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Recyclable process for sustainable adipic acid production in microemulsions

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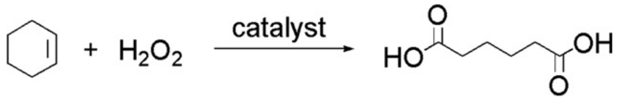
ABSTRACT

Adipic acid is an important industrial intermediate for the manufacture of nylon-6,6. We propose a recyclable and environmentally friendly process for the oxidation of cyclohexene by hydrogen peroxide in microemulsions. These organized nano-structured media have been formulated in using the molecular economy principle. The main interests of the present work are the easy recovery of pure adipic acid and the reuse of the reaction media, what are promising for developing a future green industrial process.

1. Introduction

Adipic acid is a very important industrial intermediate, since it is used as a starting reagent in the preparation of nylon-6,6, a polymeric material used in carpet fibres, tyre reinforcement, automobile parts, clothing and many other everyday life applications.[1] Adipic acid is currently industrially produced by the oxidation of a cyclohexanol/cyclohexanone mixture or cyclohexane with nitric acid.[2] Nitrous oxide, or N_2O, emission generated during the synthesis (0.3 tonne emitted per tonne of adipic acid produced) contributes to global warming and ozone depletion.[3] Therefore, the development of an industrial process that is less damaging for the environment is of crucial importance.[4]

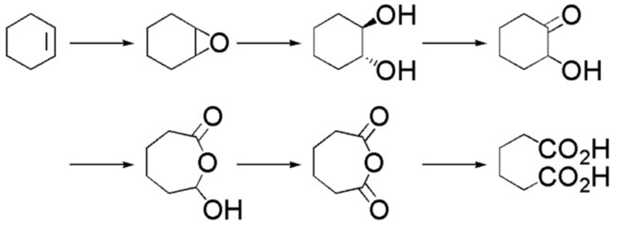
Adipic acid can be also obtained by oxidation of cyclohexene by hydrogen peroxide in presence of a catalyst (Scheme 1).



Scheme 1. Oxidation of cyclohexene with hydrogen peroxide.

Hydrogen peroxide (H_2O_2) is widely accepted as a green oxidant because it is relatively non-toxic and its decomposition leads to benign by-products like water and oxygen.[5,6] H_2O_2 has several advantages as an oxidant for industrial processes: easy handling and storage, high active oxygen content and low cost.[7] However, H_2O_2 alone is rarely sufficient to achieve the conversion and catalysts are essential.[8]

Oxidation of cyclohexene by H_2O_2 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).[9] The key step for this reaction in an aqueous medium is to bring all the reagents into close contact.



Scheme 2. Pathway for the formation of adipic acid.

Deng and co-workers[5] described the synthesis of adipic acid in a water emulsion by hydrogen peroxide oxidation of cyclohexene without surfactant and under strong stirring. In this system, addition of an organic acid as ligand (co-catalyst) and severe reaction conditions (20 h at 94 °C following to 0 °C overnight) were required to obtain a good yield of pure adipic acid. Noyori and co-workers[10] described the use of a phase transfer agent (methyltrioctylammonium hydrogenosulphate) in water to produce adipic acid with a good yield, but reuse of the system required an additional

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amount of phase transfer agent to be effective. More recently, the potential of transition metal-mesoporous materials as heterogeneous systems have been described[11] in water or organic solvent but the long reaction time and/or the low adipic acid production yield are not advantageous for an industrial process. Also, the use of surfactant-type peroxotungstates or peroxomolybdates has been studied but the reuse of these catalysts for a new reactional cycle (in the perspective of an industrial process) is never described.[12]The main difficulty in water or hydrogen peroxide is the weak contact between the hydrophobic and hydrophilic reagents. The use of microemulsions as aqueous media for organic reactions is a way to improve the compatibility between the different reagents[13] and to overcome the use of polluting organic solvent. In this paper, we present, for the first time, the use of hydrogen peroxide microemulsions as reaction media for the oxidation of cyclohexene to adipic acid with hydrogen peroxide. The establishment of the microemulsions zone, the reactivity in these media and the reuse of the system (to provide a first approach for an industrial process) will be presented and discussed.

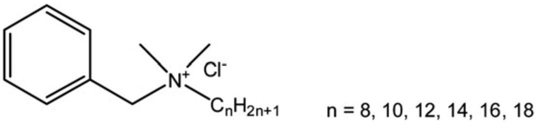
Microemulsions are transparent and thermodynamically stable dispersions of oil and water or non aqueous structured polar solvent (formamide, glycerol and their mixture with water)[14] spontaneously formed by the addition of an amphiphile: a surfactant and a co-surfactant (an amphiphile with a short chain like an alcohol, an acid or an amine).[15] There are two types of microemulsions according to the nature of the continuous phase (Fig. 1).

Their thermodynamic stability and their nanostructure are two important characteristics that distinguish them from emulsions. Direct microemulsions are usually expressed as oil-in-water microemulsions in which nanoscopic oil droplets (10–50 nm in diameter) are dispersed in water with the help of a surfactant and a co-surfactant. These microemulsions are very suitable as reaction media for a sustainable development because of their numerous properties;[16] they allow organic synthesis in water, specific localization of the reactants, interfacial orientation of the molecules and increase of local concentrations and reaction rate. Many chemical reactions have been studied in microemulsion media: oligomerization of norbornene,[17] photoamidation of olefin,[18] catalytic hydrolysis of phosphate esters,[19] olefin oxidation,[20] halogen nucleophilic substitution,[21] mustard gas oxidation,[22] Diels–Alder reaction[23] etc. Holmberg[13] has demonstrated that microemulsions can be considered as an alternative to biphasic systems with added phase transfer reagent. Generally, microemulsions are described as versatile reaction media for many organic reactions but there is still no industrial process based on microemulsions, essentially because of the difficulty to recover the products and to reuse the system.

2. Results and discussion

2.1. Establishment of the microemulsions

Microemulsions are generally ternary systems comprising water, oil, a surfactant and a co-surfactant like a medium chain alcohol.[19] With a view to environment protection and a future industrial process, we applied the principle of molecular economy, and the microemulsion was mainly composed of the reagents: cyclohexene as the oily phase and hydrogen peroxide as the aqueous phase. Furthermore, we selected a special surfactant able to form microemulsions without co-surfactants, which avoided the short chain alcohols classically used but incompatible with an oxidation reaction. Benzalkonium chlorides (BenzCl) were selected and have already been described for obtaining microemulsions without co-surfactants.[24] These surfactants, also known as alkylbenzyldimethylammonium chlorides, are quaternary ammonium salts widely used as disinfectants, biocides and detergents.[25] The general structure of such surfactants is presented in (Scheme 3).



Scheme 3. General structure of benzalkonium chloride.

Benzalkonium chlorides could be toxic for aquatic organisms,[26] so their introduction in a process implies their control and strict reuse. Also, in the aim of easily recovering pure adipic acid by precipitation at room temperature and reusing the system, we fixed the water phase at pH 1 by adding sulfuric acid.

In this study, we used a low-cost commercial mixture of BenzCl containing 60 wt% of dodecyl (n=1) and 40 wt% of tetradecylbenzyldimethylammonium chloride (n=2). In a first step, we established a ternary phase diagram to determine the microemulsion zones. Because of the stoichiometry of the reaction (4 mol of H_2O_2 per mol of cyclohexene), only the water-rich region of the phase diagram was explored (direct microemulsions). For practical reasons, hydrogen peroxide was replaced by water at pH 1 and the

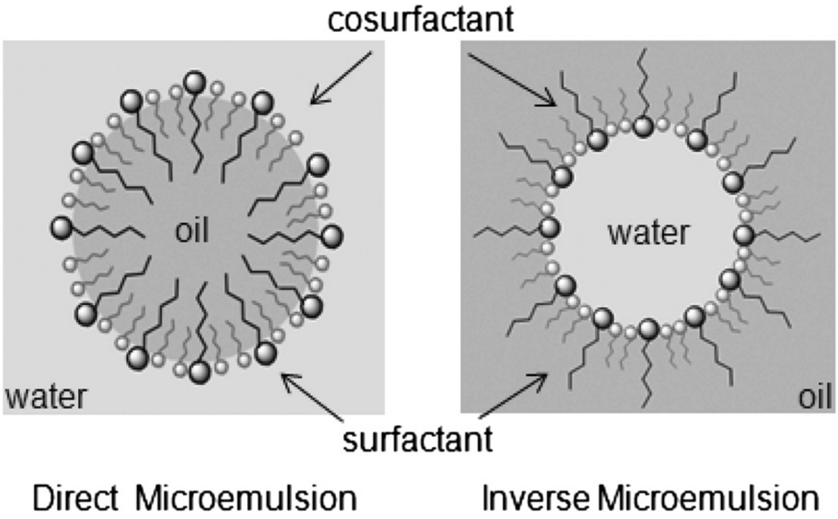


Figure 1. The two types of microemulsion.

titrations were performed at 25 °C (see details in Experimental section). We checked on several points, that we obtain the same microemulsions, by replacing water by hydrogen peroxide.

The phase diagram obtained is shown in Figure 2.

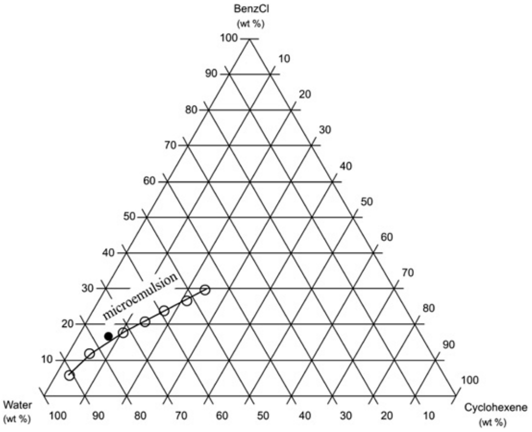


Figure 2. Ternary phase diagram (water/BenzCl/cyclohexene) at 25 °C and pH 1. The full dot (•) corresponds at the selected microemulsion mixture for the reaction.

Even without any co-surfactant, we obtained a large microemulsion area with BenzCl. In some of these microemulsions, it was possible to solubilize more than 20 wt % of cyclohexene but, in this case, a large amount of surfactant (30 wt %) was required, which drastically increased the viscosity (liquid crystal phases), limiting their use as reaction media. Although the phase diagram was established at 25 °C, we checked that the microemulsions obtained were optically clear, stable over time and in a large range of temperature (5–100 °C).

Once the ternary phase diagram had been established, we selected a point of microemulsion to study the reactivity. This point (full dot on the phase diagram) was a trade-off among the following criteria: a high concentration of cyclohexene with a relatively low concentration of surfactant (to limit the viscosity of the microemulsion) and the respect of the stoichiometry of the reaction. The composition of this point was the following: cyclohexene 8 wt % (0.975 mol L^{-1}); BenzCl 15 wt %; water 77 wt %.

2.2. Oxidation of cyclohexene in the selected microemulsion

In the context of the development of a clean oxidation process, we selected the non-polluting catalyst sodium tungstate, Na_2WO_4, which contained no heavy metal. We also took advantage of its anionic charge to associate it with the cationic surfactant at the interface of the droplets. Although this catalyst is not very active, it is widely used for many oxidation reactions in aqueous systems.[27–30] By reaction with hydrogen peroxide, sodium tungstate is transformed into sodium peroxotungstate, the active catalyst able to oxidize cyclohexene at high temperature ($T \geq 70$ °C). Also, sodium tungstate is activated in acidic conditions like those in our microemulsion.[30]

Oxidation of cyclohexene was performed in the selected microemulsion according to the following procedure: surfactant, hydrogen peroxide (30 wt %), catalyst, cyclohexene and sulfuric acid were mixed (homogeneous solution) at 70 °C for 18 h. After reaction and cooling at room temperature, adipic acid precipitated and was recovered by filtration. Pure adipic acid (analyzed by GC chromatography and NMR) was obtained after washing the crude solid with cold water. Several reaction parameters were optimized: quantities of catalyst, sulfuric acid, temperature and reaction time. Table 1 presents the effect on the reaction yield of varying the quantity of catalyst.

Table 1
Influence of catalyst ratio

Catalyst ratio	Yield (%)[a]
1.5 mol %	31
3 mol % (Initial)[b]	56
6 mol %	54

[a] Based on adipic acid recovered.
[b] 3 mol % relative to cyclohexene.

As can be observed, in the selected microemulsion, the maximum yield of pure adipic acid (56%) was reached with a catalyst ratio of 3 mol % relative to cyclohexene. An increase of this ratio did not improve the yield of adipic acid, so we fixed the catalyst ratio at 3% for the subsequent experiments. Also, we varied the percentage of sulfuric acid relative to the hydrogen peroxide, from 3 to 6 mol %, with no significant increase in the adipic acid production yield.

In the chosen conditions, we followed the decrease of the reagents during the reaction by gas chromatography analysis for the cyclohexene and by potassium permanganate titration for the hydrogen peroxide. The results are presented in Figure 3.

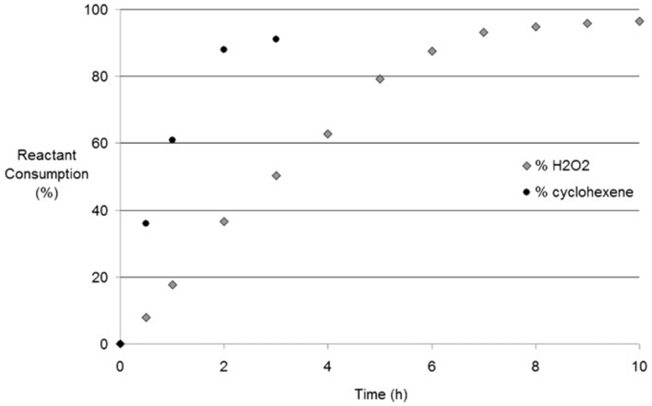


Figure 3. Consumption of the reactants during the reaction.

Conversion of the cyclohexene was completed in 2 h (limit of detection by GC at 90% of conversion) and more than 7 h were necessary to consume all the hydrogen peroxide. In accordance with the mechanism which implies four stages of oxidation, the cyclohexene (consummated during the first step of the process) is transformed in 2 h, whereas 7 h are needed in order to consummate the totality of the hydrogen peroxide.

Although the conversion of cyclohexene was total, the yield of recovered adipic acid was only 56%. In fact, an additional amount of adipic acid (equivalent to a yield of 20%) stayed soluble at room temperature but could be recovered by cooling the solution to a low temperature (5 °C). As we were looking for a reusable industrial process, we neglected this low temperature step, favouring a cumulative recovery of the adipic acid at room temperature by reusing the system.

We investigated the influence of temperature and reaction time on the adipic acid production yield. Several temperatures (room temperature to 100 °C) and reaction times (1.5–18 h) were tested and the results are listed in Table 2.

Table 2
Dependence of temperature and reaction time

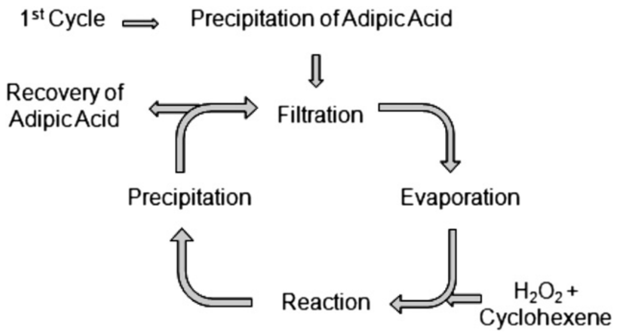
Temperature (°C)	Reaction time (h)	Yield (%)[a]
20	18	0[b]
70	5	19
70	18	56
90	5	48
100	1.5	41

[a] Based on adipic acid recovered.
[b] No precipitation occurs.

The parameter studied was the yield of pure adipic acid recovered. Firstly, it can be noted that no reaction occurred at room temperature (20 °C), confirming a minimum of 70 °C to activate the reaction. Secondly, good yields were obtained when the temperature was increased, which also considerably reduced the reaction time. However, at 100 °C and for a long reaction time (more than 3 h), by-products were formed in the precipitate, which led to a supplementary step of purification not desirable for an industrial process. These tests demonstrate the importance of the temperature on both the proposed reaction and adipic acid precipitation, so it will have to specially taken into account in the framework of an industrial process.

2.3. Study of the recyclability of the system

Our first results obtained in microemulsion demonstrate that it is possible to obtain a good yield in the production of pure adipic acid without using extreme conditions of stirring, high temperatures or fastidious purification steps. In the objective of developing an industrial process, we focused our attention on the recycling of the system at the end of the reaction. After recovery of the adipic acid by filtration, the remaining water solution (produced by reduction of hydrogen peroxide) contained unprecipitated adipic acid (due to its partial solubility, even at pH 1), surfactant, catalyst, sulfuric acid and unreacted intermediates. The fact that water remained caused two important problems. Firstly, if the water was not removed and if we started a second reaction run, dilution by addition of another volume of hydrogen peroxide shifted the microemulsion point, reducing the efficiency of the system. Secondly, the dilution decreased the precipitation of adipic acid. We bypassed these difficulties by introducing the steps illustrated in (Scheme 4).



Scheme 4. Recyclability of the system.

After precipitation and recovery of the adipic acid (formed during the first cycle), we checked the absence of peroxide in solution (hypochlorite test), then the majority of the water was evaporated at low pressure until precipitation (solubilized adipic acid and surfactant) occurred. Then, the same amounts of hydrogen peroxide and cyclohexene were introduced again and another reaction was started in the same conditions as the first cycle (18 h at 70 °C). After this second cycle, adipic acid was again recovered by filtration after cooling to room temperature and, after water removal by evaporation, another reaction cycle was started. In that way, six consecutive cycles were performed. The yields obtained (based on adipic acid recovered) after each cycle are presented in Figure 4.

As we can see, the yield increased continuously with the consecutive cycles. Adipic acid did not totally precipitate at room temperature but accumulated in the reaction medium cycle after cycle, facilitating its precipitation and recovery. Furthermore, possible unreacted intermediates could be reoxidized during the different cycles, increasing the adipic acid production yield. The yield rapidly reached extremely interesting values (up to 90% after five cycles), which are comparable to the best yield presented in the literature.[5]

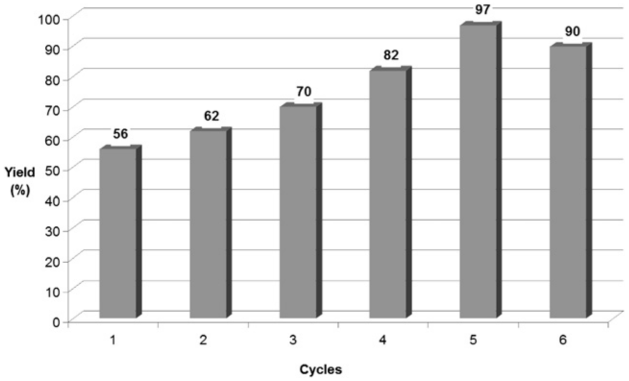


Figure 4. Recycling studies of the process.

These results demonstrate, for the first time, that it is possible to use a cyclohexene/hydrogen peroxide microemulsion to produce pure adipic acid with very good yield without using extreme conditions of temperature or long precipitation times. Within the framework of an industrial application, this process could be advantageously modified (reduced energy cost) by replacing the water evaporation step by an ultrafiltration step to concentrate the surfactant in the water phase, as described in other processes.[31]

3. Conclusion

In summary, we have described, for the first time, an original recyclable process for the synthesis of pure adipic acid by hydrogen peroxide oxidation of cyclohexene in a microemulsion, with a very good yield. In the context of an industrial approach, we used microemulsions without co-surfactant and where practically all the ingredients are also the reagents (molecular economy principle). Microemulsion provides homogeneous media for close contact between the reagents in the hydrogen peroxide phase, leading to a better reactivity without the need for strong stirring or very high temperatures. Thanks to the low pH used, the process leads to pure adipic acid that can be recovered by simple filtration at room temperature. The investigation of the system recyclability demonstrated, (i) that it was possible to reuse the system for a new cycle (after adipic acid filtration and residual water evaporation) and (ii) that an excellent yield could be obtained by cumulating the cycles. These two points are essential in the perspective of an industrial development of the process.

4. Experimental section

4.1. Materials

Benzalkonium chloride (95%, Fluka) and cyclohexene (99%, Sigma–Aldrich) were used without purification. Sulfuric acid (95–97%, Sigma–Aldrich), sodium tungstate dihydrated (99%, Sigma–Aldrich), hydrogen peroxide (30 wt %, Sigma–Aldrich), *N*,*O*-bis(trimethylsilyl)acetamide (derivatization grade, Sigma–Aldrich), decanoic acid (99.5%, Fluka) and potassium permanganate (98%, Lancaster) were used as received.

4.2. Phase diagram determination

Each point was obtained by titration with cyclohexene of various solutions of benzalkonium chloride/water (pH 1) at room temperature (18 °C). Addition of cyclohexene was stopped when a turbid solution was obtained.

4.3. Synthesis of adipic acid in microemulsion and recyclability experiments

Benzalkonium chloride (5.25 g), hydrogen peroxide (30 wt % solution, 26.95 g), sodium tungstate (410 mg), sulfuric acid (920 mg) and cyclohexene (2.80 g) were introduced in a round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar. The solution was heated at 70 °C for 18 h. After cooling at room temperature (with rapid stirring for the first 30 min), adipic acid precipitated (precipitation started at 28 °C) and was recovered by filtration. The crude product was washed with cold water (5 mL) to give a white powder. For recyclability studies, the filtrate was evaporated at 70 °C under reduced pressure (1 kPa), until solid recovery. Hydrogen peroxide and cyclohexene were introduced in the same quantities and the reaction was restarted for 18 h at 70 °C.

4.4. GC analysis

The purity of the adipic acid was checked, after derivatization with *N*,*O*-bis(trimethylsilyl)acetamide (decanoic acid was used as an internal standard), by gas chromatography (Varian CP-3800) with a flame-ionization detector and a Macherey–Nagel Optima-1-Accent-0.25 mm column (30 m×0.25 mm). The GC settings were programmed as follows: injector temperature 350 °C (1 mL/min, split ratio: 10); detector temperature 350 °C; column temperature 150 °C for 10 min.

4.5. Derivatization procedure

20 mg of crude product, 20 mg of decanoic acid, 250 mg of *N*,*O*-bis(trimethylsilyl)acetamide and 1 g of $CHCl_3$ were mixed for 1 h at 60 °C to room temperature, 1 μL of solution was analysed.

4.6. Hydrogen peroxide titration

A 2.10^{-2} M solution of potassium permanganate was obtained by dissolution of 3.4 g of solid potassium permanganate in a beaker containing 1 L of deionized 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). Consumption of hydrogen peroxide was monitored by taking 0.1 g of crude diluted in 20 mL of water with 5 mL of sulfuric acid and titrated until a persistent colouration was obtained.

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