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Geoffroy Lesage* Isariebel Quesada Peñate[†]

Patrick Cognet[‡] Martine Poux[**]

Green Process for Adipic Acid Synthesis: Oxidation by Hydrogen Peroxide in Water Micromelusions using Benzalkonium Chloride C12-14 Surfactant*

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Abstract

Adipic acid was synthesized by the oxidation of cyclohexene using 30% hydrogen peroxide in a microemulsion in the presence of sodium tungstate as catalyst. The proposed green process is environmentally friendly since catalyst and surfactant are recycled and pure adipic acid is produced in high yield (70% to 79%). Microemulsions are used as a "green solvent" and give a better contact between the phases. Alkyldimethylbenzylammonium chloride (C12-C14) was used as a surfactant for the generation of the microemulsion since it enables the use of harmful organic solvents and phase-transfer catalysts to be avoided. Optimised operating conditions (temperature, reaction time, separation process) have been defined and applied to evaluate the industrial practicability. The main interest of the present work is the easy recovery of pure adipic acid and the reuse of the reaction media (surfactant and catalyst). This shows promise for developing a future green industrial process that will enable greenhouse gas emissions (N2O), among others, to be reduced.

1. Introduction

Adipic acid (ADA) is of considerable importance commercially since it is a key intermediate in the preparation of nylon 6.6 employed in the manufacture of carpet fibers, upholstery, tire reinforcements, auto parts, and many other products (Castellan et al., 1991; Cavani et al., 2009). Currently, the oxidation of cyclohexanone and/or cyclohexanol to synthesise ADA is carried out with nitric acid in most industrial processes (Castellan et al., 1991; Usui et al., 2003). However, while this process is cost-effective the oxidant generates environmentally unfriendly materials like nitrous oxide (N_2O) in large amounts (0.3 metric ton emitted per metric ton of ADA produced, which represents 5 to 10% of human N_2O emissions) (Castellan et al., 1991; Thiemens et al., 1991; Ravishankara et al., 2009). These emissions contribute to global warming and ozone depletion (Thiemens et al., 1991). Organic solvents, which are also harmful to the environment and difficult to dispose, are also used in current industrial ADA production processes as phase-transfer agents to increase reaction rates (Noyori et al., 2003). It is therefore highly desirable and urgent to develop a less environmentally damaging process for the manufacture of ADA (Thiemens et al., 1991; Ravishankara et al., 2009). Various methods including mesostructured catalyst uses (Lapisardi et al., 2004; Cheng et al., 2007), biosynthesis (Draths et al., 1994; Niu et al., 2002), supercritical methods (Beckman, 2003; Hou et al., 2002) and ozonolysis (Bailey et al., 1995) have been designed for the clean synthesis of ADA. However, they were too expensive or too complicated to apply to industrial processes (Ren et al., 2009).

H_2O_2 is the most attractive oxidant (after dioxygen) because it is green, quite cheap, easy to handle and its oxidation produces only water and oxygen as by-products (Deng et al., 1999; Jiang et al., 2002; Karimi et al., 2005). Nevertheless the need for catalysts to achieve a satisfactory conversion has been shown for these organic oxidation reactions (Higgs et al., 2001; Gregori et al., 2008; Podgorsek et al., 2009). Clean synthesis of adipic acid with cyclohexene oxidation by hydrogen peroxide in the presence of a catalyst (Scheme 1) has been demonstrated in the past few years (Sato et al., 1998; Zhu et al., 1998; Fujitani et al., 1998; Deng et al., 1999; Jiang et al., 2002; Noyori et al., 2003; Timofeeva et al., 2008; Ravishankara et al., 2009; Ren et al., 2009; Blach et al., 2010; Peng et al., 2011). It could be an alternative green method because the use of organic solvents and phase-transfer catalysts can then be avoided. The general equation of the reactions found in the literature can be written as follows:

$$C_6H_{10} + 4\ H_2O_2 \xrightarrow[\text{H}_2\text{SO}_4]{\substack{\text{Na}_2\text{WO}_4\ \text{or}\\ \text{other catalyst}}} C_6H_{10}O_4 + 4\ H_2O$$
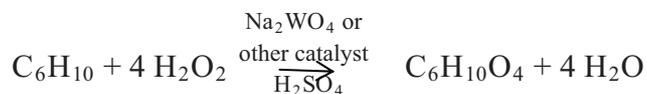
Scheme 1. Green adipic acid synthesis by cyclohexene oxidation with hydrogen peroxide in presence of a catalyst.

The main difficulty in achieving a good reaction without using polluting organic solvents is to provide a close contact between the hydrophobic and hydrophilic reactants, which is the key step for this reaction to proceed in an aqueous medium (Blach et al., 2010). Deng et al. (1999) have proposed a solution with high stirring, adding a co-catalyst (organic acid) and drastic operating conditions (20 h at 94 °C followed by 0 °C overnight). Sato et al. (1998) have worked on phase-transfer catalysis. The reaction was carried out for 8 hours (75-90 °C) with reloading of the phase-transfer agent at each cycle. Research on the clean synthesis of adipic acid has also been reported using transition metal-mesoporous materials as heterogeneous systems in water or organic solvents. In this case, the long reaction time and/or the low adipic acid production yield are not advantageous for an industrial process (Lapisardi et al., 2004). More recently, the use of surfactant-type peroxotungstates or peroxomolybdates has been studied but the reuse of these catalysts for a new reaction cycle is rarely described (Zhu et al. 2008; Blach et al., 2010; Peng et al., 2011).

Several studies have reported that microemulsions could provide a homogeneous aqueous media for close contact between the reagents involved in an organic reaction without the need for high speed stirring or very high temperatures and could lead to a better reactivity (Holmberg et al., 1994; Holmberg et al., 2003; Lapisardi et al., 2004). Indeed, synthesis in microemulsion media has many advantages (Nardello-Rataj et al., 2008; Blach et al., 2010):
- By the choice of components (surfactant and co-surfactant) from renewable materials, the use of water as solvent, and the fact that reagents and catalyst are used in very small quantities and could be recycled,
- By the process itself: the study of the phase diagram helps to determine the best proportions for the easy removal of the reaction products. The extraction and purification steps are simplified, which provide new recycling opportunities.

Blach and co-workers (2010) have reported the feasibility of the reaction described in this current study with an optimal formulation. They determined operating conditions on a small scale (50 mL) and have proved the potential recyclability of the organic phase (in which a part of the formed adipic acid is dissolved). They obtained good results with reaction mixture recycling over several cycles that resulted in high yields (above 90%), reinforcing the idea of a

possible recycling process. The major issue concerning the proposed process is the water evaporation step at 70 °C under reduced pressure (1 kPa). It is cost effective but could be dangerous on a larger scale (industrial process) because of the presence of explosive by-products or remaining reagent (peroxides).

The aim of the current study was to improve the continuity between bench-scale and the industrial environment by carrying out reactions with more consistent volumes (500 mL). However the design of a semi-industrial pilot reactor and optimisation of the operating conditions could only be achieved if the reaction kinetics were determined. Moreover, a new flow sheet is considered, whereby the adipic acid precipitate is separated by filtration on a porous media and the elimination of the water formed during the reaction by another filtration step. Another objective was to evaluate the choice of surfactant to be used in a semi-continuous, safe and clean ADA synthesis process with an easy and efficient recycling of surfactant and catalyst.

2. Materials and experimental methods

2.1. Materials

Benzalkonium chloride C12-14 (95%, Fluka), cyclohexene (99%, Sigma-Aldrich), sulfuric acid (95-97%, Sigma-Aldrich), sodium tungstate dihydrated (99%, Sigma-Aldrich), hydrogen peroxide (30 wt%, Sigma-Aldrich), sodium hydroxide (99%, Sigma-Aldrich), toluene (99%, Sigma-Aldrich), methanol (99%, Sigma-Aldrich) and potassium permanganate (98%, Lancaster) were used as received without purification.

2.2. Synthesis of adipic acid in microemulsion and recyclability experiments

Benzalkonium chloride (26.25 g), hydrogen peroxide (30 wt% solution, 134.75 g), sodium tungstate (2.05 g), and sulfuric acid (4.6 g) were introduced into a 0.5 L round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar. Temperature, pH and conductivity were monitored on line.

Firstly, the solution was stirred at 50 °C for 10 min to homogenise the system (a clear solution was obtained) and then 14 g of cyclohexene was added. This delayed addition of cyclohexene was done to minimise C_6H_{10} evaporation during the first minutes of heating. The solution was then heated at 75 °C for the first 20 min followed by a temperature rise from 75 °C to 85 °C at 0.25 °C/min (40 min to reach 85 °C) and the last reaction step was achieved at a temperature of 85 °C for the final 7 hours. After cooling at 25 °C under stirring for 2 h (with rapid stirring for the first 30 min), adipic acid precipitated (precipitation started at 28 °C) and 17.75 g of pure adipic acid (NMR results shown no surfactant in the

precipitate) was recovered by Büchner filtration. The crude product was washed with cold water (25 mL) to give a white powder. The remaining water in the solid was eliminated by drying at 50 °C in an oven over 24 h.

For recyclability studies, the filtrate was cooled at 5 °C and the precipitate (BenzCl C12-C14, sodium tungstate and the remaining adipic acid) was recovered by microfiltration or ultrafiltration. The solid was reintroduced into the reactor with hydrogen peroxide and cyclohexene in the same quantities (respectively 134.75 g and 14 g) and the reaction was restarted under the same operating conditions. It has to be noted that no vacuum pressure evaporation was done because of the possible presence of explosive by-products (peroxides).

2.3. *Analytical procedures*

2.3.1. *Cyclohexene titration*

Cyclohexene was quantified by gas chromatography (Varian CP-3800) with a flame-ionization detector and a Machereye Nagel Optima-1-Accent-0.25 mm column (30 m*0.25 mm). 500 mg of reaction medium, 50 mg of toluene (internal standard) and 500 mg of methanol were added in a vial. After stirring, 1 µL 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.

2.3.2. *Adipic acid titration*

Adipic acid was quantified by acid/base titration with NaOH (0.025 N or 0.4 N) using an automatic titrator Mettler Toledo DL50. The validity of these routine analyses has been demonstrated by GC-FID analysis (Varian CP-3800; Machery-Nagel Optima-1-Accent 0.25 mm column, 30 m x 0.25 mm) after derivatization with N,O-bis(trimethylsilyl)actetamide. The GC settings were programmed as follows: injector temperature 350 °C (1.2 mL/min, split ratio: 10); detector temperature: 350 °C; column temperature: 150 °C for 9 min. The purity of adipic acid and the concentration of by-products were determined by the same GC method. In most cases, the purity of the synthesized adipic acid was more than 99.0%. Jin et al. (2011) have reported that glutaric acid and succinic acid are the major by-products and cylohexanediol is the major intermediate of this reaction.

2.3.3. Hydrogen peroxide titration

A 2.10^{-2} M potassium permanganate solution was prepared by dissolving 3.4 g of solid potassium permanganate in 1L of deionised water. This solution was refluxed for 20 min and filtered. The exact concentration was determined by titration with potassium oxalate (0.1 g dissolved in 20 mL of water with 5 mL of sulfuric acid). Hydrogen peroxide consumption was monitored by taking 0.1 g of crude reaction mixture diluted in 20 mL of water with 5 mL of sulfuric acid and titrated until a persistent colouration was obtained.

2.3.4. NMR Analysis

The amount of surfactant in the liquid waste and in the solid product was checked by NMR analysis. 0.7 mL of MetOD and 50 mg of solid or 100 µL of liquid were added in a closed vial. The final mixture was homogenised and 500 µL transferred to an NMR vial. The temperature of the analysis was 303 K and spectra were recorded on a Varian Gemini 300 MHz. The analysis conditions were as follows: 1H NMR (300 MHz, D2O): d 1.71 (m, 4H), 2.48 (m, 4H), 4.78 (brs, 2H).

2.4. Filtration step

The solid product obtained after Büchner® filtration (Fritted glass funnels with pore size of 2-4 µm) of the reaction mixture at T=25 °C was pure adipic acid (purity > 99% confirmed by NMR analysis). The particle size study of solid adipic acid was obtained by dry method in a Malvern-Mastersizer 2000 analyser (Figure 1). The average particle size of ADA formed was around 12 µm but the granulometric distribution was relatively wide (between 0.3 and 100 µm). These results validate the use of the filtration device selected for the recovery of the adipic acid.

Other experiments of surfactant/water separation were achieved by Amicon® filtration cell (50 mL) with an MF membrane (0.2 µm, 1 bar) or UF membrane (hydrophilic coated polyvinylidenefluoride membrane, 10 pp ETNA, 2 bars) after a solid precipitation step at 5 °C. The filtration data are not shown in this paper.

3. Results and discussion

3.1. Surfactant selection and microemulsion formation

The chemical stability of the surfactant with respect to oxidation by hydrogen peroxide under acidic conditions (pH 1) and its possible complexation with the metal used as catalyst must be taken into account for the choice of the surfactant. In addition, the cost and the impact on the environment are important criteria.
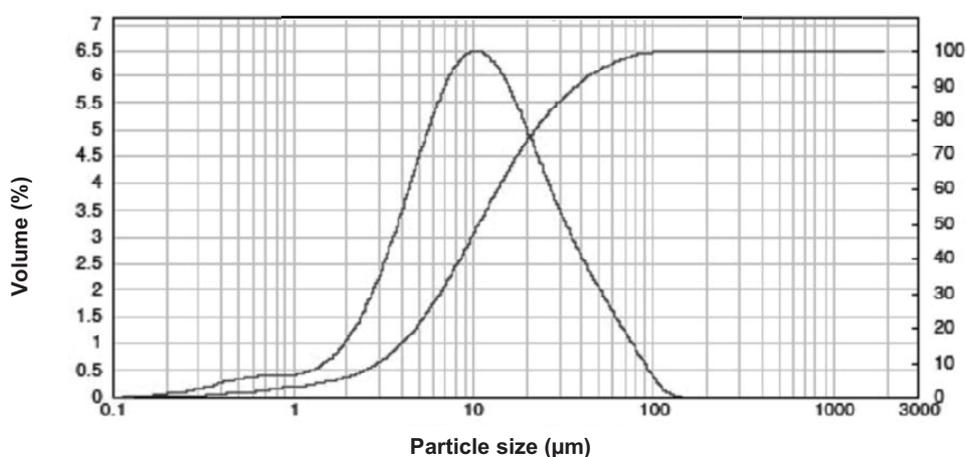
Figure 1. Particle size analysis: granulometric distribution of solid adipic acid synthesized by oxidation of cyclohexene with hydrogen peroxide and BenzCl C12-C14 as surfactant.

Benzalkonium chlorides (BenzCl), whose general structure is shown in Figure 2, are interesting because microemulsions can be easily generated without the presence of a polluting co-surfactant (Mayhan et al., 1993).
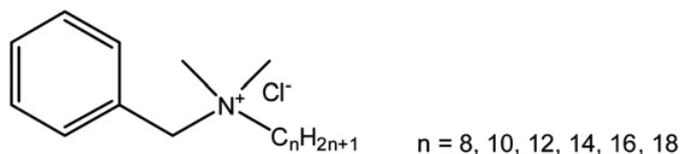
Figure 2. General formula of benzalkonium chloride (BenzCl).

The following results were obtained with BenzCl C12-14 which is actually a commercial mixture of surfactants with alkyl chains of C12 (n=1) and C14 (n=2) (in proportion 60:40). This surfactant has the advantage of being

inexpensive and commercially available in large quantities. The microemulsion formed is composed of the following reagents: cyclohexene (oily phase), H_2O_2 (aqueous phase) and the surfactant BenzCl C12-14. The ternary phase diagrams were plotted (wt %) for different temperatures and Figure 3 refers to the points of microemulsions determined for the mixture studied at 70 °C. For ternary diagram studies, hydrogen peroxide was replaced by water to avoid a reaction during the study (the same results were obtained for several points with hydrogen peroxide) and the temperature applied (70 °C) was close to the synthesis temperature (75 °C-85 °C). The proportions used in this study (H_2O_2: 77%, cyclohexene: 8% and benzCl C12-C14: 15%) were chosen in order to use a minimum of surfactant which could increase the medium viscosity but could be toxic at high concentration for aquatic organisms if released in the liquid waste (Perez et al., 2009; Ferrer et al., 2001).
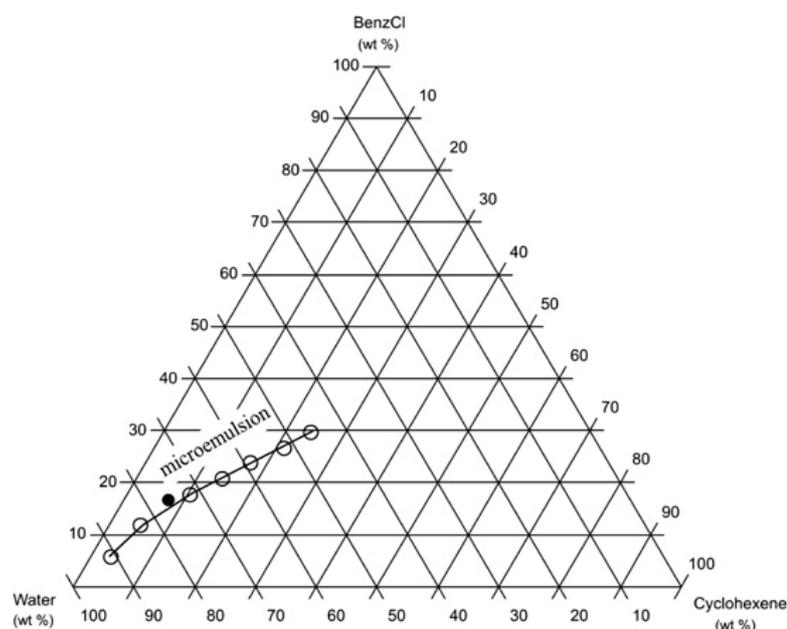
Figure 3. Ternary phase diagram (water/benzCl C12-C14/cyclohexene) at 70 °C and pH 1. The full dot (●) corresponds to the microemulsion mixture selected for the reaction. Laboratory of the Complex Fluids (Pau, France).

There is a large area of microemulsion, and this increases with the amount of hydrocarbon used. However, because of the stoichiometry of the reaction, only the region with a high H_2O_2 content (direct microemulsions) can be used in this study (4 mol H_2O_2 / 1 mol cyclohexene). The formulation has been made following the molecular economy principle (Blach et al., 2010).

3.2. Operating conditions for green adipic acid synthesis

3.2.1. Concentrations of sulfuric acid and catalyst

A constant pH of 1 was used to facilitate the adipic acid precipitation (pKa1 = 4.3) at the end of the reaction and to give appropriate conditions for the stability of H_2O_2 and enhancement of its oxidative ability (Blach et al., 2010; Peng et al., 2011). However, the sulfuric acid concentration should not be excessive to avoid degradation of the catalyst. Thus the amount of acid added at the beginning of reaction was optimized by Blach et al. (2010) in order to maintain the pH constant at a value close to 1 and to easily precipitate ADA.

Blach et al. also studied the effect of the concentration of catalyst and reported that a ratio of 3 mol% relative to cyclohexene gave the maximum yield of pure adipic acid under their conditions. Because it can be considered that these parameters are not the most sensitive (Peng et al., 2011), the pH and catalyst concentration effects were not studied in the current experiments and the results reported by Blach et al. (2010) were used to establish these parameters. On the other hand, the effects of temperature and reaction time were studied in order to increase the efficiency of the process in a larger volume.
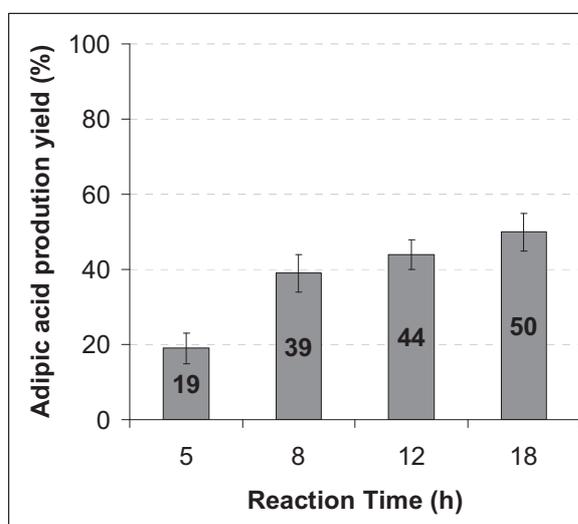

Figure 4. Production yield of adipic acid (reaction temperature: 75 °C) for various reaction times (5 h, 8 h, 12 h and 18 h).

3.2.2. Reaction time

The determination of the optimal reaction time was conducted with the new synthesis conditions with a reaction volume of 0.14 L. The results presented in Figure 4 show the ADA yield (calculated with adipic acid quantities recovered after cooling at 25 °C and Büchner filtration) at different reaction times, from 5 hours to 18 hours, at a constant temperature of 75 °C. This temperature was chosen with reference to the operating conditions described in the literature (Blach et al., 2010; Jin et al., 2011). Each reaction was carried out twice and a satisfactory repeatability of the measures was obtained (4%-5%).

As can be observed, an ADA yield of 39% was obtained in 8 hours and it did not increase significantly with longer reaction times: 44% in 12 h and 50% in 18 h. For an industrial process, a long reaction time is not desirable and so the reaction time of 8 h was chosen for the rest of the study.

3.2.3. Reaction temperature

Given that an ADA production yield of 39%, which was obtained at a reaction temperature of 75 °C, was still too low to be satisfactory, the reaction temperature needed to be optimised. Temperature plays a key role in the reaction, as it has a direct impact on the solubility of the surfactant and the reactivity is directly linked to the reaction temperature. Unsuccessful attempts were made by Blach and co-workers (2010) at room temperature and at 50 °C. In addition, the use of a tungsten catalyst requires a temperature greater than or equal to 70 °C. However, at temperatures higher than 90 °C, impurities appear during the synthesis and it would be difficult to recover high quality adipic acid without an additional purification step. As a result, the temperature has to be maintained between 70 °C and 90 °C throughout the reaction. Previous studies at temperatures of 85 °C and 90 °C were conducted and showed that it was possible to divide the reaction time by more than three with equivalent yields and purities (Blach et al., 2010). However, the experiments in these extreme conditions can be hazardous due to the presence of peroxides and cyclohexene volatility (boiling point: 82.8 °C). That is why special attention was paid to the addition of cyclohexene and the possible loss by volatilisation during the first heating stage. Consequently it was decided to proceed in two steps. Firstly, the medium is homogenised at 50 °C without cyclohexene and then, after 10 minutes of stirring at 50 °C, cyclohexene is added to start the reaction.

In order to study the reaction kinetics at different temperatures, cyclohexene oxidation in the selected microemulsion was carried out for 8 hours as described in the experimental section. The consumption of reactants (calculated from the cyclohexene and hydrogen peroxide concentrations measured in the

liquid phase during the reaction) and adipic acid production (calculated from the quantity of adipic acid recovered after cooling at 25 °C and Büchner filtration) were measured during the reaction by the analytical techniques described above (Figure 5). The reagent conversion kinetics and the appearance of product as a function of time at a constant temperature of 75 °C are presented in Figure 5(a) and the same conversion and production kinetics, with a temperature of 75 °C for the first 20 minutes, followed by a rise of temperature from 75 °C to 85 °C at a rate of 0.25 °C/min over 20 min and with a final temperature of 85 °C for the last 7 hours, are presented in Figure 5(b)

Figure 5. Kinetic curves for the oxidation of C_6H_{10} catalysed by Na_2WO_4 with 30% H_2O_2 for the synthesis of adipic acid. Production yield of ADA (■) and % conversion of C_6H_{10} (●) and H_2O_2 (Δ) over time with BenzCl C12-C14 as surfactant.

a) Reaction temperature of 75 °C for 8 hours.	b) Reaction temperature of 75 °C for the first 20 min followed by a temperature rising from 75 °C to 85°C at 0.25 °C/min (40 min to reach 85 °C) and finished at the temperature of 85 °C for the 7 last hours.

These results show that the production yield of ADA could be increased from 39% to 70% with the temperature gradient conditions and less H_2O_2 remained in the reactor after 8 h (25% of the initial amount of H_2O_2 is left in the reactor at a constant temperature of 75 °C while only 12% of the H_2O_2 initially

added remained in the medium at the end of the reaction with the new temperature reaction conditions). Also, cyclohexene conversion is faster with the gradient temperature conditions, because it takes less than 1 h to remove all the initial C_6H_{10} with the new conditions, where it takes almost 3 h to remove this amount during the synthesis at 75 °C. This could be due to the fact that at higher temperature, the reaction starts more rapidly and proceeds faster. Thus, the temperature gradient has been applied for the rest of the study.

It is important to note that after 8 hours, 12% of the initial hydrogen peroxide remains in the reaction mixture when the temperature gradient (75 °C-85 °C) is applied. This is coherent with a 5.8 H_2O_2 stoichiometric excess. At the beginning of the reaction 3.96 moles of hydrogen peroxide were added and at the end of the reaction 0.12 moles of adipic acid were obtained, which means that 0.48 moles of reactive H_2O_2 lead to adipic acid formation (12% of the H_2O_2 initially added) and that a certain amount of oxidant was lost (decomposed) during the reaction. If we assume that unproductive decomposition of H_2O_2 is negligible under such catalytic conditions, the large excess of hydrogen peroxide required is not only due to the microemulsion formation (because water could be used instead of expensive hydrogen peroxide) but the high oxidant concentration is also needed to increase the number of particle collisions and thus the level of oxidation. For an industrial application, it could be necessary to decrease the cost due to the excess H_2O_2, and thus an extensive study of oxygen oxidation could be important for the future.

Whereas a major part of the reactants are eliminated from the liquid phase during the 8 h of reaction (88% of H_2O_2 and almost 100% of C_6H_{10}), the quantity of adipic acid that was recovered after the two separation steps (cooling and filtration) was only 70% of the entire quantity that should be produced. It could be considered that a part of the initial cyclohexene is volatilised during the process and that a part of the initial hydrogen peroxide decomposes into water and oxygen. However, it has been proven that a non-negligible amount of the synthesised ADA remains solubilised in the liquid phase at the filtration temperature (25 °C). After recovering pure ADA by filtration at 25 °C, the filtrate was analysed by GC and a quantity remained that was about 12% of the theoretical ADA synthesised. Therefore, if one cycle of ADA synthesis is considered, the exact yield is about 82%, which is a very good yield for such an oxidation. This remaining ADA could be recovered by cooling the filtrate below 25 °C but the surfactant and catalyst would then precipitate together so it would be difficult to recover pure ADA. Since a recyclable process is desired, the major part of ADA remaining in the filtrate after the first cycle was precipitated at 5 °C together with the surfactant and the catalyst. The mixture was then reintroduced in the system for the second cycle. This accumulation of ADA should enhance the amount of ADA recoverable after the second reaction cycle.

3.3. Product/Surfactant/Catalyst separation and system recyclability

A green process must be designed to produce ADA under continuous or semi-continuous conditions, while allowing a recycling of the active components (surfactant and catalyst) and an easy discharge of clean waste. Scheme 2 illustrates the global recycling process:

1St Reaction
(8h, 75°C-85°C) ⟹ **ADA precipitation**
(25°C)

Recovery
of pure ADA ⟵ **Büchner Filtration**

ADA precipitation
(25°C)   **Cooling at 5°C and MF**
or UF filtration ⟶

Reaction
(8h, 75°C-85°C) ⟵ $H_2O_2 + C_6H_{10}$
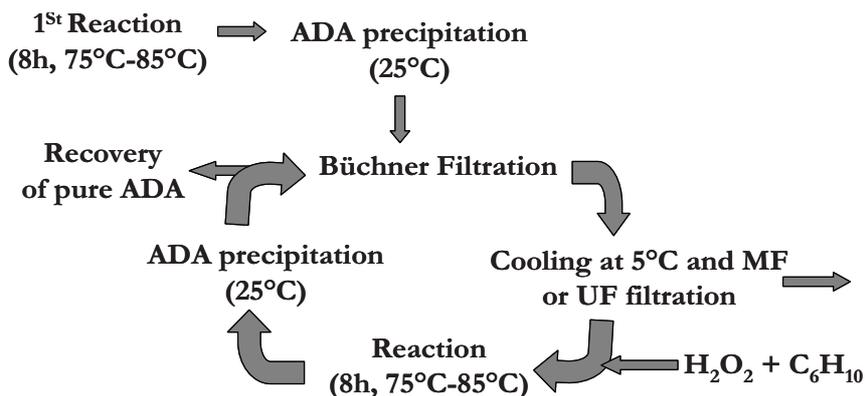
Scheme 2. Diagram for adipic acid green synthesis in microemulsions by oxidation of cyclohexene with hydrogen peroxide in the presence of BenzCl C12-C14 as surfactant. Recyclability of the system.

At the end of the first reaction carried out at 75 °C-85 °C for 8 hours, the ADA synthesised has to be recovered and the water formed by the H_2O_2 reduction must be eliminated. This separation could be achieved by precipitation/filtration/evaporation (Blach et al., 2010). Evaporation of the aqueous phase under reduced pressure has to be avoided because of the explosive character of hydrogen peroxide and possible by-products under this low pressure condition (1 kPa). Moreover, the potential of the concept of membrane-assisted crystallization using membrane technology (reverse osmosis) has been recently compared to evaporative crystallisation for solvent removal from an aqueous adipic acid solution. The use of membranes gives a better control over product quality and a drastic reduction in energy use (six times less) (Khun et al., 2009). According to the solubility and granulometric measurements, ADA has a solubility at 25 °C of 22.9 g/kg in the reaction medium (surfactant, water and sulphuric acid) and ADA mean particle size is 12 μm in the precipitate obtained after cooling at 25 °C. Thus, a major part of the pure ADA precipitated at 25 °C (about 85% of the total ADA synthesised during the reaction) and a simple Büchner filtration at 25 °C could be sufficient to achieve a satisfying separation between solid ADA and the aqueous phase. The ADA purity was checked with NMR analysis and elementary analysis and it was found that no surfactant

precipitated with ADA at 25 °C. Nevertheless, after recovering pure ADA at 25 °C, it is not possible to restart the reaction without the elimination of the water produced because the medium is consequently diluted and the microemulsion point would be shifted. Other problems would come from the volume of the solution which would be increased 2-fold at each cycle and from the decreasing quantity of ADA that would precipitate. Thus, a second separation step had to be introduced to recover the active compounds (remaining dissolved ADA, surfactant and catalyst) and to eliminate the water produced. The second precipitation was carried out at 5 °C, where a major part of the remaining ADA, surfactant and catalyst precipitated. Then the second solid/liquid separation was done in a MF or UF filtration cell. Experiments have shown that this second separation operation is efficient and 17% of the remaining ADA dissolved in the liquid phase could be recovered by this precipitation/filtration step. Although the aqueous waste still contained about 10% of the total ADA synthesised during the 8 h reaction (about 2.17 g ADA in 140 mL of liquid), this step enabled most of the surfactant and catalyst to be recovered and is a key operation for a recycling process.

To begin a new synthesis, the solid was reintroduced into the reactor with H_2O_2 and C_6H_{10} in the same amounts (respectively 134.75 g and 14 g) and the reaction was restarted with the same operating conditions (8 h, 75 °C-85 °C). Several reaction cycles have been applied and the effect of these successive cycles
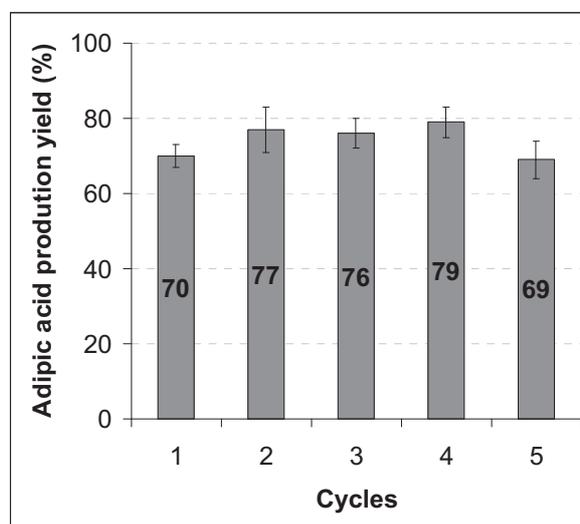

Figure 6. Process recycling studies at the 0.14 L scale. Reaction conditions: surfactant BenzCl C12-14, reaction temperature 75 °C for the first 20 min followed by a rise from 75 °C to 85 °C at 0.25 °C/min (40 min to reach 85 °C) and finished at the temperature of 85 °C for the 7 last hours.

on the ADA production yield has been evaluated (Figure 6). Once again, the experiments were done twice (with a good repeatability between 4% and 6%) and the ADA production yield is calculated from the quantity of pure ADA which was recovered after the first precipitation/separation step at 25 °C.

It is important to remember that if the total amount of ADA synthesised (solid form and dissolved part) was taken into account, the total ADA production yield would have been increased from 70% to 82% for the first cycle. For the second cycle, the synthesis efficiency increases from 70% to 77%, this indicates that enough surfactant and catalyst were recycled. Moreover this increased yield could be due to the accumulated ADA in the reaction medium which should facilitate its precipitation and recovery and/or to the possible unreacted intermediates, which are recycled with the surfactant and the catalyst and which could be re-oxidized during the second cycle (Peng et al., 2011). As we can see in Figure 6, the ADA production yield remained stable at about 70% to 79% for the first four cycles, which are very interesting values and of the same order of magnitude as the yields described in the literature (Blach et al., 2010). As observed in other studies (Jiang et al., 2002; Blach et al., 2010) the ADA production yield decreased slightly after the fourth cycle to 69% for the fifth cycle. This could be due to the possible loss of catalyst and surfactant in the liquid waste.

4. Conclusion

An original recyclable process has been described here for the synthesis of pure adipic acid by hydrogen peroxide oxidation of cyclohexene in a microemulsion using BenzCl C12-C14 as surfactant. A good adipic acid conversion of 82% was obtained without using high speed stirring, long reaction times or very high temperatures and between 69% and 79% of pure solid ADA could be recovered for each of 5 successive cycles. Nevertheless, because of the ADA solubility in water, the yield after the first cycle is only 70%. This value is slightly increased during the following cycle and could reach almost 80% after 4 cycles. This work could be helpful in developing a pioneering industrial process based on microemulsions, because it could overcome the problems of product recovery and system (surfactant/catalyst) reuse.

It is important to note that the major green chemistry principles for chemical synthesis (Anastas and Warner, 1998; Warner et al., 2004) have been applied to this new process design: molecular economy for the reaction formulation, a less harmful synthesis, reduced use of organic solvents, increased production yield and recycling of polluting compounds (surfactant and catalyst).

5. Acknowledgements

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