous processes, the investments necessary for its implementation are very important. This is due to the cost of recovering and recycling the acetic acid, the regeneration of the catalyst and the cooling devices required to manage the high exothermicity of the reaction. All this explains the weak industrial development of this process.

BASF has developed a process based on the carbonylation of butadiene [10]. It operates in two steps: first, butadiene reacts with carbon monoxide and methanol at 120 °C and 60 MPa. Dicobalt octocarbonyl (Co<sub>2</sub>(CO)<sub>8</sub>) is used as catalyst in the presence of a heterocyclic nitrogen base. At the end, methyl pentene-3-ole is formed with a selectivity of 98 mol%. In a second step, the olefinic ester is treated with a new quantity of carbon monoxide and methanol. The reaction is carried out at 185 °C under 3 MPa. Methyl adipate is then formed with a yield of 75 mol%. Glutarate and methyl succinate ethyl are also formed. The methyl adipate is then purified by distillation and then hydrolyzed to adipic acid. Despite the large investments due to the high pressures implemented in the first stage, this process is economically comparable to the conventional methods.

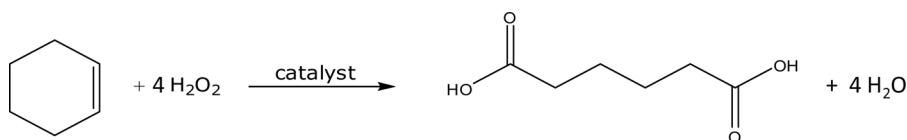
An alternative process is based on the dimerization of acrylates. As the previous method, the dimerization of acrylates has the advantage of not sourcing the adipic acid from benzene but from olefins. In fact, methyl acrylate results from the oxidation of propylene to acrylic acid, which is then esterified with methanol. The dimerization of the acrylate then takes place in the presence of palladium chloride and benzonitrile as catalyst. The reaction is carried out at 80 °C under a nitrogen atmosphere. For a contact time of 35 min per pass, a conversion of 45% together with a 92% selectivity into linear dimer are obtained. The ester formed is then purified by fractionation, hydrogenation and hydrolysis to adipic acid. This process is advantageous compared to conventional routes due to the low cost of raw materials.

All these processes are not sustainable and green and the development of a new process less damaging for the environment is of crucial importance [11–15].

Adipic acid can be also obtained by oxidation of cyclohexene by hydrogen peroxide in the presence of a catalyst [16] (Scheme 1). Recent works show the last advances on the development specially either on the choice of the catalyst or the type of process (batch and continuous) [17,18].

In a previous work, we have shown the interest to introduce microemulsions as a new green solvent for the production of adipic acid [19] using hydrogen peroxide and benzalkonium chlorides as surfactant.

A microemulsion is a system formed of water, oil, amphiphilic agents, which is transparent and thermodynamically stable. Physical and chemical properties of the microemulsion are interesting, in particular from the point of view of thermodynamic stability, low formation barrier kinetics, low viscosity and excessively low interfacial tension. Given these particular properties, microemulsions become more significant in both research and industry. A microemulsion distinguishes by the size of its dispersed droplets in the range between 50 and 1000 Å. The dispersed molecules merge with the water molecules and are defined as transparent liquid / liquid dispersions of water and oil. They are not very viscous and their formation is spontaneous and requires very little energy.



**Scheme 1.** Oxidation of cyclohexene with hydrogen peroxide.

Since many years, microemulsions have been used as reaction media for numerous chemical reactions [20–25]. Often considered as a simple solvent, microemulsions are employed to overcome reactant solubility problems in water. On the other hand, because of their particular interfacial properties which create a nanoscale contact between hydrophilic and hydrophobic reactants, microemulsions could be used as “chemical reactors”. Microemulsions allow a more homogenous solubilisation of oil in water than emulsions based on micellar solutions. Also, the concentration of the reactants at the interface has been exploited to induce regio-specificity or stereo-selectivity in an organic reaction [26]. Use of microemulsions as reaction media is also compatible with a catalytic process [27–35]. Nowadays, microemulsions are versatile reactions media for many organic syntheses but at this time, no industrial reaction process based on microemulsions exists.

We already described a reusable green process for the synthesis of adipic acid in very good yield and purity by hydrogen peroxide oxidation of cyclohexene in a microemulsion [36] in a previous work. The originality of the process was based on the use of microemulsions as reaction media without cosurfactant and on the molecular economy principle, almost all the compounds acting as reagents too. Microemulsions allow working in a macroscopic homogeneous media for a better reactivity and pure adipic acid is obtained without any difficulty by simple filtration using a low pH.

In the present work, we propose the use of a microemulsion as reaction medium at 85 °C, including hydrogen peroxide as aqueous oxidant phase, cyclohexene as reagent and oil phase and benzalkonium chloride C18 as surfactant. The Krafft temperature [37] of this surfactant allows a precipitation at 27 °C. Maintaining the pH at 1 (+ H<sub>2</sub>SO<sub>4</sub>) and the temperature at 40 °C allowed us to precipitate pure adipic acid. The surfactant and the catalyst (Na<sub>2</sub>WO<sub>4</sub>) are then recovered by filtration at room temperature for a new reaction cycle.

## 2. Materials and methods

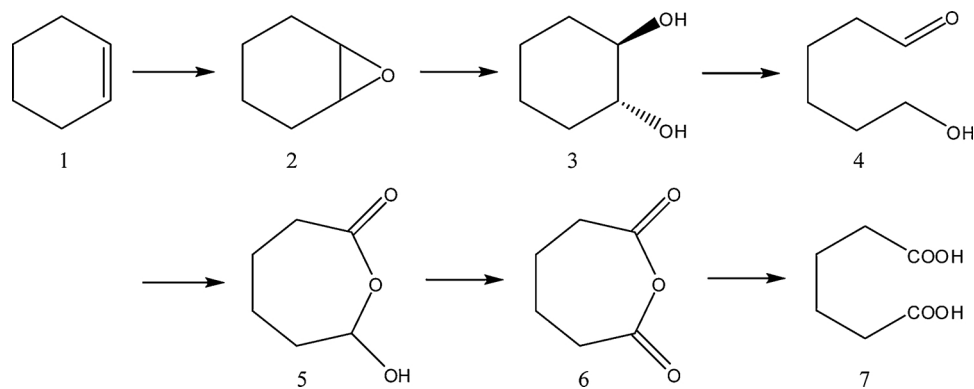
### 2.1. Materials

Benzalkonium chloride C18 (90%, Sigma-Aldrich), cyclohexene (99%, Sigma-Aldrich), sulfuric acid (95–97%, Sigma-Aldrich), dihydrated sodium tungstate (99%, Sigma-Aldrich), hydrogen peroxide (30 wt%, Sigma-Aldrich), were used for the reaction experiments as received without purification. Methanol (99.9%, Fluka) and toluene (99.9%, Sigma-Aldrich) were used for cyclohexene GC analysis. Potassium permanganate (98.5%, Sigma-Aldrich) was used for hydrogen peroxide titration. Sodium hydroxide solution (30%, Analar Normapur) was used for adipic acid titration.

### 2.2. Synthesis of adipic acid in microemulsion

Reactions were carried out in a 1.4 L cylindrical water-jacketed glass reactor equipped with a magnetic stirring bar and a reflux condenser. BenzCl C18 (82.5 g), hydrogen peroxide (30% solution, 1321.5 g), sodium tungstate (20.5 g) and sulfuric acid (46 g) were introduced at one time. The mixture was strongly stirred at 70 °C until total dissolution and then 150 g of cyclohexene were added. The solution was maintained at 85 °C during 8 h [36].

Oxidation of cyclohexene by H<sub>2</sub>O<sub>2</sub> typically involves epoxidation of the double bond, its opening and transformation to a diol, and then a Baeyer-Villiger oxidation and multiple hydrolysis steps resulting in adipic acid (Scheme 2) [38,39].



**Scheme 2.** Different steps of the formation of adipic acid : epoxidation of cyclohexene 1 - rapid hydrolytic ring opening of the bicyclic epoxide 2 - dehydrogenation of the secondary alcohol 3 – formation of hemiacylal 5 - Baeyer-Villiger oxidation and hydrolysis to the adipic acid 7.

### 2.3. Filtration step

After cooling at 40 °C for 1 h, adipic acid precipitated and was recovered by Büchner filtration (fritted glass funnels with pore size of 2–4 μm). The crude product was washed with cold water (10 mL) and the white powder was then dried at 40 °C (cycle 1). For recyclability studies, the filtrate was cooled at 20 °C and the solid (BenzCl C18, sodium tungstate and remained adipic acid) was recovered by Büchner filtration. This mixture was reintroduced into the reactor with hydrogen peroxide and cyclohexene (with the same quantities as for the first cycle) for a new cycle (8 h at 85 °C (Fig. 1)).

In order to improve the solid/liquid separation step, some preliminary ultrafiltration experiments were carried out. The study was performed with a dead-end filtration unit (Berghof) with a hydrophilic coated polyvinylidene fluoride membrane (ETNA 10 P P). The effective membrane area was  $3.52 \times 10^{-3} \text{ m}^2$  and the total effective volume was about 300 mL. Stirring speed (200 rpm) and temperature (20 °C) were maintained constant in all tests. The cell was filled with 100 mL of the liquid waste containing adipic acid, surfactant and catalyst. The filtration was conducted until a volume reduction factor (VRF) of 3 (33 mL of permeate had been collected). Then, the resulting concentrate (the volume remaining in the storage) was added at the beginning of the reaction cycle with the reactants.

### 2.4. Analytical procedures

#### 2.4.1. Cyclohexene titration

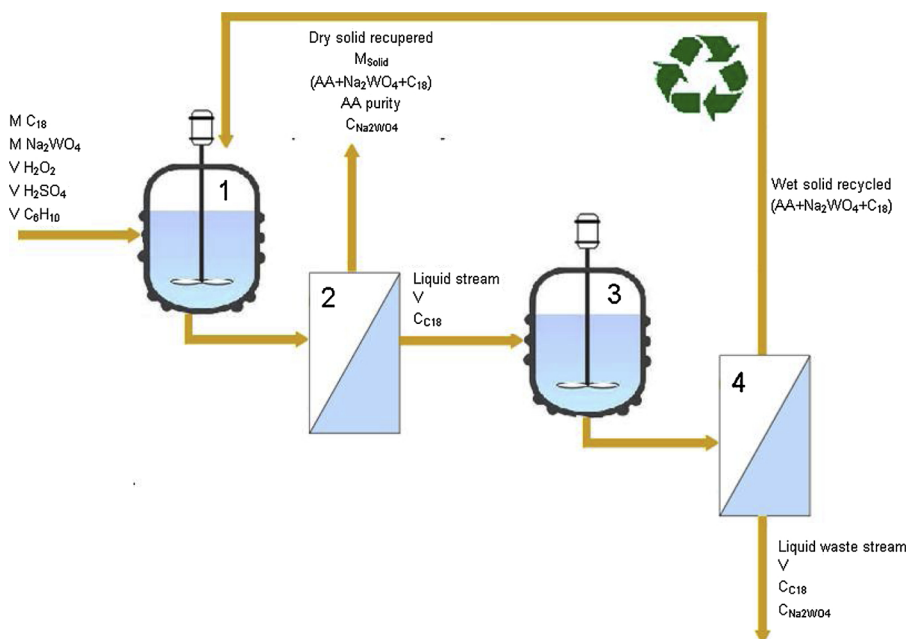
Gas chromatography (Varian CP-3800) with a flame-ionization detector was used to determine the quantity of remaining cyclohexene. Separation was accomplished using a MachereyNagel Optima-1-Accent-0.25 mm column (30 m, 0.25 mm). 1 μL of a solution prepared with 500 mg of crude reaction mixture, 50 mg of toluene (internal standard) and 500 mg of methanol was injected. The GC settings were programmed as follows: injector temperature 150 °C (1 mL/min, split ratio: 10); detector temperature 350 °C; column temperature 50 °C for 5 min. The detection limit was  $1 \text{ mg L}^{-1}$ . The accuracy for measurements of samples containing a concentration of  $30.4 \text{ mg L}^{-1}$  was  $\pm 1.3 \text{ mg L}^{-1}$ .

#### 2.4.2. Adipic acid titration

Adipic acid concentration was determined by acid-base titration. A 0.025 N NaOH solution was prepared and was standardized with a  $\text{H}_2\text{SO}_4$  solution (0.025 N) in an automatic titrator Mettler Toledo DL50. Adipic acid formation was followed by NaOH titration. Measurements were performed at least three times.

#### 2.4.3. Adipic acid purity

The adipic acid purity was determined by HPLC in a Waters Alliance



**Fig. 1.** Simplified diagram for adipic acid synthesis in microemulsion with BenzCl C18. 1: reaction of cyclohexene oxidation by hydrogen peroxide at 85 °C and first adipic acid precipitation at 40 °C; 2: filtration at 40 °C; 3: second precipitation at 20 °C (adipic acid, catalyst, possible by-products and surfactant); 4: filtration at 20 °C.

2695 Separation Module with a 2487 UV detector. Analysis were carried out at 210 nm with an Xbridge Shield RP C18 column (2,1 × 150 mm, 3.5 μm particles). The mobile phase consisted of acetonitrile (A) and aqueous acetic acid (0.1%) (B) at a flow rate of 0.3 mL min<sup>-1</sup>. A gradient separation mode was used as follows: 0 min: 9% A, 91% B; 5 min: 9% A, 91% B, 15 min 100% B.

#### 2.4.4. Hydrogen peroxide titration

The hydrogen peroxide solution concentrations were determined by permanganometry. A standard 0.02 M potassium permanganate (KMnO<sub>4</sub>) solution was prepared (3.4 g of solid KMnO<sub>4</sub> in 1 L of deionized water). This solution was refluxed for 1 h, filtered and stored in a dark colored bottle. The KMnO<sub>4</sub> solution was standardized with primary standard grade potassium oxalate (0.1 g dissolved in 20 mL of water with 5 mL of sulfuric acid). Hydrogen peroxide consumption was followed by taking 0.1 g of crude mixture diluted in 20 mL of water with 5 mL of sulfuric acid and titrated with KMnO<sub>4</sub> solution until persistent coloration of the solution. Measurements were performed at least three times.

#### 2.4.5. Sodium tungstate titration

Sodium tungstate concentrations in reaction media were determined by inductively coupled plasma mass spectrometry (ICP-MS), according to ISO 17294-1:2005 and ISO 17294-2:2003 and carried out by Antellis (Toulouse, France). Sample dilution has been done in nitric acid.

#### 2.4.6. BenzCl C18 titration

Liquid samples were characterized using a HPLC equipped with a UV/vis detector (ACCELA-Thermo Fisher). Benzyldimethylstearylammionium (CAS number : 206752-43-4) was separated from other products on a Phenomenex Gemini C18 column (100.0 mm × 2.0 mm, particle size 3 μm) with a Phenomenex Securityguard Gemini C18 precolumn (4.0 mm × 2.0 mm, particle size 5 μm) (Torrence, Ca, USA). The mobile phase consists of a mixture of methanol-aqueous potassium phosphate (pH 3.0; 7.5 mM) (80:20, v/v). The flow rate of the mobile phase was kept at 200.0 μl/min. The column temperature was maintained at 50 °C and the optimum wavelength was monitored at a value of 210 nm. The injection volume was 5 μl for the assay determination. The mobile phase was used as diluent for both standards and samples preparation [40].

### 3. Results and discussion

#### 3.1. Reaction kinetics

Reagents consumption and product formation has been followed with the described analytical method and results are presented in Fig. 2 (molar ratios) and Fig. 3 (concentration profiles). Fig. 2 shows that cyclohexene is almost all consumed in 2 h whereas hydrogen peroxide content continuously decreases during the 8 h of the experiment. In the meanwhile, adipic acid is continuously formed, even after the total cyclohexene consumption. This corroborates the proposed mechanism which implies the formation of intermediates from cyclohexene, which further react with H<sub>2</sub>O<sub>2</sub> to produce adipic acid.

Oxidation of cyclohexene by hydrogen peroxide implies a complex reaction scheme. Kinetic modeling requires the quantification of all oxidation intermediates generated during the transformation. In this work, we only followed hydrogen peroxide, cyclohexene and adipic acid concentrations. Nevertheless, a few observations can be made, according to the observed concentration profiles 3).

First, initial H<sub>2</sub>O<sub>2</sub> consumption rate can be estimated using the initial slope of H<sub>2</sub>O<sub>2</sub> concentration curve. It has been estimated to 10.16 mol L<sup>-1</sup> h<sup>-1</sup>. The same procedure for cyclohexene consumption leads to a 0.84 mol L<sup>-1</sup> h<sup>-1</sup> value, which is 12 times lower. The overall oxidation process requires 4 mol of H<sub>2</sub>O<sub>2</sub> for each cyclohexene mole, to produce adipic acid (Scheme1).

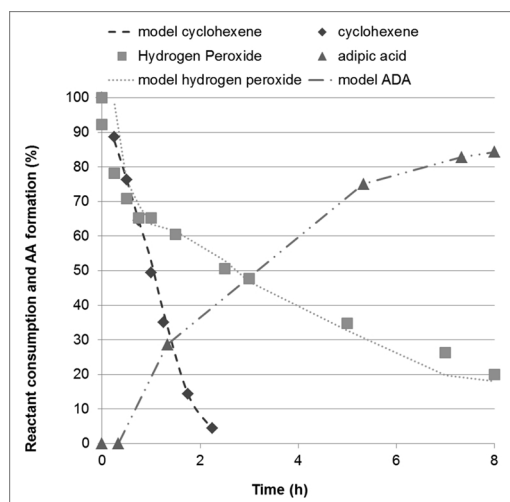


Fig. 2. Time evolution of cyclohexene oxidation. Temperature, 85 °C; reaction time, 8 h; reaction volume, 0,14 L.

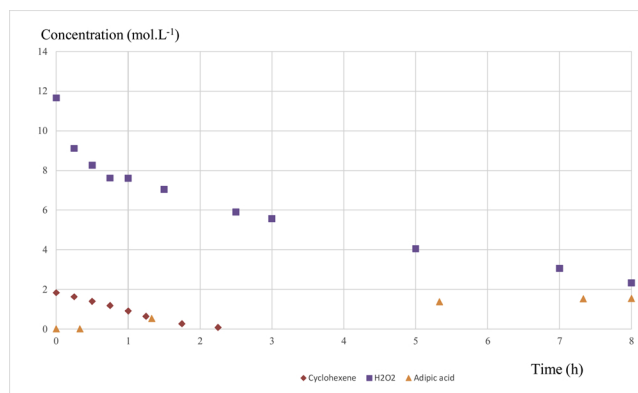


Fig. 3. Concentrations of cyclohexene, H<sub>2</sub>O<sub>2</sub> and adipic acid versus time. Temperature, 85 °C; reaction time, 8 h; reaction volume, 1.4 L.

We can so conclude that a large part of H<sub>2</sub>O<sub>2</sub> is consumed during its degradation and other oxidation reactions. Finally, it can be remarked that after 30 min, C<sub>6</sub>H<sub>10</sub> and H<sub>2</sub>O<sub>2</sub> concentration curves seem to be almost parallel, which is consistent with the hypothesis of a 1:1 stoichiometric reaction between C<sub>6</sub>H<sub>10</sub> and H<sub>2</sub>O<sub>2</sub> to form epoxide. Then side reactions using H<sub>2</sub>O<sub>2</sub> would rather occur at the very beginning of the reaction. That's why the kinetic constant was estimated, based only on the cyclohexene consumption and assuming that the first step of the cyclohexene oxidation is:

Assuming a second order kinetic law, order 1 with respect to each reagent, the kinetic constant *k* was estimated, based on the molar balance on cyclohexene, in a batch reactor:

$$-\frac{d(C_6H_{10})}{dt} = k(C_6H_{10}) \cdot (H_2O_2) \quad (1)$$

Introducing *M*, the ratio between the initial H<sub>2</sub>O<sub>2</sub> concentration and the initial cyclohexene concentration (C<sub>6</sub>H<sub>6</sub>)<sub>0</sub> and *X*, the cyclohexene conversion rate, Eq. (1) becomes:

$$\frac{dX}{dt} = k(C_6H_{10})_0 \cdot (1-X)(M-X) \quad (2)$$

Which leads to:

$$X = \frac{M \{ \exp[(M-1)k(C_6H_{10})_0 t] - 1 \}}{\{ M \cdot \exp[(M-1)k(C_6H_{10})_0 t] - 1 \}} \quad (3)$$

Finally, *k* value was estimated by minimizing the quadratic difference between the cyclohexene concentration obtained by simulation



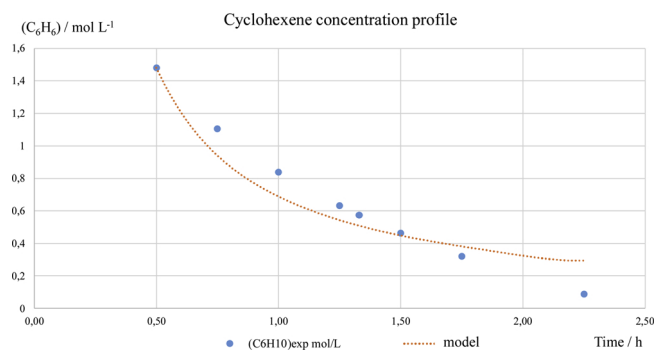


Fig. 4. experimental cyclohexene concentration and simulated cyclohexene concentration profile using 2<sup>nd</sup> order kinetic law.

$(C_6H_6)_{cal}$  and the cyclohexene measured concentration  $(C_6H_6)_{exp}$ . The initial value of  $H_2O_2$  concentration in Fig. 3 corresponds to the amount of hydrogen peroxide introduced initially in the reactor. It can be assumed that a part of  $H_2O_2$  is consumed during stirring before adding cyclohexene. It can be due to reactions with reagent impurities or catalyst: the decomposition of hydrogen peroxide can be catalyzed with incompatible soluble substances, even at very low levels (a few ppm). This decomposition occurs with a wide range of pollutants, particularly metal salts including tungsten. Additionally, a thermal decomposition at 70 °C, can also explain that the slope of the  $H_2O_2$  concentration changes dramatically. As the  $H_2O_2$  concentration was not measured just after cyclohexene introduction, it was decided to use the first measured concentration at 0.5 h reaction time for  $k$  calculations.

The value of  $k$  was found to be equal to  $0.245 \text{ L mol}^{-1} \text{ h}^{-1}$ .

Comparison between experimental and simulated cyclohexene concentration profiles can be seen on Fig. 4. The model overestimates the cyclohexene consumption before 1.5 h reaction time and underestimates it after that time.

Considering the behavior of cyclohexene concentration profile, which seems almost linear, a zero order kinetic model was also attempted. It can be shown on Fig. 5 that modeling is quite better (regression coefficient of 0.98). Then, the cyclohexene consumption rate is considered constant equal to  $0.822 \text{ mol.L}^{-1} \text{ h}^{-1}$ .

The zero order kinetic law means that the reaction rate is independent on both cyclohexene and hydrogen peroxide concentrations. It can be explained by the availability of the reactants in the micelles, where the reaction takes place. In this case, as long as the reagents are present in the micelles, the reaction does not depend on the bulk reagent concentrations. A zero order kinetics has already been observed in micro emulsions, for example in the case of enzymatic reactions [41]. Further experiments, varying experimental conditions, have to be further carried out to confirm this result.

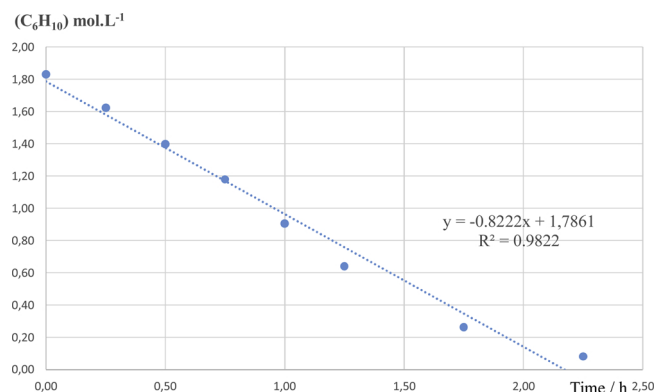


Fig. 5. cyclohexene concentration profile and zero order kinetic simulated concentration profile (linear profile).

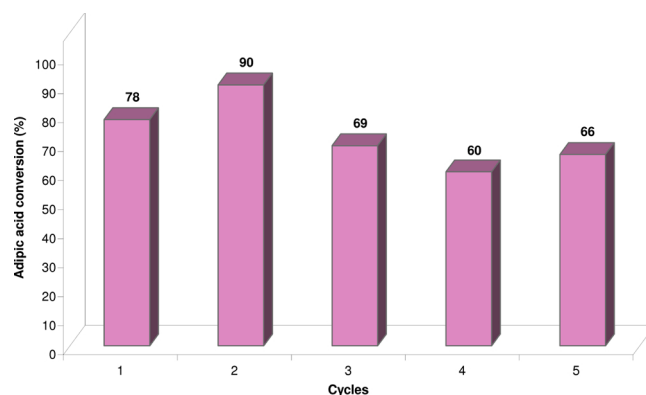


Fig. 6. Process recycling study: adipic acid yield. Reaction operating conditions: temperature, 85 °C; reaction time, 8 h; separation step, Büchner filtration; reaction volume, 1.4 L.

### 3.2. Adipic acid yields and mass balance

In this section, the adipic acid yield (number of moles of adipic acid divided by the initial number of moles of cyclohexene) over five consecutive cycles was calculated at the first time (Fig. 6) and then mass balance was carried out in order to evaluate the loss of catalyst and surfactant in the liquid waste and to identify the needs for process optimisation.

As shown in Fig. 6, the conversion was increased from the first to the second cycle and then a decreased was observed (yields values between 60% and 70%). It is very difficult to establish the reasons for this behavior but it can be partially attributed to the loss of surfactant and catalyst in the liquid wastes, thus changing the reaction conditions. In fact the two Büchner filtration operations used for liquid/solid separation steps were not effective for total adipic acid, catalyst and surfactant recovery.

The exact quantities of surfactant and catalyst entering each cycle were calculated by mass balance from the known variables of the system presented on Fig. 1. Catalyst and surfactant mass evolutions are presented in Fig. 7. As we can see, 34% of catalyst is lost during the recycling process (5 cycles) while 90% of surfactant leaves the reaction medium after the first cycle. This surfactant loss is in accordance with the adipic acid particle size distribution study published in our previous study<sup>17</sup>. The co-precipitation of surfactant with adipic acid during the first solid-liquid separation step results in a larger final product particle size distribution.

Because the two Büchner filtration operations used for liquid/solid separation were not effective neither for total adipic acid recovery nor for surfactant recovery, some preliminary studies were carried out by

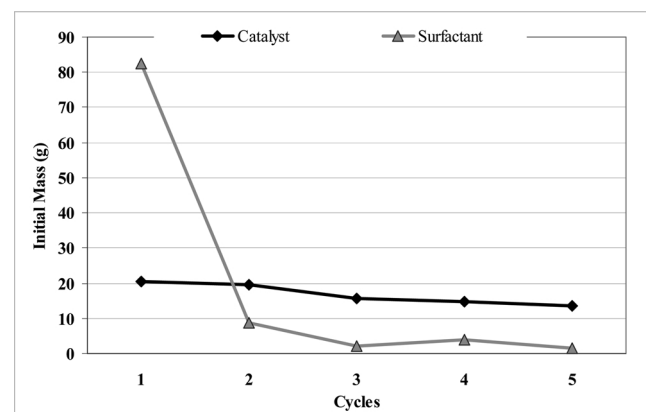
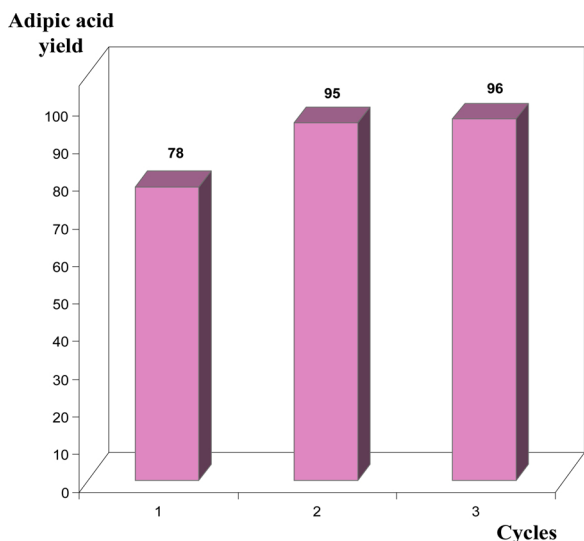


Fig. 7. Catalyst and surfactant evolution in function of the cycle numbers. temperature, 85 °C; reaction time, 8 h; Büchner filtration; reaction volume, 1.4 L.



**Fig. 8.** Process recycling study: adipic acid yield. Reaction operating conditions: temperature, 85 °C; reaction time, 8 h; separation step, ultrafiltration; reaction volume, 1.4 L.

modifying the filtration step at the lab scale by using ultrafiltration. The results presented in Fig. 8 show that special attention has to be paid to the solid/liquid separation step and that using ultrafiltration allows better adipic acid yields. The crude powder obtained after reaction and ultrafiltration was analyzed and the adipic acid purity obtained was 90%, 96% and 97% for the 3 successive cycles instead of 77%, 83%, 87% when using Büchner filtration.

#### 4. Conclusion

Adipic acid has been successfully synthesized by oxidation of cyclohexene by hydrogen peroxide, in microemulsion. The latter can be considered as a green solvent since it is mainly composed of water, hydrogen peroxide. A first attempt of kinetic modelling was done. A zero order kinetic law seems to correctly represent the cyclohexene behaviour but this result has to be confirmed. The identification and quantification of intermediary products are necessary to go further into this complex reaction modelling. It has been shown that both surfactant and catalyst can be separated from the medium after conversion of cyclohexene to adipic acid. Recycling of these two components is crucial to maintain a good yield of adipic acid in the objective of an industrial process. Using ultrafiltration allows to obtain a product yield of 95%, even after two recycling steps. The purity of the crude product was also maintained greater than 90% with this separation technique. Further study will be devoted to the optimisation of the separation step and the increase of the number of cycles.

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#### References

[1] Y. Usui, K. Sato, *Green Chem.* 5 (2003) 373–375, <https://doi.org/10.1039/B305847F>.  
 [2] Z.P. Pai, A.G. Tolstikov, P.V. Berdnikova, G.N. Kustova, T.B. Khlebnikova,

N.V. Selivanova, A.B. Shangina, V.G. Kostrovskii, *Russ. Chem. Bull.* 54-8 (2005) 1847–1854, <https://doi.org/10.1007/s1172-006-0047-z>.  
 [3] A.R. Ravishankara, J.S. Daniel, R.W. Portmann, *Science* 326 (2009) 123–125, <https://doi.org/10.1126/science.1176985>.  
 [4] D.E. Only, C.R. Campbell, 3rd ed., ‘Kirk-Othmer Encyclopedia of Chemical Technology’ 1 J. Wiley & Sons, New York, 1978, p. 51.  
 [5] U.S. Pat. 3,932,513 (Jan. 13, 1976), J. L. Russell (to Halcon International, Inc.).  
 [6] Jpn. Pat. 45-16444 (June 8, 1970), G. Inoue and co-workers (to Asahi Chemical Industries, Ltd.).  
 [7] Jpn. Pat. 50-116415 (Sept. 11, 1975), S. Furuhashi (to Asahi Chemical Industries, Ltd.).  
 [8] Jpn. Pat. 51-29427 (Mar. 12, 1976), M. Nishino and co-workers (to Toray Industries).  
 [9] U.S. Pat. 4,032,569 (June 28, 1977), A. Onopchenko and co-workers (to Gulf Research and Development Corp.).  
 [10] R. Platz, R. Kummer, H.W. Schneider, K. Wirten (to B.A.S.F.), *Ger. Offen* 2 (1978) 630,086, Jan. 12.  
 [11] O. Bolm, O. Beckmann, O.A.G. Dabard, *Angew. Chem., Int. Ed.* 38 (1999) 907–909, [https://doi.org/10.1002/\(SICI\)1521-3773\(19990401\)38:7<907::AID-ANIE907>3.0.CO;2-#](https://doi.org/10.1002/(SICI)1521-3773(19990401)38:7<907::AID-ANIE907>3.0.CO;2-#).  
 [12] C.M. Che, W.P. Yip, W.Y. Yu, *Chem. Asian J.* 1 (2006) 453–458, <https://doi.org/10.1002/asia.200600091>.  
 [13] S. Van de Vyver, Y. Román-Leshkov, *Catal. Sci. Technol.* 3-6 (2013) 1465–1479, <https://doi.org/10.1039/C3CY20728E>.  
 [14] A. Castellan, J.C.J. Bart, S. Cavallaro, *Catal. Today* 9-3 (1991) 237–254, [https://doi.org/10.1016/0920-5861\(91\)80049-F](https://doi.org/10.1016/0920-5861(91)80049-F).  
 [15] T. Polen, M. Spelberg, M. Bott, *J. Biotechnol.* 167-2 (2013) 75–84, <https://doi.org/10.1016/j.jbiotec.2012.07.008>.  
 [16] Y. Deng, Z. Ma, K. Wang, J. Chen, *Green Chem.* 1-6 (1999) 275–276, <https://doi.org/10.1039/a908889j>.  
 [17] C. Hongen, Z. Boran, Y. Yufan, X. Lin, Y. Lei, X. Qing, *Chinese J. Catal.* 39-5 (2018) 899–907, [https://doi.org/10.1016/S1872-2067\(18\)63050-5](https://doi.org/10.1016/S1872-2067(18)63050-5).  
 [18] W. Yiqiang, W. Xiangyu, W. Huijuan, L. Baojun, J. Peng, L. Limin, *Green Chem.* 14-10 (2012) 2868–2875, <https://doi.org/10.1039/C2GC35677E>.  
 [19] P. Blach, Z. Böstrom, S. Franceschi-Messant, A. Lattes, E. Perez, I. Rico-Lattes, *Tetrahedron* 66 (2010) 7124–7128, <https://doi.org/10.1016/j.tet.2010.06.093>.  
 [20] K. Holmberg, *Curr. Opin. Colloid Interface Sci.* 8 (2003) 187–196, [https://doi.org/10.1016/S1359-0294\(03\)00017-7](https://doi.org/10.1016/S1359-0294(03)00017-7).  
 [21] K. Holmberg, *Adv. Colloid Interface Sci.* 51 (1994) 137–174, [https://doi.org/10.1016/0001-8686\(94\)80035-9](https://doi.org/10.1016/0001-8686(94)80035-9).  
 [22] A. Lattes, I. Rico, *Colloids Surf.* 35-2 (1989) 221–235, [https://doi.org/10.1016/0166-6622\(89\)80297-5](https://doi.org/10.1016/0166-6622(89)80297-5).  
 [23] I. Rico, A. Lattes, *Nouv. J. Chim.* 8 (1984) 429–431.  
 [24] Z. Saidi, C. Boned, J. Peyrelasse, C. Helm, M. Lösche, H. Möhwald (Eds.), *Trends in Colloid and Interface Science VI. Progress in Colloid & Polymer Science*, vol 89, 1992, pp. 156–159, <https://doi.org/10.1007/BFb0116301> Steinkopff 89.  
 [25] J. Peyrelasse, C. Boned, Z. Saidi, P. Bothorel, E.J. Dufourc (Eds.), *Trends in Colloid and Interface Science III. Progress in Colloid & Polymer Science*, vol. 79, 1989, pp. 263–269, <https://doi.org/10.1007/BFb0116219> Steinkopff 79.  
 [26] V. Nardello-Rataj, L. Caron, C. Borde, J.M. Aubry, *J. Am. Chem. Soc.* 130 (2008) 14914–14915, <https://doi.org/10.1021/ja805220p>.  
 [27] M. Häger, K. Holmberg, A. M. d’A. Rocha Gonsalves, A.C. Serra, *Colloids Surf. A Physicochem. Eng. Asp.* 183-185 (2001) 247–257, [https://doi.org/10.1016/S0927-7757\(01\)00552-0](https://doi.org/10.1016/S0927-7757(01)00552-0).  
 [28] M. Haumann, H. Koch, R. Shomäcker, *Appl. Catal. A: Gen.* 236 (2002) 173–178, [https://doi.org/10.1016/S0926-860X\(02\)00284-3](https://doi.org/10.1016/S0926-860X(02)00284-3).  
 [29] M. Fantì, F. Mancin, P. Tecilla, U. Tonellato, *Langmuir* 16 (2000) 10115–10122, <https://doi.org/10.1021/la0009238>.  
 [30] B. Nuthakki, J.M. Bobbitt, J.F. Rusling, *Langmuir* 22 (2006) 5289–5293, <https://doi.org/10.1021/la0600191>.  
 [31] H. Ohde, C.M. Wai, H. Kim, J. Kim, M. Ohde, *J. Am. Chem. Soc.* 124 (2002) 4540–4541, <https://doi.org/10.1021/ja012232j>.  
 [32] E.A. Ofstead, J.P. Lawrence, M.L. Senyek, N.J. Calderon, *J. Mol. Catal.* 8 (1980) 227–242, [https://doi.org/10.1016/0304-5102\(80\)87021-0](https://doi.org/10.1016/0304-5102(80)87021-0).  
 [33] E. Perez, N. Alandis, J.P. Laval, I. Rico, A. Lattes, *Tetrahedron Lett.* 28 (1987) 2343–2346, [https://doi.org/10.1016/S0040-4039\(00\)96119-7](https://doi.org/10.1016/S0040-4039(00)96119-7).  
 [34] G. Barak, Y. Sasson, *Chem. Soc. Chem. Commun.* 16 (1987) 1266–1267, <https://doi.org/10.1039/C39870001266>.  
 [35] N. Alandis, I. Rico-Lattes, A. Lattes, *New J. Chem.* 18 (1994) 1147–1153.  
 [36] I.Q. Peñaite, G. Lesage, P. Cognet, M. Poux, *Chem. Eng. J.* 200–202 (2012) 357–364, <https://doi.org/10.1016/j.cej.2012.06.041>.  
 [37] R.G. Laughlin, *Surfactant solubility*, in: G. Broze, Marcel Dekker (Eds.), *Handbook of Detergents*, 2000 New York, Ch. 4.  
 [38] S. Ren, Z. Xie, L. Cao, X. Xie, G. Qin, J. Wang, *Catal. Commun.* 10-5 (2009) 464–467, <https://doi.org/10.1016/j.catcom.2008.10.013>.  
 [39] S.O. Lee, R. Raja, K.D.M. Harris, J.M. Thomas, B.F.G. Johnson, G. Sankar, *Angew. Chem.* 42-13 (2003) 1520–1523, <https://doi.org/10.1002/anie.200250351>.  
 [40] L.P. Labranche, S.N. Dumont, S. Levesque, A. Carrier, *J. Pharm. Biomed. Anal.* 43-3 (2007) 989–993, <https://doi.org/10.1016/j.jpba.2006.09.022>.  
 [41] F. Lopez, G. Cinelli, M. Colella, A. De Leonardis, G. Palazzo, L. Ambrosone, *Biotechnol. Prog.* 30-2 (2014) 360–366, <https://doi.org/10.1002/btpr.1892>.