



HAL
open science

Clean synthesis of adipic acid from cyclohexene in microemulsions with stearyl dimethyl benzyl ammonium chloride as surfactant: From the laboratory to bench scale

Isariebel Quesada-Peñate, Geoffroy Lesage, Patrick Cognet, Martine Poux

► To cite this version:

Isariebel Quesada-Peñate, Geoffroy Lesage, Patrick Cognet, Martine Poux. Clean synthesis of adipic acid from cyclohexene in microemulsions with stearyl dimethyl benzyl ammonium chloride as surfactant: From the laboratory to bench scale. *Chemical Engineering Journal*, 2012, vol. 200-202, pp. 357-364. 10.1016/j.cej.2012.06.041 . hal-00879077

HAL Id: hal-00879077

<https://hal.science/hal-00879077v1>

Submitted on 31 Oct 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 9999

To link to this article : DOI:10.1016/j.cej.2012.06.041
URL : <http://dx.doi.org/10.1016/j.cej.2012.06.041>

To cite this version : Quesada Peñate, Isariebel and Lesage, Geoffroy and Cognet, Patrick and Poux, Martine *Clean synthesis of adipic acid from cyclohexene in microemulsions with stearyl dimethyl benzyl ammonium chloride as surfactant: From the laboratory to bench scale.* (2012) Chemical Engineering Journal, vol. 200-202 . pp. 357-364. ISSN 1385-8947

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Clean synthesis of adipic acid from cyclohexene in microemulsions with stearyl dimethyl benzyl ammonium chloride as surfactant: From the laboratory to bench scale

Isariebel Quesada Peñate, Geoffroy Lesage, Patrick Cognet, Martine Poux*

Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4, Allée Emile Monso, F-31432 Toulouse, France
CNRS, Laboratoire de Génie Chimique, F-31432 Toulouse, France

- ▶ Adipic acid was obtained from cyclohexene oxidation in microemulsions.
- ▶ Stearyl dimethyl benzyl ammonium chloride is used as surfactant.
- ▶ Non-polluting catalyst sodium tungstate, which contains no heavy metal, is used.
- ▶ Reaction without organic ligand and without phase transfer catalyst.
- ▶ The surfactant and catalyst can be reused through many cycles.

A B S T R A C T

Adipic acid, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, is a white crystalline solid used primarily in the manufacture of nylon-6,6 polyamide. In industry, adipic acid is mainly produced by oxidation of cyclohexane with air and nitric acid following a homogeneous two-step route. However, this process leads to the formation of nitrous oxide, a greenhouse gas that has to be decomposed. The aim of this study was the development of a clean technology at pilot scale in order to obtain and recover pure adipic acid, and the evaluation of its industrial practicability. Adipic acid was synthesized from cyclohexene and hydrogen peroxide in microemulsions with stearyl dimethyl benzyl ammonium chloride as surfactant. The non-polluting catalyst sodium tungstate, which contains no heavy metal, was used and the reaction conducted under mild conditions (85 °C, 8 h). Yields of up to 81% were reached at the 0.14 L scale. However at the end of the reaction the catalyst and the surfactant must be separated and recycled for subsequent cycles. The reuse of the reaction media enabled the conversion to be increased up to 92% but a loss of surfactant and/or catalyst through the cycles progressively reduced the yields. Yields at the bench scale (1.4 L) increased during the two first cycles and then decreased to conversions of between 60% and 70%. Globally the yield is a little lower at bench scale. The results obtained show that the synthesis of adipic acid by a heterogeneous one-step oxidation of cyclohexene in the presence of hydrogen peroxide is an attractive route for developing a future green industrial process.

Keywords:
Adipic acid
Hydrogen peroxide
Microemulsion
Surfactant
Sustainable chemistry

1. Introduction

Adipic acid is a chemical used primarily in the manufacture of nylon-6,6 polyamide [1]. It is also used in the manufacture of some low-temperature synthetic lubricants, synthetic fibers, coatings, plastics, polyurethane resins, and plasticizers, and to give some imitation food products a tangy flavor [2]. The rising demand for engineering plastics necessitates an increasing production for this product [3].

Adipic acid production is the largest potential source of industrial nitrous oxide (N_2O) emissions (0.3 kg N_2O per kg adipic acid) that are commonly thought to cause global warming, ozone depletion, acid rain and photochemical smog [4,5]. N_2O is expected to be the dominant ozone-depleting substance emitted in the 21st century [6]. Overall, total N_2O emissions from adipic acid production were substantially limited in 2000 because of the abatement measures that have been implemented in the US, the world's major producer, but emissions will grow through 2020 in the absence of additional activities to reduce them [3]. Therefore, the development of an environmentally friendly industrial process for adipic acid production is very important.

* Corresponding author at: Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4, Allée Emile Monso, F-31432 Toulouse, France. Tel.: +33 534323684; fax: +33 532343600.

E-mail address: Martine.Poux@ensiacet.fr (M. Poux).

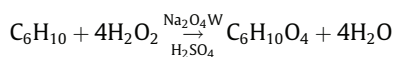
Adipic acid historically has been manufactured from either cyclohexane or phenol. Oxidation of cyclohexane is a low efficiency industrial chemical process. Conversions are usually in the range of 3–8% with a mean selectivity of 80% for the cyclohexanone/cyclohexanol mixture [7]. Various alternative methods including biosynthesis [8–10], supercritical fluid methods [11,12] and ozonolysis [13] have been elaborated for the clean synthesis of adipic acid.

In the other hand, the one-step oxidative cleavage of cyclohexene to adipic acid with hydrogen peroxide is considered as one of the most promising and environmentally friendly processes [14]. Hydrogen peroxide is a clean oxidant and its decomposition leads to benign by-products like water and oxygen [15,16]. However, it is often limited by a poor rate of production of active oxygen in organic oxidation reactions [17] and thus the use of catalysts is essential [18]. Furthermore, the relative prices of hydrogen peroxide (US\$ 0.58/kg) and adipic acid (US\$ 1.43/kg) should be considered. Thus, if the efficiency of the reaction is less than 40%, the value of the oxidant is higher than the cost of the product [19]. Nevertheless academia and industry develop new alternatives for reducing cost in H₂O₂ production [20–22]. The main difficulty in this type of reaction is the poor contact between the hydrophobic and the hydrophilic reagents [23]. Different methods have been proposed in order to improve this contact. The synthesis of adipic acid in a water emulsion by hydrogen peroxide oxidation of cyclohexene without surfactant and under strong stirring was proposed by Deng and co-workers [15]. In their work a good yield of pure adipic acid was obtained only by addition of an organic acid as ligand (co-catalyst) and harsh reaction conditions (20 h at 94 °C). The use of a phase transfer agent (methyltrioctylammonium hydrogenosulphate) in water to produce adipic acid with a good yield was proposed by Sato and co-workers [14] but the reuse of the system required an additional amount of phase transfer agent to be effective.

The use of microemulsions as aqueous media for organic reactions is a way to improve the contact between the different reagents [24,25] and to overcome the use of polluting organic solvents. Although microemulsions are described as versatile reaction media for many organic reactions, there is still no industrial process based on microemulsions, essentially because of the difficulty in recovering the products and reusing the system [23].

Blach and co-workers [23] have described the use of hydrogen peroxide microemulsions as reaction media for the oxidation of cyclohexene to adipic acid. The microemulsion was obtained by using a low-cost commercial mixture of benzalkonium chloride containing 60 wt.% of dodecyl- and 40 wt.% of tetradecylbenzyltrimethylammonium chloride (BenzCl C12–14). The process leads to pure adipic acid that can be recovered by simple Büchner filtration at room temperature, but in order to recycle the system, a water evaporation step at 70 °C under reduced pressure (1 kPa) is needed.

In this paper, the synthesis of adipic acid by oxidation of cyclohexene in a microemulsion system with hydrogen peroxide as oxidant is presented. In order to avoid the evaporation step and to improve the efficiency of the reaction, stearyldimethylbenzylammonium chloride (BenzCl C18), a longer chain surfactant, was used. The general equation describing the reaction is:



2. Materials and methods

2.1. Materials

BenzCl C18 (90%, Sigma–Aldrich), cyclohexene (99%, Sigma–Aldrich), sulfuric acid (95–97%, Sigma–Aldrich), dihydrated sodium tungstate (99%, Sigma–Aldrich), and hydrogen peroxide (30%,

Sigma–Aldrich), were used for the reaction experiments as received. Methanol (99.9%, Fluka) and toluene (99.9%, Sigma–Aldrich) were used for the GC analysis of cyclohexene. Potassium permanganate (98.5%, Sigma–Aldrich) was used for the hydrogen peroxide titration and sodium hydroxide solution (30%, Analar Normapur) was used for the adipic acid titration.

2.2. Synthesis of adipic acid in a microemulsion and recyclability experiments

Reactions were carried out in a 0.5 L cylindrical water-jacketed glass reactor equipped with a magnetic stirring bar and a reflux condenser. BenzCl C18 (8.25 g), hydrogen peroxide (30% solution, 132.15 g), sodium tungstate (2.05 g) and sulfuric acid (4.6 g) were added all together. The mixture was rapidly stirred at 70 °C until total dissolution and then 15 g of cyclohexene were added and the mixture maintained at 85 °C for 8 h. After cooling to 40 °C for 1 h, adipic acid precipitated and was recovered by Büchner filtration (fritted glass funnels with a pore size of 2–4 µm). The crude product was washed with cold water (10 mL) to give a white powder that was dried at 40 °C (cycle 1).

For recyclability studies, the filtrate was cooled to 20 °C and the solid (BenzCl C18, sodium tungstate and remaining adipic acid) was recovered by Büchner filtration. It was reintroduced into the reactor with hydrogen peroxide and cyclohexene (the same quantities as the first cycle) and a new cycle was started for 8 h at 85 °C.

Two different reaction volumes were used in order to scale up the process: 0.14 L and 1.4 L. For 1.4 L, the same procedure was followed but 82.5 g of BenzCl C18, 1321.5 g of hydrogen peroxide solution (30%), 20.5 g of sodium tungstate, 46 g of sulfuric acid and 150 g of cyclohexene were used instead.

2.3. Analytical methods

The adipic acid concentration was determined by acid–base titration. A 0.025 N NaOH solution was prepared and was standardized with a H₂SO₄ solution (0.025 N) in an automatic titrator (Mettler Toledo DL50). Adipic acid formation was followed by NaOH titration. The measurements were performed at least three times.

The adipic acid purity was determined by HPLC in a Waters Alliance 2695 Separation Module with a 2487 UV detector. Analyses 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. A gradient separation mode was used as follows: 0 min: 9% A, 91% B; 5 min: 9% A, 91% B, 15 min: 100% B.

The concentrations of the hydrogen peroxide solutions were determined by permanganometry. A standard 0.02 M potassium permanganate (KMnO₄) solution was prepared that was refluxed for 1 h, filtered and stored in a dark colored bottle. The KMnO₄ 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 verified by taking 0.1 g of crude mixture diluted in 20 mL of water with 5 mL of sulfuric acid and titrated with KMnO₄ solution until persistent coloration of the solution. The measurements were performed at least three times.

The cyclohexene consumption was checked by gas chromatography (Varian CP-3800) with a flame-ionization detector and a MachereyNagel Optima-1-Accent-0.25 mm column (30 m, 0.25 mm). 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, 500 mg of crude reaction mixture, 50 mg of toluene (internal standard) and 500 mg of methanol were mixed and then 1 µL of this solution was analyzed.

The particle size distribution of solid adipic acid obtained was followed by a dry method in a Malvern-Mastersizer 2000 analyzer.

For the ultrafiltration experiments, a hydrophilic coated polyvinylidene fluoride membrane (ETNA 10PP) was used.

3. Results and discussion

3.1. Surfactant selection and microemulsion zones

BenzCl C18 was used as surfactant in order to avoid the evaporation step and to improve the efficiency of the reaction compared with the previous results obtained by Blach and co-workers [23] with BenzCl C12–C14. BenzCl C18 is a quaternary ammonium salt (Fig. 1) that is widely used as an active ingredient for conditioners, antistatic agents, detergent sanitisers, softeners for textiles and paper products, as phase transfer catalyst and various other uses. It is able to form microemulsions without co-surfactants. The microemulsion studied was mainly composed of the following reagents: cyclohexene as the oily phase, water diluted hydrogen peroxide as the aqueous phase and the surfactant BenzCl C18.

The physico-chemical properties of the system were previously studied by the Laboratory of Complex Fluids (Pau, France). The ternary phase diagram determining the microemulsion zones at 70 °C is presented in Fig. 2.

As we can be seen, even without any co-surfactant, a large microemulsion area was obtained with BenzCl C18 but because of the reaction stoichiometry (4 mol H₂O₂/1 mol cyclohexene), only a water-rich region of the diagram can be used. The ternary phase diagram shows the superiority of BenzCl C18 in solubilising the oily phase compared with BenzCl C12–C14 [23]. With 85% water, 5% BenzCl C18 can solubilize 10% of the cyclohexene whereas 10% BenzCl C12–C14 solubilizes only 5% of the oily phase [23].

Even if it was possible to solubilize 15% of the cyclohexene in the water-rich region ($\geq 75\%$ water), a large amount of surfactant (25%) would be required, which would drastically increase the viscosity of the system. On the other hand, it is well-known that benzalkonium chlorides could be toxic for aquatic organisms at high concentrations [26]. For these reasons the selected point was the one with the minimal quantity of surfactant: 85% water, 10% cyclohexene and 5% BenzCl C18. Although the phase diagram was established at 70 °C and the reaction temperature of this study was 85 °C, the comparison between the phase diagrams at 25 °C (not reported here) and 70 °C (Fig. 2) showed that the microemulsion zone increases with temperature.

3.2. Oxidation of cyclohexene in BenzCl C18 microemulsion

Although hydrogen peroxide is a clean oxidant, organic oxidation reactions using H₂O₂ show low reaction rates and therefore the use of a catalyst and an excess of this product are needed. The non-polluting catalyst sodium tungstate (Na₂WO₄), which contains no heavy metal was selected. By reacting with hydrogen peroxide, sodium tungstate is transformed into sodium peroxotungstate and the active catalyst is then able to accelerate cyclohexene oxidation at high temperature. In order to easily recover

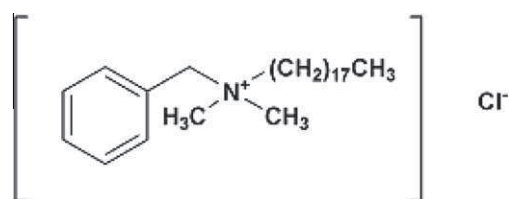


Fig. 1. General structure of stearyl dimethylbenzylammonium chloride (BenzCl C18).

pure adipic acid by precipitation, the pH was fixed at 1. This condition is favorable for catalyst activation [27].

Cyclohexene oxidation was performed as described in the experimental section and the consumption of the reactants during the reaction was followed by gas chromatography and potassium permanganate titration respectively.

Although previous studies on adipic acid formation by the cyclohexene oxidation reaction (with the hydrogen peroxide) indicate that other acids could be formed [14,28], it has been found that those by-products were present at very low concentrations [29–31]. Jin and co-workers [29] reported that glutaric and succinic acid were the major by-products but their production yields were lower than 5%. Ren and co-workers [30] obtained an acid production yield lower than 1% and Jiang and co-workers [31] found only 2% of glutaric acid as by-product at the end of the reaction. Based on those results, the acid by-products that could be formed were not considered in our study and the adipic acid formation was determined by chemical titration with standard NaOH solution. Fig. 3 shows the consumption of the reactant and adipic acid formation with reaction time.

The cyclohexene kinetics had the same behavior as those obtained by Blach and co-workers with BenzCl C12–C14 where C₆H₁₀ was completely consumed in 2 h. Nevertheless, in our study, a greater conversion of adipic acid was obtained (84% in 8 h vs. 56% in 18 h). It is important to note that after 8 h, 24% of the initial hydrogen peroxide remained in the reaction mixture. This is in agreement with the use of a 1.6 times stoichiometric excess of H₂O₂. The H₂O₂ and adipic acid kinetics follow similar trends. At the beginning of the reaction, 1.17 mol of hydrogen peroxide were added and at the end of the reaction 0.18 mol of adipic acid were obtained, which means that 0.73 mol of reactive H₂O₂ led to adipic acid formation (62% of the H₂O₂ initially added) and that a certain quantity of the oxidant was lost (decomposed) during the reaction time. The kinetics of H₂O₂ consumption obtained using BenzCl C18 are quite different from those with BenzCl C12–C14 as surfactant. Indeed Blach and co-workers found that only 5% of the oxidant remained in the system, after 8 h of reaction [23].

In order to reduce the quantity of hydrogen peroxide remaining at the end of the reaction, one experiment (duplicated) was carried out with a lower oxidant stoichiometric excess (1.3 times). To stay at the same point on the ternary diagram (Fig. 4), the H₂O₂ removed was replaced by water.

A decreasing oxidant concentration of 20% leads to a decrease in the conversion from 84% to 66%. It means that the micro-emulsion formation is important but not sufficient and that the number of collisions between molecules is also relatively important. Thus the oxidant concentration must be maintained at a certain level of excess. Although a low oxidant concentration could be found in the waste, it is important to note that nearly all organisms (specifically, all obligate and facultative aerobes) have enzymes known as peroxidases, which harmlessly and catalytically decompose hydrogen peroxide to water and oxygen.

These preliminary studies of the adipic acid synthesis by oxidation of cyclohexene with hydrogen peroxide as oxidant in a microemulsion system using BenzCl C18 surfactant are very promising. The advantages of this reaction compared with using BenzCl C12–C14 are the high adipic acid yield (1.5 times higher) and the shorter reaction time (2.25 times shorter) compared with the microemulsions using BenzCl C12–C14. Nevertheless for the complete evaluation of the system improvement, a recyclability study was essential.

3.3. System recyclability

The use of aqueous hydrogen peroxide for clean oxidation is one of the three identified key developments in green chemistry [32]

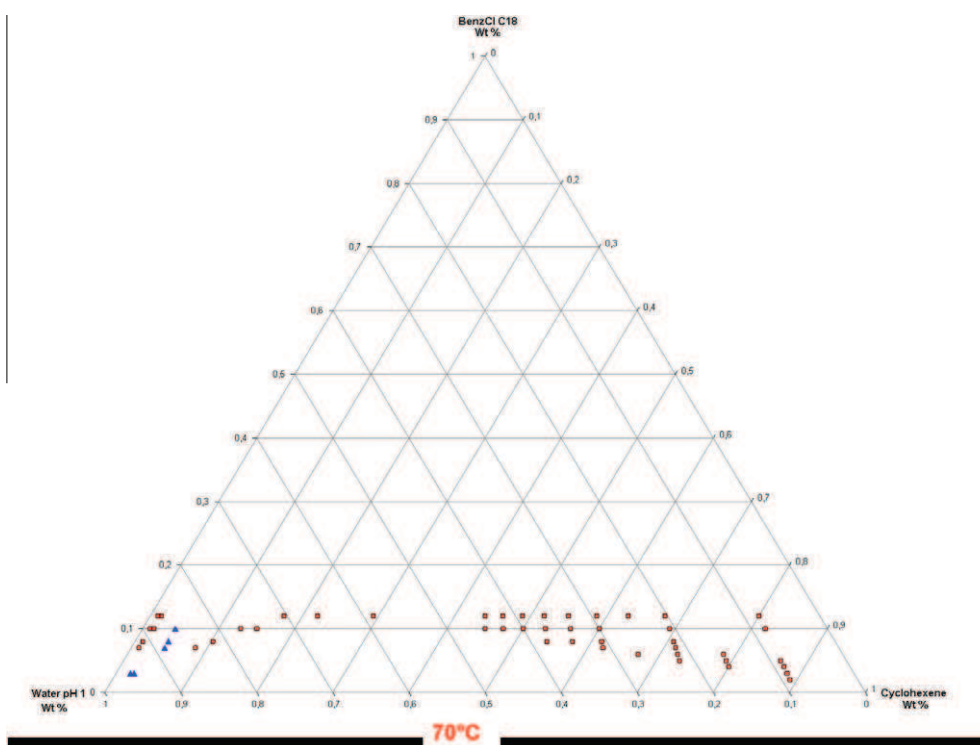


Fig. 2. Ternary phase diagram of water/BenzCl C18/cyclohexene at 70 °C and pH 1. With permission of the Laboratory of Complex Fluids (Pau, France). ▲ Birefringent microemulsion, ■ microemulsion.

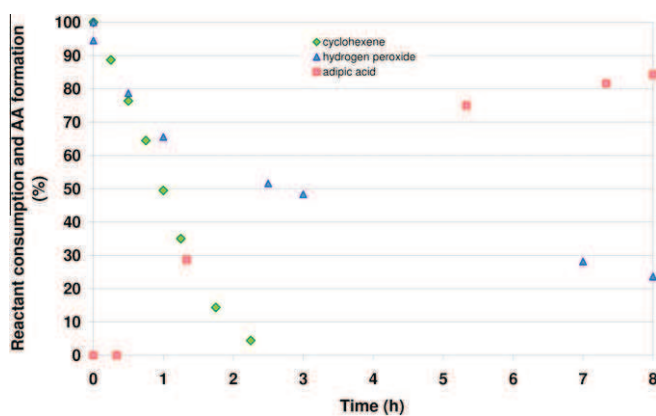


Fig. 3. Time course of cyclohexene oxidation by H_2O_2 in the BenzCl C18 microemulsion. Temperature, 85 °C; reaction time, 8 h; reaction volume, 0.14 L.

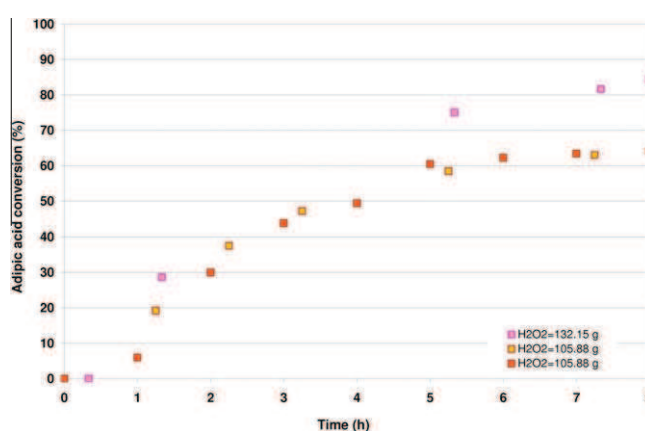


Fig. 4. Experimental adipic acid kinetics in experiments with different initial H_2O_2 concentrations. Operating conditions: surfactant, BenzCl C18; temperature, 85 °C; reaction time, 8 h; reaction volume, 0.14 L.

but benzalkonium chlorides used as surfactants could be toxic for aquatic organisms at high concentrations [27] so their introduction in this process implies their control and strict reuse. The operating procedure for this study was described in the experimental section. After the reaction step, two important objectives must be achieved: the first one is the adipic acid recovery and the second one is the surfactant and catalyst reuse (Fig. 5). It is very important to note that the solid/liquid separation step is quite different from that used with the BenzCl C12-C14 system. In the presence of BenzCl C18, adipic acid precipitation appears at 46 °C instead of 20 °C (value reported by Blach and co-workers [23]). Moreover, the progressive cooling of the reaction mixture down to 20 °C generates the simultaneous precipitation of the remaining adipic acid, catalyst and the surfactant that will be re-used in the next reaction cycle. These properties of adipic acid and BenzCl C18 enable two different precipitation steps to be used for adipic acid and

surfactant separation and avoid the potentially dangerous evaporation step described by Blach and co-workers [23].

The adipic acid yield (number of moles of adipic acid divided by the initial number of moles of cyclohexene) based on adipic acid titration, over five consecutive cycles is given in Fig. 6. As shown, the conversions to adipic acid increase continuously during the three first cycles and then a decrease is observed. Although the synthesis of adipic acid in BenzCl C18 microemulsions reaches higher values in the three first cycles compared with those obtained by Blach and co-workers [23] using BenzCl C12-C14 as surfactant, this trend changes in further cycles. This difference could be very well explained by the different methods of surfactant recovery. While BenzCl C12-C14 was recovered by an evaporation step allowing the total mass of surfactant to be returned to the

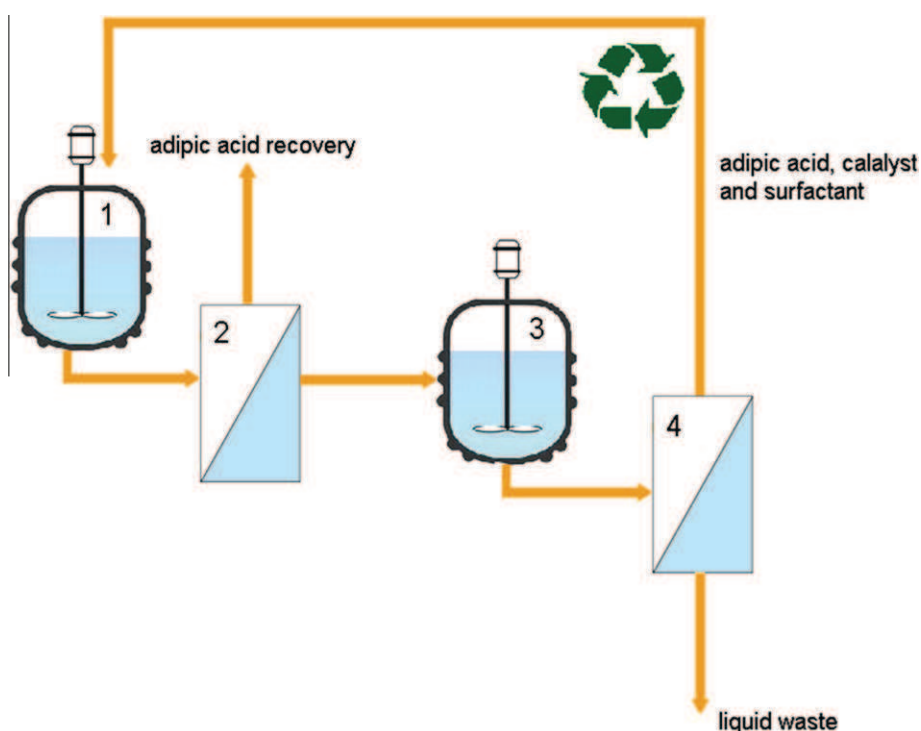


Fig. 5. Simplified diagram for adipic acid synthesis in a microemulsion with BenzCl C18. 1: Reaction of cyclohexene oxidation by hydrogen peroxide at 85 °C and first adipic acid precipitation at 40 °C; 2: Filtration at 40 °C; 3: Second precipitation at 20 °C (adipic acid, catalyst, possible by-products and surfactant); 4: Filtration at 20 °C.

reactor, BenzCl C18 was recovered by filtration and thus is partially lost in the liquid waste.

In order to verify the influence of surfactant concentration on adipic acid production yields, a new experiment was carried out with 7.42 g of surfactant instead of 8.25 g used in the first experiment. Although the fraction of surfactant in the ternary phase diagram changes only from 5.3% to 4.8%, the adipic acid yield decreased from 84% to 47% (data not shown). These results are in agreement with those obtained in the Laboratory of Complex Fluids (Pau, France) showing a complex ternary phase diagram with discontinuity zones for the mixture water/BenzCl C18/cyclohexene at 70 °C. A minimal decrease in surfactant concentration shifts the working point in the ternary diagram and thus the efficiency of the system.

The two Büchner filtration operations used for liquid/solid separation were not effective neither for total adipic acid recovery nor

for surfactant recovery and so crystallization was used. Thus the separation steps must be optimized.

To choose the most efficient liquid/solid separation step, a particle size analysis of adipic acid crude powder obtained during the first four cycles were carried out by the dry method. Fig. 7 shows the average particle size of three repeatable measurements for each cycle.

The adipic acid particles obtained during the first cycle have a wider size distribution, between 3.55 μm and 153 μm and with an average particle size of 14 μm . After the first cycle, the size distribution becomes narrower and the average particle size decreases from 14 μm to 6 μm . There are two possible reasons for these behaviors: the first one is that adipic acid crystal size largely depends on the composition of the bulk mixture at the end of the reaction and the second one is that coprecipitation of adipic acid, surfactant and catalyst may occur. The decrease in the crystal size

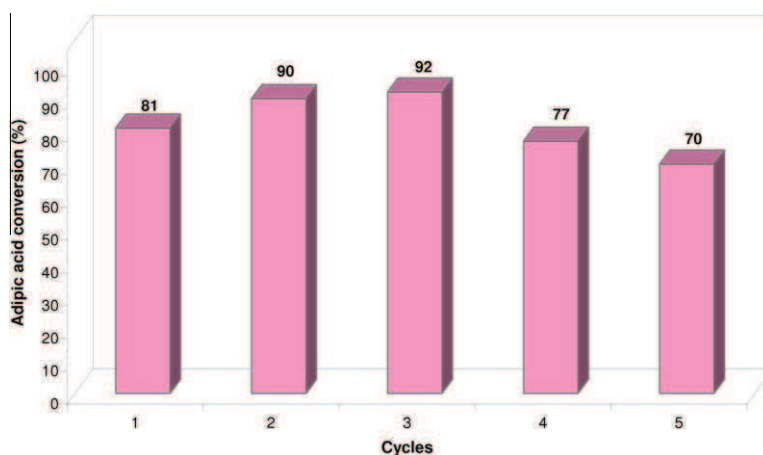


Fig. 6. Process recycling study. Reaction operating conditions: surfactant, BenzCl C18; temperature, 85 °C; reaction time, 8 h; reaction volume, 0.14 L.

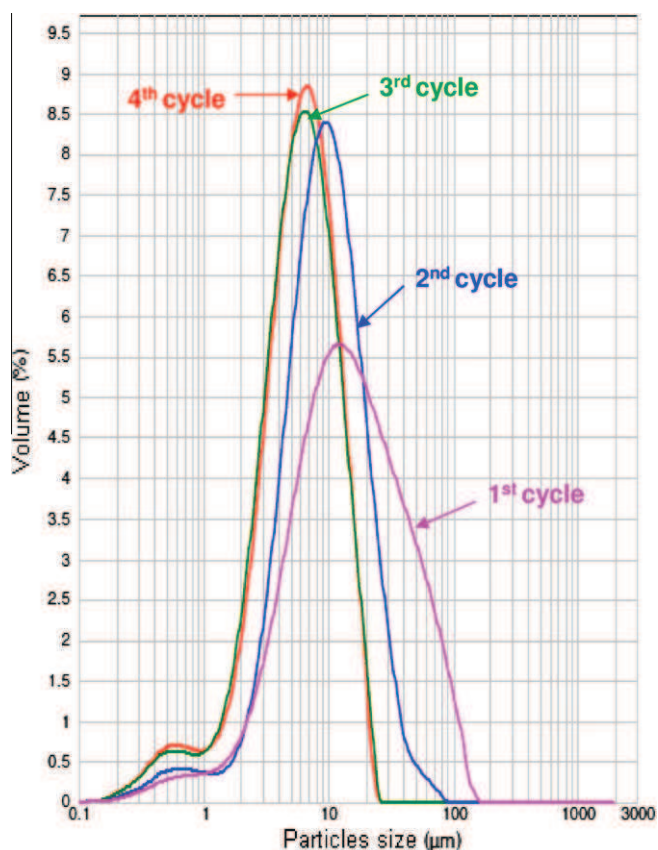


Fig. 7. Particle size analysis of solid adipic acid (crude powder) obtained after four successive reaction cycles at the 0.14 L scale.

could induce significant progressive release of adipic acid after the filtration if this operation is not fully efficient. Taking into account these results an ultrafiltration step was implemented, using a composite ETNA10 PP membrane at a filtration pressure of 2 bars. The experiments were conducted with the liquid waste from the four cycles (containing different adipic acid concentrations) and the filtrate of this separation step was completely adipic acid free. It is important to note that the concept of membrane-assisted adipic acid crystallization has been reported by Juhn and co-workers [33] and a six times lower energy conversion was obtained compared to evaporative crystallization [33].

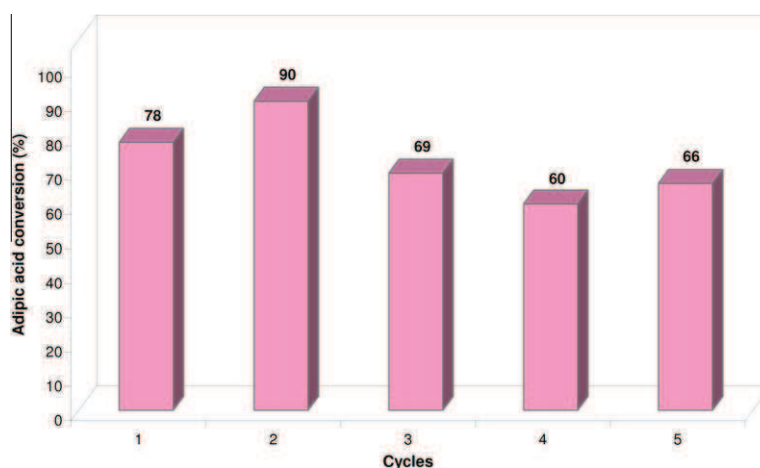


Fig. 8. Process recycling studies at the 1.4 L scale. Reaction operating conditions: surfactant, BenzCl C18; temperature, 85 °C; reaction time, 8 h.

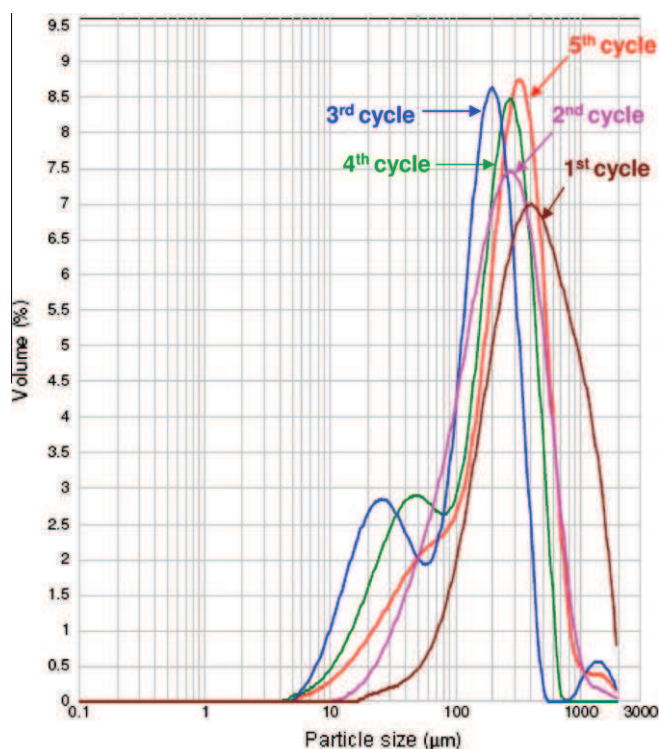


Fig. 9. Particle size analysis of solid adipic acid (crude powder) synthesized in the 1.4 L scale process.

3.4. Preliminary studies at bench scale

Because this chemical process was firstly carried out at a small laboratory scale (0.14 L), its subsequent development was done by conducting the reaction at a larger scale of 1.4 L. The geometric similarity approach was used for the scale-up.

Although at the 0.14 L scale, the total cyclohexene addition was done at the beginning of the reaction, this was not possible at the bench scale (1.4 L) due to the high reaction exothermicity. Because the geometric similarity approach gives less heat transfer in the 1.4 L vessel, the cyclohexene was added with in pulses over mode during 1 h in order to avoid a thermal runaway. However, for the precipitation and separation steps, no changes were made in the protocol.

Table 1

Comparison between operation parameters of adipic acid synthesis by cyclohexene oxidation with hydrogen peroxide in a microemulsion and the current cyclohexane oxidation.

Parameters	Current process: cyclohexane oxidation [34]	This study: cyclohexene oxidation with hydrogen peroxide in a microemulsion
Type	Two-stage process	One-stage process
Reaction	(1) $C_6H_{12} + O_2 \Rightarrow C_6H_{12}O + C_6H_{11}OH$ (2) $2C_6H_{12}O + 7HNO_3 + 2C_6H_{11}OH \Rightarrow 3,5N_2O + 4C_6H_{10}O_4 + 5,5H_2O$ (3) $C_6H_{12}O + 2HNO_3 \Rightarrow N_2O + C_6H_{10}O_4 + 2H_2O$	$C_6H_{10} + 4 H_2O_2 \Rightarrow C_6H_{10}O_4 + 4H_2O$
Pressure	(1) 1000–1800 kPa (2) 100–400 kPa	1 kPa
Temperature	(1) 100–170 °C (2) 60–90 °C	80 °C
Catalyst	(1) Cobalt naphthenate or cobalt octoate (2) Vanadium catalysts	Sodium tungstate
Yields	(1) 3–8% (2) 92–96%	60–92%
Wastes	Three major waste streams: – Off-gas containing oxides of nitrogen and CO ₂ – Water containing traces of nitric acid and organics from the water removal column – Dibasic acid purge stream containing adipic, glutaric, and succinic acids	One major waste stream: – Water containing adipic acid, catalyst, surfactant and glutaric, and succinic acids

It can be seen from the comparison of Figs. 6 and 8 that adipic acid conversions follow similar trends at both scales. The conversion was increased during the first two cycles and then decreased to between 60% and 70%. Globally, the adipic acid production yields are a little lower at 1.4 L scale. This behavior could be explained by the cyclohexene feeding mode which has slightly reduced the total reaction time.

The crude powder obtained after reaction and filtration at 40 °C was analyzed as described in the experimental section. The adipic acid purity was 77%, 83%, 87%, 81% and 83% in cycles 1, 2, 3, 4 and 5 respectively.

It is important to note that the adipic acid purity is closely related to the particle size distribution (Fig. 9). The highest purity and the narrowest size distribution (20–316 μm) were obtained for the third cycle and on the contrary, the lowest purity and the widest size distribution corresponded to cycle 1 (130–1142 μm). The lower adipic acid purity in cycle 1 is certainly related to the co-precipitation of surfactant, catalyst and adipic acid which could lead to a larger particle size distribution. In the future industrial process, this crude powder could be purified by recrystallization.

All these results demonstrate that it is possible to use a cyclohexene/hydrogen peroxide microemulsion with BenzCl C18 to produce pure adipic acid with very good yield and acceptable purity. The use of this process has the following advantages:

- Total elimination of N₂O emissions.
- Reaction yields in the same order of magnitude as the actual manufacture process.
- Reaction can be achieved without using extreme conditions of temperature, pressure, mixing and reaction times.
- Solid/liquid separation can be efficiently achieved by ultrafiltration instead of a potentially dangerous evaporation step used in the synthesis with BenzCl C12–C14.

The following Table 1 shows a comparison between some operating parameters for the adipic acid synthesis by cyclohexene oxidation with hydrogen peroxide in a microemulsion and the current oxidation technology using nitric acid in the final oxidation stage.

4. Conclusions

An original recyclable process has been described for the synthesis of adipic acid by cyclohexene oxidation with hydrogen peroxide in a microemulsion system using BenzCl C18 as surfactant. Microemulsions using BenzCl C18 provide better adipic acid

production yields than BenzCl C12–C14 systems. Reactions were carried out without using strong stirring, long reaction times or very high temperatures. Adipic acid yields ranged from 60% to 92% and the product purity reached values between 77% and 87%. The recyclability study demonstrated that it is possible to re-use surfactant, catalyst and remaining adipic acid but special attention has to be paid to the solid/liquid separation step in order to obtain better yields and higher purities. The partially cyclohexene oxidation by molecular oxygen and the membrane-assisted adipic acid crystallization studies have to be carried out in order to improve the efficiency of this new “green process”.

Acknowledgments

The authors gratefully thank the French ANR CP2D for financial support, Magdalena Kristiawan for the physico-chemical analysis, Jean Louis Nadalin for the experimental set-up construction, Paul Montagne for his valuable help in the experimental work, Jean-Christophe Garrigues for the HPLC analysis and finally Professors Emile Perez and Sophie Franceschi-Messant for their valuable comments.

References

- [1] D.D. Davis, D.R. Kemp, Adipic Acid in ECT, 2000. <http://onlinelibrary.wiley.com/doi/10.1002/0471238961.0104091604012209.a01.pub2/pdf>.
- [2] G.S. Chen, Y.M. Zhou, X. Wang, *Jiangsu Chem. Ind.* 33 (2005) 69.
- [3] H. Mainhardt, Good practice guidance and uncertainty management in national greenhouse gas inventories. <http://www.ipcc-nggip.iges.or.jp/public/gp/bgp/3_2_Adipic_Acid_Nitric_AcidProduction.pdf>.
- [4] R.E. Dickinson, R.J. Cicerone, *Nature* 319 (1986) 109.
- [5] J. Li, G. Luo, Y. Chu, F. Wei, *Chem. Eng. J.* 184 (2012) 168.
- [6] Y. Wang, J. Geng, G. Guo, C. Wang, S. Liu, *Chem. Eng. J.* 172 (2011) 999.
- [7] D. Lončarević, J. Krstić, J. Dostanić, D. Manojlović, Ž. Čupić, D.M. Jovanović, *Chem. Eng. J.* 157 (2010) 181.
- [8] K.M. Draths, J.W. Frost, *J. Am. Chem. Soc.* 116 (1994) 399.
- [9] W. Niu, K.M. Draths, J.W. Frost, *Biotechnol. Progr.* 18 (2002) 201.
- [10] J.M. Thomas, R. Raja, B.F.G. Johnson, T.J. O'Connell, G. Sankar, T. Khimyak, *Chem. Commun.* 10 (2003) 1126.
- [11] E.J. Beckman, *Environ. Sci. Technol.* 37 (2003) 5289.
- [12] Z. Hou, B. Han, L. Gao, Z. Liu, G. Yang, *Green Chem.* 4 (2002) 426.
- [13] A.J. Bailey, W.P. Griffith, B.C. Parkin, *J. Chem. Soc. Dalton Trans.* (1995) 1833.
- [14] K. Sato, M. Aoki, R.A. Noyori, *Science* 281 (1998) 1646.
- [15] Y. Deng, Z.M. Wang, J. Chen, *Green Chem.* 1 (1999) 275.
- [16] B. Karimi, M. Ghoreishi-Nezhad, J.H. Clark, *Org. Lett.* 7 (2005) 625; H. Jiang, H. Gong, Z. Yang, X. Zhang, Z. Sun, *React Kinet Catal Lett* 75 (2002) 315.
- [17] W. Zhu, H. Li, X. He, Q. Zhang, H. Shu, Y. Yan, *Catal. Commun.* 9 (2008) 551.
- [18] D.E. Higgs, M.I. Nelen, M.R. Detty, *Org. Lett.* 3 (2001) 349; A. Podgorsek, M. Zupan, J. Iskra, *Angew. Chem. Int. Ed.* 48 (2009) 8424; F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri, G. Sartori, *J. Mol. Catal. A: Chem.* 286 (2008) 124.

- [19] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinacé, E.L. Pires, *Appl. Catal. A: General* 211 (2001) 1.
- [20] P. Biasi, F. Menegazzo, F. Pinna, K. Eränen, T.O. Salmi, P. Canu, *Chem. Eng. J.* 176–177 (2011) 172.
- [21] T. Inoue, Y. Kikutani, S. Hamakawa, K. Mawatari, F. Mizukami, T. Kitamori, *Chem. Eng. J.* 160 (2010) 909.
- [22] S. Ma, G. Li, X. Wang, *Chem. Eng. J.* 156 (2010) 532.
- [23] P. Blach, Z. Böstrom, S. Franceschi-Messant, A. Lattes, E. Perez, I. Rico-Latte, *Tetrahedron* 66 (2010) 7124.
- [24] K. Holmberg, *Colloid Interface Sci.* 8 (2003) 187; K. Holmberg, *Adv. Colloid Interface Sci.* 51 (1994) 137.
- [25] J. Sjöblom, R. Lindberg, S.E. Friberg, *Adv. Colloid Interface Sci.* 95 (1996) 125.
- [26] P. Pérez, E. Fernández, R. Beiras, *Water Air Soil Pollut.* 201 (2009) 319; I. Ferrer, E.T. Furlong, *Environ. Sci. Technol.* 35 (2001) 2583.
- [27] C. Venturello, M.J. Ricci, *Org. Chem.* 51 (1986) 1599.
- [28] G. Lapisardi, F. Chiker, F. Launay, J-P. Nogier, J-L. Bonardet, *Catal. Commun.* 5 (2004) 277.
- [29] P. Jin, Z. Zhao, Z. Dai, D. Wei, M. Tang, X. Wang, *Catal. Today* 175 (2011) 619.
- [30] S. Ren, Z. Xie, L. Cao, X. Xie, G. Qin, J. Wang, *Catal. Commun.* 10 (2009) 464.
- [31] H. Jiang, H. Gong, Z. Yang, X. Zhang, Z. Sun, *React Kinet Catal Lett* 75 (2002) 315.
- [32] R. Noyori, *Chem. Commun.* 14 (2005) 1807.
- [33] K. Juhn, R. Lakerveld, K. Juhn, H. Kramer, J. Grievink, P. Jansens, *Ind. Eng. Chem. Res.* 48 (2009) 5360.
- [34] K. Othmer, *Encyclopedia of Chemical Technology, Adipic Acid*, vol. 1, forth ed., Interscience Encyclopedia, Inc., New York, 1991, p. 553.