

**CERIUM MEDIATED ELECTROSYNTHESIS OF p-ANISALDEHYDE**

by

Robin Roussel

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Department of CHEMICAL ENGINEERING  
The University of British Columbia  
Vancouver, Canada

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## ABSTRACT

The objective of this project was to study the synthesis of p-anisaldehyde (PMA,  $C_8H_8O_2$ ) via an indirect (mediated) in-cell electro-oxidation of p-methoxytoluene (PMT,  $C_8H_{10}O$ ). The electro-oxidation was carried out in a batch recycle system without co-solvents and with an acid aqueous cerium (mediator) methanesulfonate solution.

The batch recycle system is mainly made up of an electrochemical reactor (a laboratory FM01-LC cell from ICI) connected to a thermochemical reactor (CSTR) in a closed loop. The main advantage to studying the electro-oxidation of PMA via an in-cell versus an ex-cell method is the potential for reduction in the capital cost of the electrochemical process.

Two important reactions are involved in the indirect in-cell electrosynthesis of PMA: the chemical oxidation of PMT and the electrochemical regeneration of cerics ions (Ce(IV)). Before investigating the mediated in-cell electro-oxidation of PMT in the batch recycle system, the chemical and electrochemical steps were separately investigated in order to have a better understanding of the kinetics of these two reactions.

A factorial design was performed to study the chemical oxidation of PMT in a conventional thermochemical batch reactor (batch reaction). Acidity, temperature, molar ratio Ce(IV)/ PMT, and residence time were studied in the range of 0.5-1.5 M, 20-60°C, 2-6, and 1-10 minutes, respectively. Over the range of the variables studied, acidity and the interaction acidity-temperature had the greatest influence on the yield of PMA. The highest yield of PMA (78%) was obtained at high temperature (60°C) and low acidity (0.5 M).

An undivided cell with a Pt/ Ti mesh anode and a three dimensional porous graphite cathode was deemed effective (without fouling problems) to accomplish the electro-oxidation of PMT. A second factorial design was conducted to investigate the performance of the electrochemical reactor for the oxidation of cerous methanesulfonate

solutions (generation of Ce(IV) ions) in the batch recycle system. Acidity, temperature, and current applied were studied in the range of 0.2-0.8 M, 20-60°C, and 10-20 A (superficial current densities, 1563-3125 A/ m<sup>2</sup>), respectively. The current efficiency (78%) for Ce(IV) was not much influenced by these variables.

Finally a third factorial design was performed to study the indirect in-cell electro-oxidation of PMT in the batch recycle system in which both reactions (chemical and electrochemical) occur simultaneously. Acidity, temperature, volume ratio Org./ Aq., and conversion of PMT were studied in the range of 0.2-0.8 M, 20-60°C, 0.03-0.06, and 10-30 %, respectively. Over the range of the variables studied, three important effects influence the yield of PMA, namely temperature, acidity and conversion of PMT. The interaction acidity-temperature was also significant. From an empirical model, it was concluded that the highest yield of PMA (28%) was obtained at low temperature (30°C), low acidity (0.2 M) and low conversion of PMT (10%).

A rough economic estimation of the cost of electrosynthesis of PMA via indirect ex-cell and in-cell methods was also done in this work. Comparisons of the two methods showed that the cost of energy and raw material was three times higher for in-cell than the ex-cell process. This economic study was done without optimisation of the electrochemical processes.

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## NOMENCLATURE

AC	amortised capital cost (\$/ kg)
B	width of the electrode (m)
C <sub>AC</sub>	cost of electricity (\$/ kWh)
C <sub>B</sub>	concentration of the reduced species or oxidised species in the bulk electrolyte for an anodic or cathodic reaction, respectively (mol/ m <sup>3</sup> )
CC	total capital cost (\$)
CE	current efficiency x 100 (%)
d <sub>E</sub>	equivalent diameter (m)
D	diffusion coefficient (m <sup>2</sup> / s)
DP	depreciation period (years)
E	cost of energy (\$/ kg)
F	Faraday constant (96487 Coulombs/ mole of e <sup>-</sup> )
i	total current density applied to the cell (A/ m <sup>2</sup> )
i <sub>D</sub>	current density driving the primary reaction (A/ m <sup>2</sup> )
i <sub>E</sub>	current density driving the secondary reaction (A/ m <sup>2</sup> )
i <sub>L</sub>	mass transfer limited current density (A/ m <sup>2</sup> )
i <sub>LD</sub>	mass transfer limited current density of the primary reaction (A/ m <sup>2</sup> )
I	total current applied to the cell (A)
K <sub>F</sub>	mass transfer coefficient due to convection (m/ s)
K <sub>G</sub>	mass transfer coefficient due to gas evolution (m/ s)
K <sub>m</sub>	mass transfer coefficient (m/ s)
MM	molar mass (g/ mol)

$n$	stoichiometry number of moles of electron per mole of Ce(IV) ions produced
$P$	production rate of the product* (mol/ s)
$PC$	total unit product cost (\$/ kg)
$R$	production rate of the Ce(IV) ions (moles of Ce(IV)/ s)
$RM$	cost of raw material (\$/ kg)
$S$	gap between the electrodes, or gap between an electrode and a diaphragm or an ionic exchange membrane (m)
$SE$	specific energy (kWh/ kg of product)
$U$	linear velocity of fluid in the cell (m/ s)
$V_{CELL}$	cell voltage (V)
$V_{OC}$	open circuit potential (V)
$V_{ohm}$	ohmic voltage drop through the cell (V)

Dimensionless numbers :

$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number

Greek symbols :

$\eta_C$	cathodic overpotential (V)
$\eta_A$	anodic overpotential (V)
$\mu$	viscosity of the solution (kg/ (m s))

---

\* In this work, PMA or p-anisalcohol

- $\rho$  density of the solution ( $\text{kg/ m}^3$ )
- $\theta$  production rate per year ( $\text{kg/ year}$ )

Abbreviations :

- AQ anthraquinone
- Ce(III) cerous ions
- Ce(IV) ceric ions
- Ce(tot) cerium total
- CP center point
- CSTR continuous stirred tank reactor
- DCE dichloroethane
- FM01-LC laboratory electrochemical reactor from ICI
- MSA methanesulfonic acid
- NQ naphthoquinone
- PFR plug flow reactor
- PMA para-anisaldehyde
- PMT para-methoxytoluene
- Pt platinum
- Ti titanium

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## Chapter 1

### INTRODUCTION

P-anisaldehyde is the common name of p-methoxybenzaldehyde (PMA). Over the past twenty years, much research has gone into the synthesis of PMA. During this period, two new industrial processes were developed to synthesise PMA, which at present, has a world production of four thousands tons per year [39].

PMA has a wide variety of uses in industry; mainly in the fabrication of perfumes, colognes, soaps and cosmetics. PMA also serves as an intermediate for the synthesis of many pharmaceutical compounds as well as brighteners in electroplating processes. Other less important applications are the use of PMA as a corrosion inhibitor, a component in agricultural pesticides and insecticides, and an anticancer reagent, to name just a few [48].

Depending on the initial material, PMA can be synthesised by a variety of chemical processes. To date, the oxidation of p-methoxytoluene (PMT) remains the most attractive option for the preparation of PMA. At present, three variations of this process are used globally to industrially synthesise PMA. In each process, PMA is produced via different methods of PMT oxidation. The commercial price of PMT is around one dollar per kilogram and that of PMA is thirteen dollars per kilogram [3].

The majority of PMA is made by the oxidation of PMT with manganese dioxide ( $\text{MnO}_2$ ). The oxidation occurs in an aqueous sulfuric acid solution with temperatures ranging from 50 to 100°C [16]. The major inconvenience of this method is related to the reuse of the oxidising agent. In fact, it is difficult to regenerate  $\text{MnO}_2$ , and the reagents require disposal after use. Nevertheless, manganese dioxide is inexpensive, available in steady quantities and is increasingly recognised as an oxidising agent in the fine chemicals and pharmaceutical industries [33].

In 1985, Nippon Shokubai succeeded in commercialising a process for the production of PMA by vapor phase catalytic oxidation of PMT [36]. The key technology of this process depended on the development of a high performance catalyst. Nippon discovered that PMT can be oxidised to PMA with good yields in the presence of catalyst based on vanadium, oxygen and a few other elements. The oxidation process is carried out in a reactor packed with the specific catalyst at 300 to 500°C. A mixed gas of PMT and oxygen is continuously passed through the reactor with a residence time of a few seconds. The released gas from the reactor is immediately cooled to avoid the auto-oxidation of PMA to p-methoxybenzoic acid. The crystals of this acid bring about numerous difficulties such as clogging of piping, hindrance in the operation of the process and a decrease in the yield of PMA. However, these problems are mostly avoided through optimised operation of the process [44]. The life time of the catalyst is strongly affected by the feed concentration of PMT. A concentration of less than 3 % by volume is required for PMT in the feed gas mixture to avoid catalyst decay caused by coke [35].

BASF has commercialised a new process for the synthesis of PMA through direct anodic oxidation of PMT. The electrochemical process is carried out in undivided cells with graphite anodes. The electrolyte contains 70 to 90% by weight methanol, 9 to 30 wt.% PMT, and 0.05 to 1.5 wt.% of a supporting electrolyte. In such an electrolyte, PMT is electro-oxidised to p-anisaldehyde dimethyl acetals and subsequently hydrolysed to p-anisaldehyde and methanol in a separate system. The electrolysis temperature is restricted by the boiling point of methanol, hence the process is preferably operated from 20 to 60°C [10, 11]. The electrochemical process provides the possibility of achieving substantial conversion of PMT with excellent yields for the synthesis of p-anisaldehyde dimethyl acetals (yields > 85%) [16]. Maintenance of the electrodes is the major inconvenience of the process. In direct electro-organic synthesis, the electrodes have a very undesirable tendency to form a deposit, particularly when the electrolyte is recycled. However, the electrochemical oxidation of PMT can be carried out for a relatively long time without serious problems.

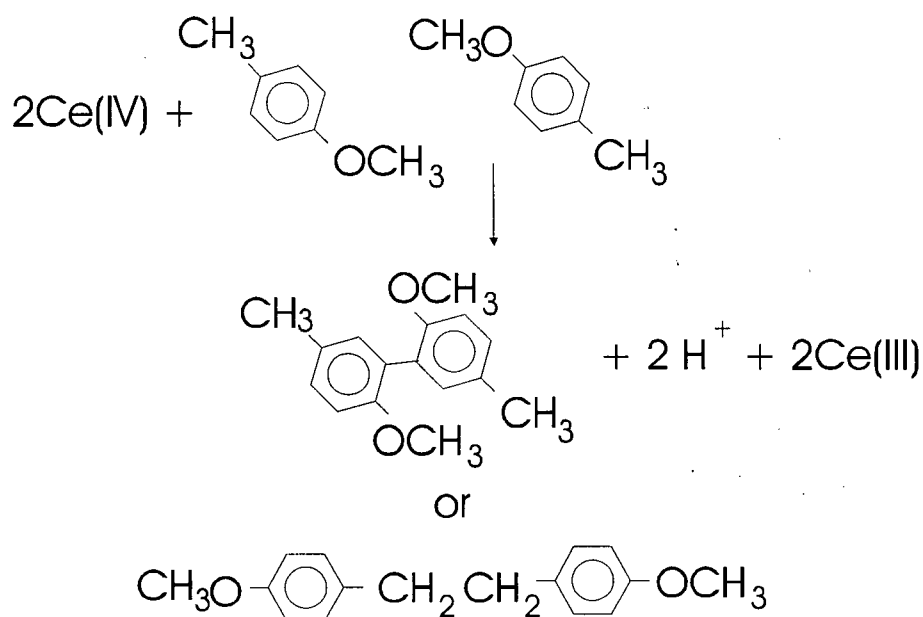


In collaboration with Hydro-Québec, the project of this thesis is based on the electrosynthesis of PMA by the ceric oxidation of PMT. In 1987, Hydro-Québec built a new industrial laboratory to explore emerging opportunities in research and development. Electrosynthesis of anthraquinone (AQ) via ceric oxidation was one of the projects which has been validated, optimised, and scaled-up to a pilot plant by Hydro-Québec. Having the necessary equipment on site, this company is particularly interested to synthesise other aromatic compounds such as PMA, butylbenzaldehyde, phenoxbenzaldehyde, chrobenzaldehyde, hydroquinone, etc [39].

The specific objectives of this thesis are related to the electrosynthesis of PMA through the oxidation of PMT with an aqueous cerium methanesulfonate solution. These objectives will be stated after background information is introduced to the reader.



Other chemicals than p-anisalcohol and p-anisic acid have been identified in previous works as secondary products of the oxidation of PMT [42]. These products are presented in Figure 2.2 and are formed by dimerisation of molecules of PMT. A plausible mechanism for the formation of these dimers involves the formation of p-methoxybenzylic radicals in the early stage of the oxidation process. More complex compounds have been detected which have not been identified. It has been proposed that the cation radical probably forms numerous secondary products by polymerisation [24].



**Figure 2.2 :** Secondary products from the oxidation of PMT

The equilibrium distribution coefficients of the oxidation products (PMA, p-anisalcohol, p-anisic acid) between an acidic aqueous solution (1 M  $\text{H}_2\text{SO}_4$ , 0.15 M  $\text{Ce}_2\text{SO}_4$ ) and PMT as well as the solubility of PMT have been evaluated by previous workers [43]. The distribution coefficients showed that the oxidation products favour their extraction into PMT from the aqueous phase, in which the solubility of PMT varies roughly from  $10^{-3}$  to  $10^{-2}$  M for temperatures of 20 to 70°C. The values of the distribution coefficients are presented in Appendix 1 .

## 2.2 Electrosynthesis.

### 2.1.1. Electrochemical reactors and figures of merit

The electrochemical reactor is the key unit of an electrochemical process. The minimum components required for an electrochemical reactor (or cell) are an anode, a cathode, an ionic contact between the electrodes (via an electrolyte) and an electronic contact between them, i.e. an external electrical circuit. Oxidation reactions occur on the anode surface whereas reduction reactions proceed on the cathode.

The performance of an electrochemical reactor is evaluated by the calculation of various figures of merit. These are important tools to facilitate comparisons between electrochemical processes and particularly useful to determine the economic viability of an electrochemical process. These figures of merit are:

$$\text{Current efficiency} \quad CE = \frac{i_D}{i} \quad \text{or} \quad \frac{n F R}{I} \quad (\times 100 \%) \quad \{1\}$$

$$\text{Specific energy} \quad SE = \frac{n F |V_{\text{cell}}|}{3600 CE MM} \quad \text{or} \quad \frac{|V_{\text{cell}}| I}{3600 P MM} \quad (\text{kWh/ kg}) \quad \{2\}$$

$$\text{where} \quad V_{\text{cell}} = V_{\text{oc}} - |\eta_C| - |\eta_A| - V_{\text{ohm}} \quad \{3\}$$

$n$  - stoichiometry number of moles of electron per mole of Ce(IV) ions produced

$F$  - Faraday constant (96487 Coulombs/ mole of  $e^-$ )

$R$  - production rate of the Ce(IV) ions (moles of Ce(IV)/ s)

$I$  - total current applied to the cell (A)

$i$  - total current density applied to the cell ( $A/ m^2$ )

$V_{\text{cell}}$  - cell voltage (V)

$i_D$  - current density driving the generation of Ce(IV) ions ( $A/ m^2$ )

$P$  - production rate of the product\* (mol/ s)

$V_{\text{oc}}$  - open circuit potential (V)

---

\* In this work, PMA or p-anisalcohol

$V_{ohm}$  - ohmic voltage drop through the cell (V)

$\eta_C$  - cathodic overpotential (V)

$\eta_A$  - anodic overpotential (V)

MM - molar mass of the product (g/ mol)

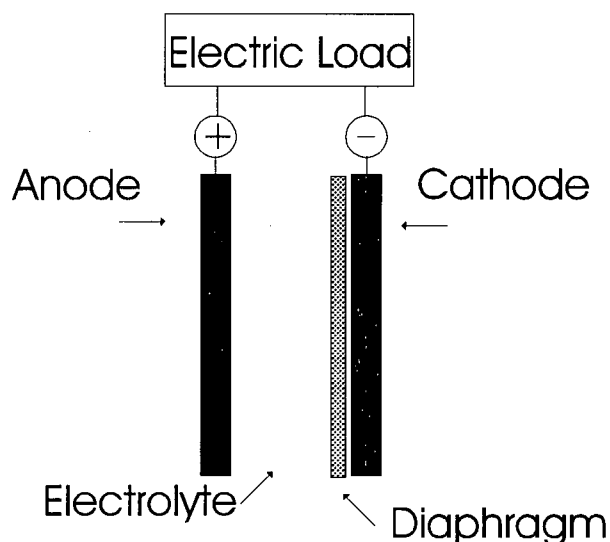
Ideally, the electrochemical reactor should be operated at high current density with high current efficiency and low specific energy [28].

The cell may be undivided or divided by a separator (usually an ion exchange membrane) to form two chambers in the cell. The separator acts as an extra resistance for the current and increases specific energy (SE) during operation of the cell. The capital and operating costs of an electrochemical reactor are increased by incorporating a separator between the electrodes and a separator should only be used if it is essential.

### 2.2.2 Separators

There are two classes of separators: ionic exchange membranes and diaphragms. Ionic exchange membranes function as barriers to convection and diffusion while permitting selective migration of ions. Ion exchange membranes always divide the cell into two hydraulically separate compartments containing an anolyte (electrolyte on the anodic side) and a catholyte (electrolyte on the cathodic side). Normally, the membrane is a thin sheet of polymer which is designed to allow the passage of anions or cations, but not both.

Diaphragms are porous or microporous polymers (Teflon, polypropylene) or ceramics (asbestos, glass frits) which act purely as a physical barrier to slow convection and diffusion of ions to the electrodes. Although diaphragms could be used to divide the cell in two hydraulically separate compartments, they may be used directly over the electrodes and permit operation of the cell with only one electrolyte. An undivided cell separated by a diaphragm is presented in Figure 2.3 .



**Figure 2.3 :** Undivided cell separated by a diaphragm

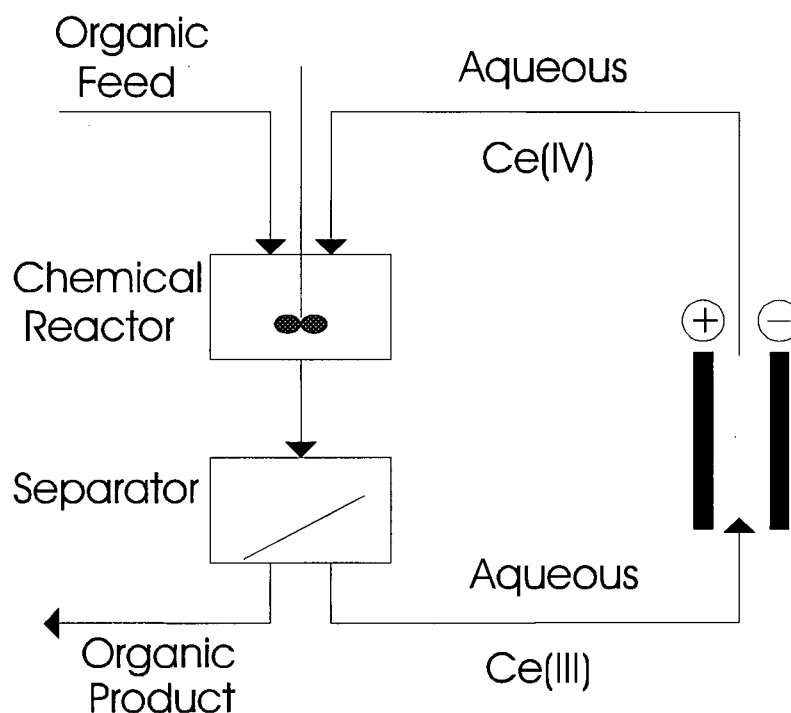
### 2.2.3 In-cell versus ex-cell and direct versus indirect organic electrosynthesis

The electrosynthesis of organic compounds can be classified as either in-cell or ex-cell. This classification is related to the presence (in-cell) or not (ex-cell) of the organic reactant with the electrolyte (liquid in contact with the electrodes) and should not be confused with the definition of a direct or an indirect organic electrosynthesis.

An indirect (or mediated) organic electrosynthesis is a process involving electrochemical generation of a reducing or oxidising agent, which is used to oxidise or reduce the organic reactant. Figure 2.4 shows a continuous cyclic process for the indirect ex-cell preparation of PMA using Ce(IV) as oxidising agent [19].

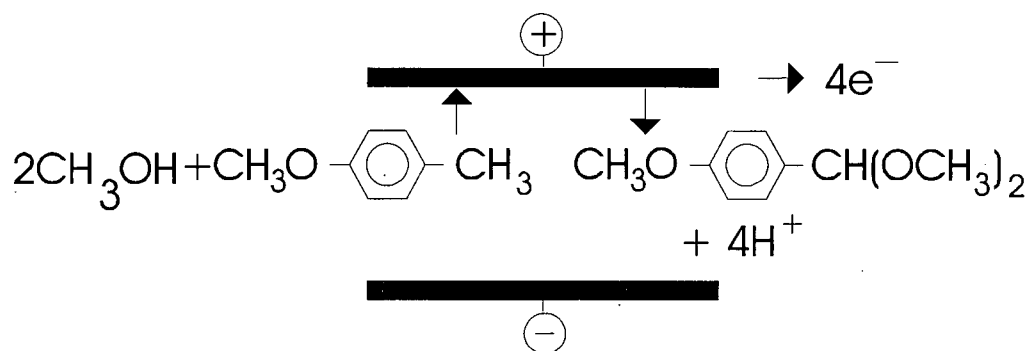
An aqueous phase containing Ce(IV) is contacted with PMT in a conventional thermochemical reactor (CSTR) to synthesise PMA. The aqueous phase containing the spent redox agent Ce(III) is separated from the organic phase and returned to the electrochemical reactor for the regeneration of Ce(IV). In such a design, the organic material is not in contact with the electrodes (in principle at least except for highly soluble

organics in electrolyte) and consequently this process is classified as an indirect ex-cell electrosynthesis system.



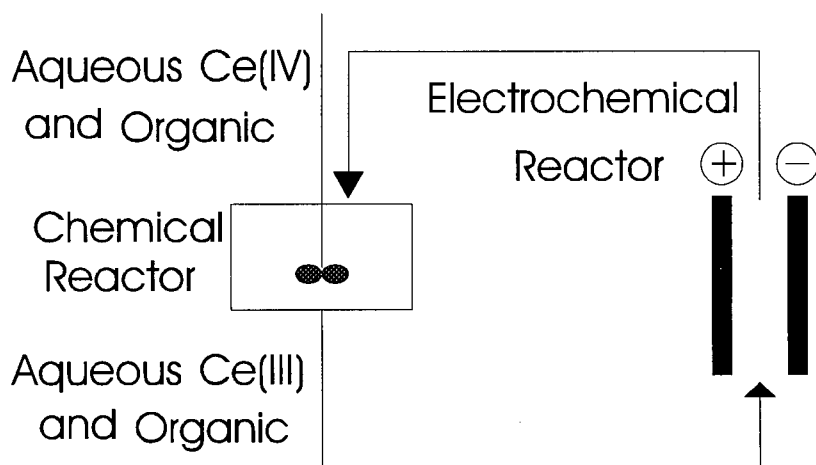
**Figure 2.4 :** General scheme for an indirect ex-cell electrosynthesis

A direct organic electrosynthesis refers to the organic reactant being directly oxidised or reduced on the electrodes of the cell. BASF used a direct method for preparing PMA by the oxidation of PMT on graphite anodes in a non-aqueous electrolyte (methanol). No electrochemical mediator is present in the electrolyte to oxidise the organic material. A general scheme for the direct oxidation of PMT to benzaldehyde dimethyl acetals is illustrated in Figure 2.5 .



**Figure 2.5 :** Direct oxidation of PMT to benzaldehyde dimethyl acetals.

A batch recycle system was used in the present project to investigate the electrosynthesis of PMA via ceric oxidation of PMT. This system (see Figure 2.6) is mainly made up of two operating units: an electrochemical reactor and a thermochemical reactor. In such a system, the aqueous cerous-ceric solution and the organic compounds are both mixed in the thermochemical reactor and pumped directly to the electrochemical reactor. Although both direct and indirect oxidation of the organic material can occur in the cell, this process is classified as an indirect in-cell electrosynthesis system.

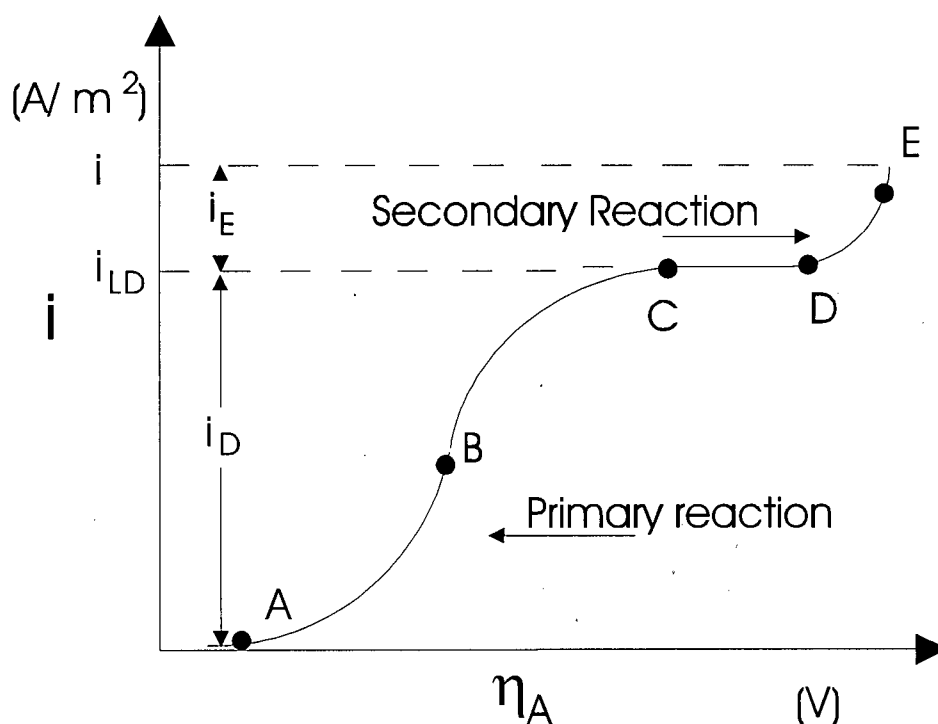


**Figure 2.6 :** Indirect, in-cell batch recycle system



### 2.2.4 Mass transfer-limited current density

In electrochemical processes, the rate of the desired reaction on an electrode may be under pure kinetic control, pure mass transport control or mixed kinetic and mass transport control. The maximum rate is determined by the current under pure mass transport control which is the maximum Faradic current supported by the reduced species for an anodic oxidation, or by the oxidised species for a cathodic reduction. This is called the mass transfer limited current density ( $i_L$ ). Figure 2.7 shows the relationship between current density and the anodic potential for a typical electrode reaction.



**Figure 2.7 :** Electrode reaction influenced by kinetics and mass transport

- A-B     Pure kinetic control of primary electrode reaction
- B-C     Mixed kinetic and mass transport control of primary reaction
- C-D     Pure mass transport control of primary reaction
- D-E     Secondary electrode reaction

where;

- $i_D$  - current density driving the primary reaction ( $A/m^2$ )
- $i_E$  - current density driving the secondary reaction ( $A/m^2$ )
- $i$  - current density applied on the electrode ( $A/m^2$ )
- $i_{LD}$  - mass transfer limited current density of the primary reaction ( $A/m^2$ )
- $\eta_A$  - anodic overpotential (V)

In the present work, the desired electrochemical reaction is the anodic oxidation of the ionic reduced species Ce(III) to its oxidised form Ce(IV), which constitutes the primary electrode reaction. A potential secondary anodic reaction is the evolution of oxygen through the oxidation of water.

There are many disadvantages in operating an electrochemical reactor with  $i$  greater than  $i_{LD}$ . Under these conditions, a portion of the current applied on the electrode ( $i$ ) is used to drive a secondary reaction ( $i_E$ ) which involves a diminution of the current efficiency of the primary reaction. Moreover, the absolute values of the overpotentials ( $\eta_A$  and  $\eta_C$ ) are increased, thereby increasing the energy consumption of the electrochemical process.

The theoretical determination of  $i_L$  is evaluated by the following equation:

$$i_L = n F K_m C_B \quad \{4\}$$

$C_B$  - concentration of the reduced species or oxidised species in the bulk electrolyte for an anodic or cathodic reaction, respectively ( $mol/m^3$ )

$K_m$  - mass transfer coefficient ( $m/s$ )

The mass transfer coefficient is determined through empirical correlations related to the geometry of the electrochemical reactor, fluid dynamic particularities and transport properties. The present work is concerned with mass transfer in a plug flow reactor with

an expanded metal mesh anode, under near turbulent or turbulent regimes. For this case, the following correlations can be used [28, 46]:

$$K_m = K_F [1 + (K_G / K_F)^2]^{0.5} \quad \{5\}$$

$K_F$  - mass transfer coefficient due to convection (m/ s)

$K_G$  - mass transport coefficient due to gas evolution (m/ s)

The limiting anodic mass transfer current density for the regeneration of Ce(IV) was determined without considering the mass transfer effects due to oxygen evolution. The production of oxygen was not precisely evaluated in this work and consequently a conservative value of  $K_m$  was calculated by assuming that  $K_m$  equals  $K_F$ .

$$K_F = \frac{Sh D}{d_E} \quad \{6\}$$

$d_E$  - equivalent diameter (m)

$Sh$  - Sherwood number

$D$  - diffusion coefficient (m<sup>2</sup>/ s)

where 
$$d_E = \frac{2 B S}{B + S} \quad \{7\}$$

$B$  - width of the electrode (m)

$S$  - gap between the electrodes or  
gap between an electrode and a diaphragm or an ionic exchange membrane (m)

and 
$$Sh = 0.82 Re^{0.61} Sc^{0.33} \quad \{8\}$$
  
valid for  $10^2 < Re < 2 \times 10^3$

$Re$  - Reynolds number

$Sc$  - Schmidt number

$$\text{Re} = \frac{U d_E \rho}{\mu} \quad \{9\}$$

$U$  - linear velocity of fluid in the cell (m/ s)

$\rho$  - density of the solution (kg/ m<sup>3</sup>)

$\mu$  - viscosity of the solution (kg/(m s))

$$\text{Sc} = \frac{\mu}{\rho D} \quad \{10\}$$

### 2.2.5 Chemical reaction in two-phase medium

There are two important steps for the electrosynthesis of organic compounds by an indirect process: the regeneration of the mediator in the electrochemical reactor (electrochemical reaction) and the chemical reaction of the organic reactant in the thermochemical reactor (CSTR or PFR). The most significant step is the chemical reaction. The synthesis of aromatic compounds is usually optimised in a CSTR before it is coupled to an electrochemical reactor. Previous work has been conducted on the oxidation of aromatic compounds in batch mode with aqueous solutions containing an electrochemical mediator. The presence of two phases had important effects on the rate of the chemical reaction. A general overview of the effects observed in previous works are summarised in this section.

The degree of phase dispersion is an important variable for chemical reactions occurring in two-phase media. In the present work, PMT must dissolve in the aqueous phase before reacting with Ce(IV) ions, and this presents a potential mass transfer resistance for the rate of the chemical oxidation [24]. Therefore, good stirring conditions are required to generate a high specific surface for mass transfer through formation of organic droplets in the aqueous phase (emulsion).

Co-solvents such as methanol and acetonitrile are soluble in water and have been used to increase the concentration of PMT in the aqueous phase [19]. The concentration of the organic reactant in the aqueous phase is critical because low concentrations may significantly decrease the rate of the reaction. This is explained by a lower probability of the organic reacting with Ce(IV) ions.

Immiscible co-solvents are usually used to slow down the chemical oxidation in very reactive media. Kerosene, dichloroethane, methylene chloride and hexane are a few examples of immiscible co-solvents which have been used for the indirect electrosynthesis of aromatic compounds [23, 24, 47]. The phase volume ratio of the organic and the aqueous phase may have important effects on the selectivity and yields for the synthesis of the desired product. It has been proposed that the presence of an immiscible co-solvent in the medium protects the organic product from further oxidation in the aqueous phase by re-extraction [24].

Temperature has a particularly important role in the distribution coefficients of organic materials. In two-phase media, the solubility of organic compounds is increased in the aqueous phase by an elevation of temperature and promotes mass exchange between phases. Temperature also has an important effect on the kinetics of chemical reactions (via the Arrhenius equation) and on the solubility of cerous-ceric salts.

The influence of cerous and ceric ions has been studied for the chemical oxidation of PMT via Ce(IV) ions in dilute aqueous sulfuric acid solution (1 M  $\text{H}_2\text{SO}_4$ ) in a conventional batch reactor [42]. The results obtained clearly indicated that the concentration of Ce(III) has no significant influence on the synthesis of PMA. However, the chemical oxidation should be performed with a concentration of Ce(III) at the saturation level, considering that the regeneration of the ceric solutions in the electrochemical reactor could be mass transfer limited. Although two different researchers concluded the PMA yield increased when the initial concentration of Ce(IV) decreased, the interpretation of the results obtained is questionable. The initial molar ratio of Ce(IV)/

PMT was not constant (varying from 1 to 10) during these investigations. The experiments were carried out at different conversions of PMT which certainly had an influence on the yield of PMA.

The aqueous phase is usually an acidic solution. The type of acid and its concentration strongly influence the kinetics of the chemical reactions and the solubility of the cerium salts. In general, the solubility of ceric ions as well as the rate of the chemical reactions increase with an increase of the acid concentration in the aqueous phase, whereas high solubility of cerous ions is obtained at low acid concentrations. The acidity of the aqueous solution can be problematic in fitting the electrochemical and chemical steps together. High organic chemical conversion, yield and selectivity are sometimes obtained only at high acid concentrations. On the other hand, the current efficiency of the electrochemical reaction decreases with increasing acid concentration in regards to the regeneration of Ce(IV).

### **2.3 Indirect in-cell/ ex-cell oxidant in organic electrosynthesis**

There are a few polyvalent metal salts that have been extensively investigated as indirect oxidants for the synthesis of aromatic aldehydes, ketones, and quinones. These include oxidant salts of cobalt(III), manganese(III), cerium(IV) and chromium(VI). The stoichiometric use and disposal of these reagents are undesirable from both economic and environmental standpoints. Consequently, more effort has been invested recently in regeneration of such oxidants via electrochemical processes. Each of these metal ion oxidants has certain properties which cause them to make the indirect oxidation process effective at different levels. In the present work, the term yield is related to the moles of organic products obtained (for instance PMA) from the moles of organic reactant consumed (PMT) (see section 3.1.2).

### 2.3.1 Chromium (VI)

Chromium(VI) has the lowest reduction potential of the above metal oxidants and could be the easiest to regenerate electrochemically. However, chromium ions have poor selectivity in the oxidation of aromatic compounds and have not been successfully used for the preparation of aromatic aldehydes [32]. On the other hand, the oxidation of a quinone (2-methyl-naphthalene) has been found to be enhanced by the presence of catalytic amounts of chromium(VI) in a cerium solution. Apparently, a coupled cerium and chromium compound is involved at some stage of the oxidation of 2-methyl-naphthalene and gives a higher yield for the synthesis of 2-methyl-1,4-naphtoquinone than with cerium or chromium alone [20].

### 2.3.2 Cobalt (III)

Cobalt(III) has been used in aqueous sulfuric acid solutions for the synthesis of a few aromatic aldehydes. One important drawback of using a cobalt salt in such media is the instability of the cobaltic ions. Comninellis *et al.* [8] have suggested that this instability is due to the decomposition of cobalt(III) sulfate by reaction with water. Many other authors have observed this degradation of cobalt(III) ions but prefer to be careful concerning the reaction mechanisms involved [2].

In spite of this problem, cobalt(III) has shown good results as an oxidising agent for the preparation of aromatic aldehydes. Comninellis *et al.* [8] obtained 80 % yield for the indirect ex-cell synthesis of o-nitrobenzaldehyde via oxidation of o-nitrotoluene. The oxidation (via a conventional batch reactor) was carried out with an aqueous cobaltic solution in 60 wt.% sulfuric acid, at 12°C, with a reaction time of 25 to 35 minutes. However, the electrolytic preparation of the cobaltic solution involved some difficulties. The current efficiency was relatively low (30-60%), even at a low current density (500 A/m<sup>2</sup>) and a low conversion of the cobaltous ions [5]. Moreover, these results have been obtained with an electrochemical batch reactor without any specification concerning the

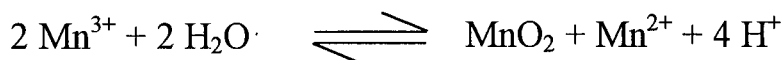
mass transfer coefficient. Wendt *et al.* [47] affirmed that a good current efficiency must be obtained for the preparation of cobaltic solutions in perchloric acid under well-defined mass transfer conditions.

Halter *et al.* [13] have prepared PMA by indirect divided in-cell oxidation of PMT with an aqueous cobalt solution in 50% weight acetic acid at room temperature. An in-cell method is advantageous to minimise the instability of the cobalt(III) ion which can react simultaneously with organic material after its regeneration in the cell [2]. The preparation of the aromatic aldehyde was performed with 80% yield and a current efficiency for cobalt (III) from 50 to 70%. However, during the operation of the electrochemical process, the cell operating voltage was high (21-23 volts for a cell divided by an anionic exchange membrane) under a low applied current density (500 A/ m<sup>2</sup>) and consequently involved a high energy consumption.

### 2.3.3 Manganese (III)

Manganese(III) has been used in aqueous solutions of sulfuric acid for the oxidation of aromatic organic compounds. Periasamy *et al.* [31] have obtained good yields (up to 80%) for the preparation of quinones. The experiments were carried out in a thermochemical batch reactor with temperatures between 20 and 50°C and a concentration of sulfuric acid around 30 wt.%. In such relatively mild conditions, the time of reaction was high (3 to 10 hours) and the oxidation was performed without being exposed to bright light to avoid disproportionation of manganese(III) ions.

It has been reported that manganese(III) sulfate is unstable in dilute or moderate concentrations of sulfuric acid in an aqueous solution and reacts with water according to the following reaction:





The equilibrium constant of this reaction was evaluated to be  $1.8 \times 10^6 \text{ (mol/L)}^3$  for solutions with a concentration of sulfuric acid from 2.5 - 7 M and manganese(II) between 0.15 - 0.35 M at 15°C. Other reports state that the manganese(III) sulfate is particularly stable only over 60 wt.% sulfuric acid [1].

The main inconvenience concerning the oxidation of organic compounds in mild conditions is the long time of reaction. Increasing the temperature as well as the acidity of the solution can increase the rate of the reactions. However, some problems are involved in the regeneration of manganic ions in concentrated sulfuric acid solution. The solubility of manganese(II) ions is relatively low in concentrated sulfuric acid and consequently high current efficiency can only be obtained at low current density with low conversion of the manganous ions. Nevertheless, Givaudan & Cie *et al.* [45] have developed an industrial indirect ex-cell process for the synthesis of p-tert-butyl benzaldehyde (yield 80%) via oxidation of p-tert-butyl toluene with manganic ions in 60 wt.% sulfuric acid. The current efficiency for manganese (III) is about 55% for high conversion of manganese(II) with a current density around 500 A/ m<sup>2</sup>.

Halter *et al.* [13] have prepared PMA by indirect in-cell oxidation of PMT with an aqueous manganous solution in 3-6 wt.% sulfuric acid at room temperature. The organic oxidation was performed with divided and undivided cells. For both cell arrangements, 50% yield was obtained for the preparation of the aromatic aldehyde with a current efficiency of 85-100%. The current density applied was 800 A/ m<sup>2</sup> with an operating cell voltage of 4-6 volts.

#### 2.3.4 Cerium (IV)

The oxidation of aromatic compounds with ceric ions has been studied in various acidic solutions. Kramer and Robertson used an aqueous ceric solution in perchloric acid to prepare a few aromatic aldehydes [18]. Even if good yields have been obtained (up to

80% via conventional batch reaction), the explosion hazard presented by mixing organics and perchloric acid has undoubtedly prevented further work with such a medium.

Nitric acid has been used to solubilise cerium salts for the preparation of aromatic compounds. Rennie *et al.* [34] obtained significant quantities of nitrated by-products with the presence of nitrate anion in the reactive medium. On the other hand, Syper reported excellent yields (95-100 %) for the preparation of aromatic aldehydes [38]. Unfortunately, nothing has been found for the regeneration of the ceric solutions in these investigations.

Cerium(IV) has been extensively used in aqueous sulfuric acid solutions for the oxidation of aromatic compounds. Formation of slurry due to the low solubility of cerous sulphate in sulfuric acid medium is problematic and has prohibited the commercial scale trial of a NQ (Naphthoquinone) process [30]. High current efficiencies (90%) with good conversion of the cerous ions (50%) are obtained only at low current density ( $500 \text{ A/m}^2$ ) [6]. This problem has been overcome somewhat by using slurries of cerous sulfate, so that the concentration of Ce(III) remained at saturation level during electrolysis. However, this resulted in Ce(III) solids following the oxidation of organic material, a difficult three phase separation [19].

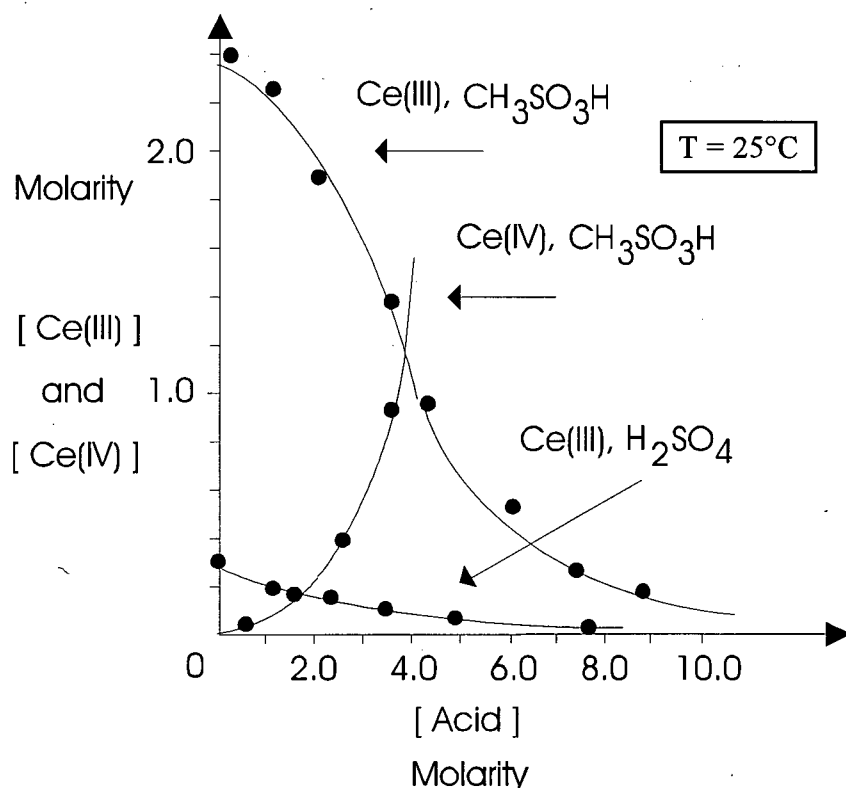
Kreysa *et al.* [24] obtained 90-95 % yields for the synthesis of PMA via oxidation of PMT with ceric sulfate solutions in a conventional batch reactor. The experiments were carried out in low sulfuric acid concentrations (0.5-1.5 M) and moderate temperatures (25-40 °C) using methylene chloride as an organic solvent. The reaction times were high (1-4 hours for complete conversion of Ce(IV) corresponding to 50-95% conversion of PMT) due to the mild conditions, low dispersion (225 RPM) and dilution of the organic reactant in methylene chloride (0.2 M). The high solubility of PMT in the organic solvent decreases the concentration of PMT in the aqueous medium, slowing the overall oxidation process.

Tzedakis and Savall have also studied the oxidation of PMT via ceric sulfate solutions in a conventional batch reactor with similar conditions to Kreysa *et al.* but without using an organic solvent. Around 80% yields have been obtained for the preparation of PMA with a reaction time of less than 5 minutes at 50°C. However, these oxidations were carried out with a stoichiometric excess of Ce(IV) without specifications for the conversion of Ce(IV) and PMT [42].

Many other aqueous acid mediums have been unsuccessfully used for the ceric oxidation of aromatic compounds. Problems include instability of the counteranions of the acid (benzenesulfonate and chloride), reactivity with the organic reactant and products (nitrate, chloride, perchlorate), and marginal solubility (sulfate, acetate, trifluoroacetate) [19, 23]. Kreh *et al.* [21, 22] found that methanesulfonic acid (MSA) or trifluoromethanesulfonic acid solubilises the Ce(III)/ Ce(IV) couple without presenting any of the difficulties above.

Figure 2.8 shows the solubility of Ce(III) and Ce(IV) salts as a function of the methanesulfuric acid concentration in aqueous solution. The high solubility of Ce(III) presents the possibility of operating the electrochemical reactor at high current densities (4000 A/ m<sup>2</sup>) with high current efficiencies (90%). The solubility of Ce(III) in sulfuric acid medium is also presented in Figure 2.8 to show the high solubility of Ce(III) ions in methanesulfonic acid. The solubility of Ce(IV) is limited at low concentration of methanesulfonic acid and can produce slurries during the electrochemical generation of Ce(IV). However, these slurries are effective for the oxidation of organic material, generating cerous ions which are soluble at low concentrations of methanesulfonic acid.

The ceric methanesulfonic solutions exhibit the desired properties for a commercially attractive process. Hydro-Québec plans to commercialise the production of anthraquinone and benzoquinone by using such solutions before the year 2000 [39].



**Figure 2.8 :** Solubility of cerous-ceric salts in aqueous acidic mediums

Kreh *et al.* [23] have prepared PMA by oxidation of PMT with ceric methanesulfonic solutions in a conventional batch reactor. The chemical oxidation was carried out at low temperature ( $5^{\circ}\text{C}$ ) with moderate acidity of the aqueous solution (3.5 M MSA) which was diluted with methanol prior to the addition of the PMT. About a 71% yield was obtained for the synthesis of the aromatic aldehyde with a 40 minute reaction time. The major inconvenience of this method is related to the use of methanol as a co-solvent. Methanol is not stable in the presence of  $\text{Ce(IV)}$  ions and results in the generation of secondary products. Using acetonitrile and dichloroethane (DCE) as organic co-solvents, an 84% yield is achieved with a lower acid concentration in the aqueous solution (0.8 M MSA) [19].

The indirect ex-cell oxidation of PMT has been carried out in various solvents by Torii *et al.* [40, 41], and has shown good results for the synthesis of PMA. Ceric ammonium nitrate in solution with pure methanol oxidises PMT with a 93 % yield at room

temperature for a contact time of a few minutes. Using a mixture of methanol and water, PMA was synthesised with a 76% yield. An indirect in-cell method has been also examined by these researchers. A ceric ammonium nitrate salt in methanol with a supporting electrolyte afforded the aromatic aldehyde with a 77% yield.

However, there are many problems concerning the regeneration of the ceric salt and the separation of the products contained in the reactive medium. Using methanol as a solvent rapidly corrodes platinised titanium anodes and shows instability problems with the reaction involving the ceric ions. Furthermore, separating PMA and regenerating the mediator involves the evaporation of methanol from the single phase medium mixture. Subsequently, the organic reactant and products must be separated and the solid residue (a Ce(III) complex) must be adequately processed before being regenerated by electrochemical means.

## **2.4 Objectives of research**

The objective of this project was to study the synthesis of PMA via an indirect (mediated) in-cell electro-oxidation of PMT in a batch recycle system (see Figure 2.6) without co-solvents (miscible or immiscible in water) and with an electrolyte of an aqueous cerium methanesulfonate solution.

## Chapter 3

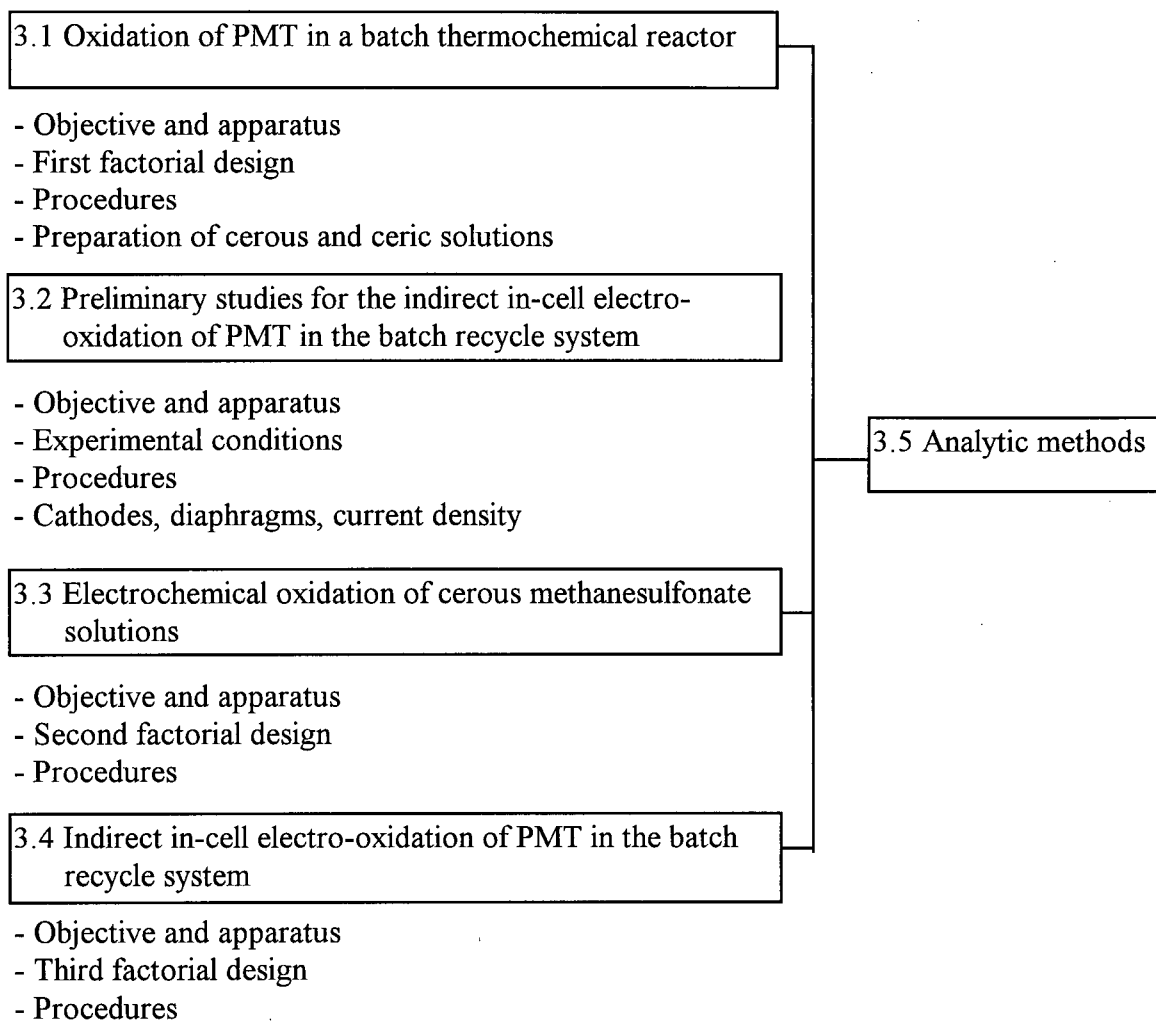
### EXPERIMENTAL APPARATUS AND PROCEDURES

Two important reactions are involved in the indirect in-cell electrosynthesis of PMA: the chemical oxidation of PMT and the electrochemical regeneration of Ce(IV) ions. Before investigating the mediated in-cell electro-oxidation of PMT in the batch recycle system, the chemical and electrochemical steps were separately investigated in order to have a better understanding of the kinetics of these two reactions.

A factorial design was performed to study the chemical oxidation of PMT in a conventional thermochemical batch reactor (batch reaction). To precede the oxidation of PMT via conventional batch reactions, it was first necessary to prepare some ceric solutions. These solutions were obtained by electro-oxidation of cerous methanesulfonate solutions in the batch recycle system. A simple undivided cell (without separator) was used to prepared the ceric solutions.

Preliminary studies for the indirect in-cell electro-oxidation of PMT in the batch recycle system showed that a simple arrangement of the cell could not be used because of fouling problems on the cathode. Consequently, a more complex arrangement (involving a diaphragm and a three dimensional porous cathode) was used to carry out the electrochemical-oxidation of PMT. A second factorial design was conducted to investigate the performance of the complex arrangement of the electrochemical reactor for the oxidation of cerous methanesulfonate solutions (generation of Ce(IV) ions).

Finally a third factorial design was performed to study the indirect in-cell electro-oxidation of PMT in the batch recycle system in which both reactions (chemical and electrochemical) occur simultaneously. A flowsheet of Chapter 3 is given in Figure 3.1 .



**Figure 3.1 : Flowsheet of Chapter 3**

### 3.1 Oxidation of PMT in a batch thermochemical reactor

#### 3.1.1 Objective and apparatus

A factorial design was performed to study the kinetics of the thermochemical oxidation of PMT by ceric methanesulfonate solutions. The experimental apparatus consisted of a batch thermochemical reactor equipped with temperature and agitation control. A small thermochemical reactor (nominal volume of 500 ml) was used to consume a small volume of chemicals. The baffles and turbine impeller were designed to achieve vigorous agitation without formation of vortex in the vessel. A detailed design of the thermochemical reactor (with baffles and turbine propeller) is given in Appendix 2 .

#### 3.1.2 First factorial design

Four variables were investigated: acidity, temperature, initial molar ratio Ce(IV)/ PMT and residence time. The ranges of the variables studied are listed in the Table 3.1 . The concentration of Ce(tot)\*, the initial concentration of Ce(IV) and agitation speed were kept constant at 1M, 0.1 M and 1000 RPM, respectively. These variables were not investigated for the following reasons:

- Previous work has demonstrated that the yield of PMA is not affected by the concentration of Ce(tot) [42]. However, this variable has an important role in the preparation of ceric solutions obtained by electro-oxidation of cerous solutions. The initial molarity of Ce(tot) was chosen to ensure that the electrochemical oxidation of the cerous ion was not mass transport limited (see Appendix 16).
- The solubility of Ce(IV) ion is strongly affected by the concentration of MSA in the aqueous solution (see Figure 2.8). The initial concentration of Ce(IV) was selected to avoid any precipitation of the ceric ions within the acidity range of the study. It was

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\*  $[\text{Ce}(\text{tot})] = [\text{Ce}(\text{III})] + [\text{Ce}(\text{IV})]$



convenient to modify the molar ratio Ce(IV)/ PMT by varying the initial number of moles of PMT without drastically changing the total volume of solution in the reactor.

- Agitation speed is related to the optimisation of a thermochemical reactor design in which many parameters could be studied, such as: type of propeller and baffles, number of propellers and baffles, diameter of propeller versus inside diameter of the propeller, etc. Optimisation of the performance of the thermochemical reactor on the oxidation of PMT is beyond the scope of this thesis. So, agitation speed was set to ensure vigorous mixing (visual observation), generating a high specific surface for mass transport of PMT through formation of organic droplets in the aqueous phase (see section 2.2.5).

**Table 3.1 :** Variables investigated in the first factorial design

Variables	Range
Acidity	0.5-1.5 M
Temperature	20-60 °C
Molar ratio Ce(IV)/ PMT	2-6
Residence time	1-10 min

Studying four variables at two levels, a half factorial design would require a total of eight runs (i.e.  $2^{4-1}$ ). A center point was taken to test the linearity of the response variables. The reproducibility of the runs was obtained by repeating the center point four times. Thus, a total of twelve runs were required for this experimental design, in which the response variables observed were the yield of PMA, the conversion of PMT and the conversion of Ce(IV) defined as follows:

$$\text{Yield of A}^* = \frac{\text{moles of A obtained} \times 100}{\text{moles of PMT consumed}} \quad (\%)$$

$$\text{Conversion of A}^{**} = \frac{\text{moles of A consumed} \times 100}{\text{initial moles of A}} \quad (\%)$$

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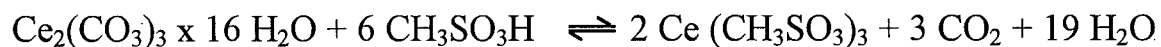
\* PMA or p-anisalcohol, \*\* PMT or Ce(IV)

### 3.1.3 Procedures

Precautions were taken to ensure the thermochemical reactor was totally closed to the atmosphere. A precise volume of 400 ml of a ceric methanesulfonate solution was introduced in the vessel, stirred and heated to the desired temperature. Then, a precise volume of PMT was injected in the thermochemical reactor, and simultaneously a chronometer was started. Depending on the molar ratio under investigation, the quantity injected was in the range of 850 to 2500  $\mu\text{l}$ . After the residence time had elapsed, the agitation was turned off and the solution was transferred directly into a funnel, in which 75 ml of 1-2 dichloroethane (DCE) was added for the extraction of the organic material. Trace chemicals in the conventional batch process were removed by washing the thermochemical reactor, baffles, and the impeller with DCE used for the second and third extraction. A total of three extractions of the aqueous phase were performed with a decanting time of 7 minutes. To determine the final concentration of Ce(IV), a sample of the aqueous phase was taken two minutes after the initial decanting time for each extraction.

### 3.1.4 Preparation of cerous and ceric solutions

An aqueous cerous methanesulfonate solution was prepared by dissolving cerium carbonate in distilled water, followed by the addition of methanesulfonic acid. The acid reacts with the cerium carbonate as follows:

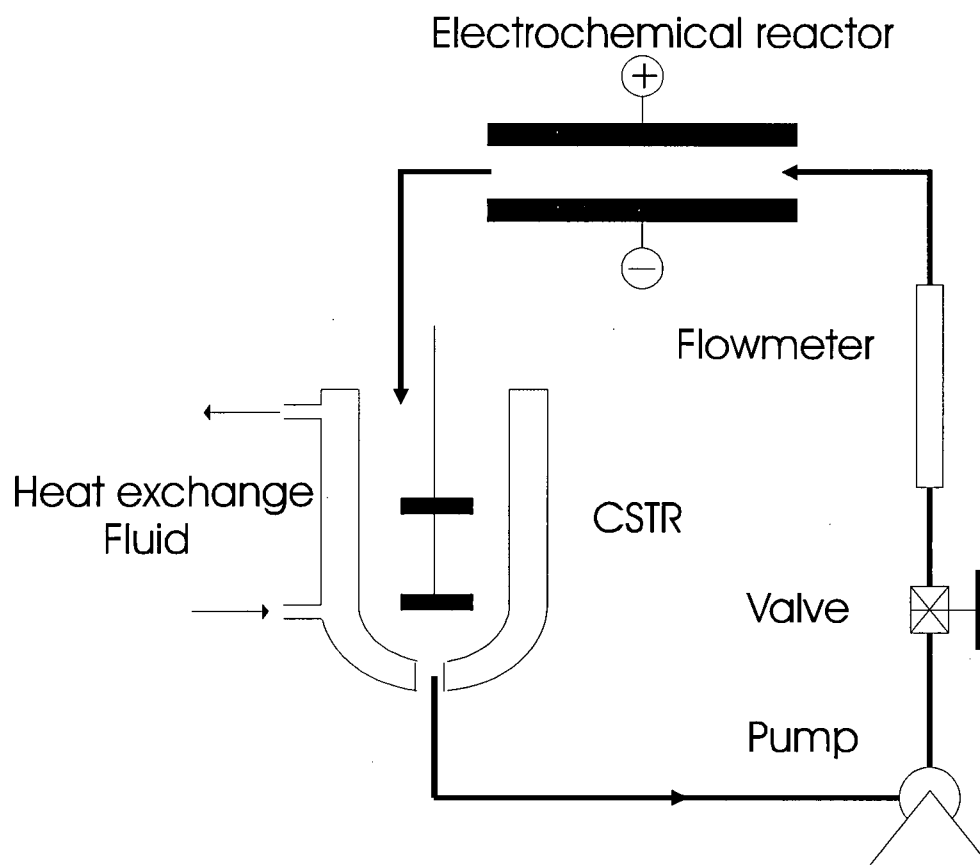


An example calculation for the preparation of a solution of 0.5 M MSA and 1M Ce(III) is given in Appendix 3 . The aqueous solution was filtered\* and electro-oxidised in the batch recycle system.

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\* Whatman 4, qualitative filter papers

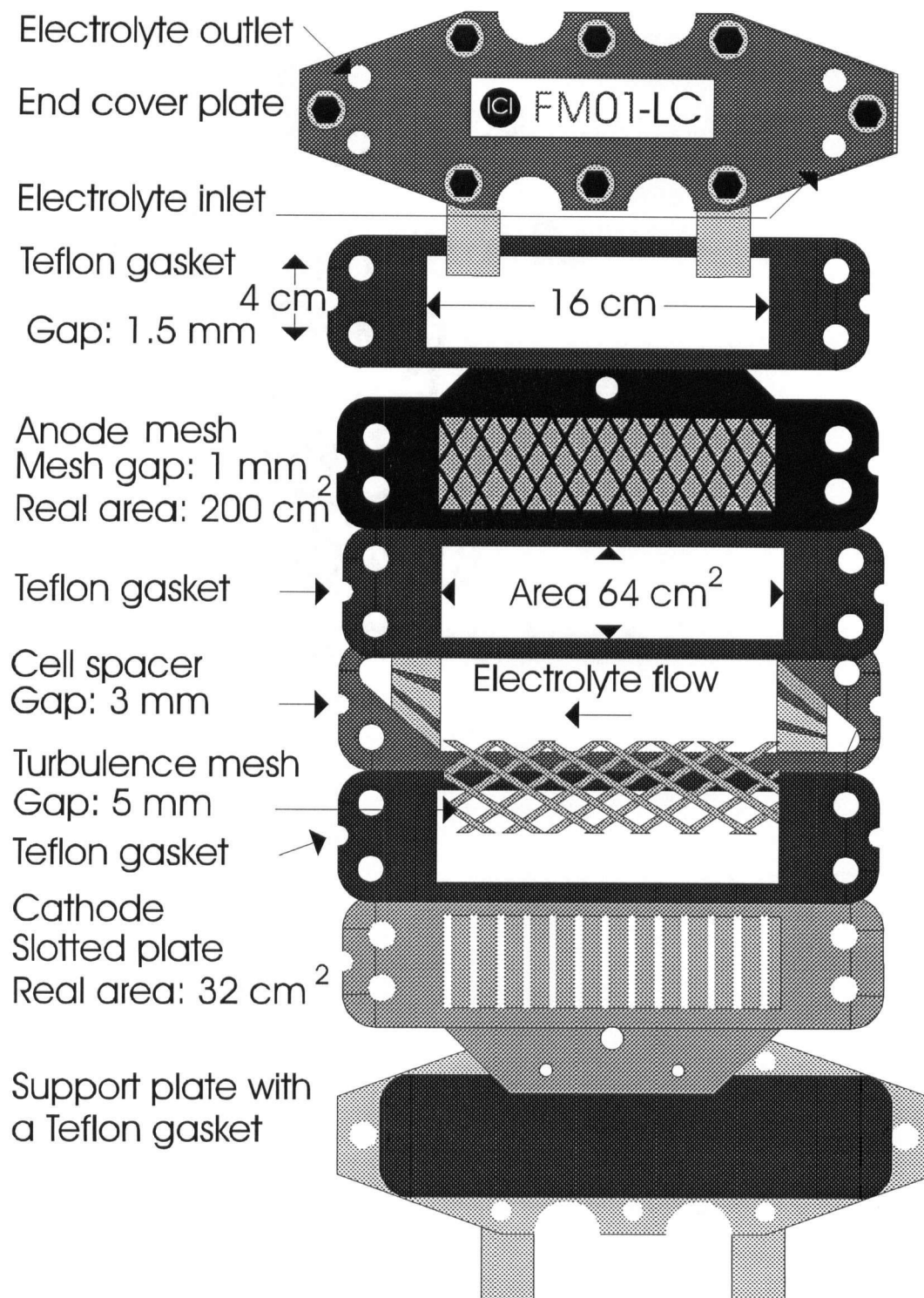
The batch recycle system is illustrated in Figure 3.2 . The thermochemical reactor (CSTR) acted as a retention tank as well as a gas disengagement vessel. This thermochemical reactor was equipped with a heat exchanger to control the temperature of the electrolyte which was pumped to an electrochemical reactor. The electrochemical system was completed by the connection of the cell to an external electrical circuit including a load, ammeter, coulometer and voltmeter.



**Figure 3.2 : Batch recycle system**

The electrochemical reactor is an ICI FM01-LC cell. The laboratory cell is based on the filter press arrangement. The design consists of plate electrodes separated by gaskets and spacers which form compartments for the electrolyte. Turbulence-promoting Teflon mesh is used within spacers to improve the transport of ions to the electrodes. A typical (simple)

arrangement of an undivided cell is shown in Figure 3.3 including dimensions (electrode sizes, areas) and the flow of electrolyte within the cell.

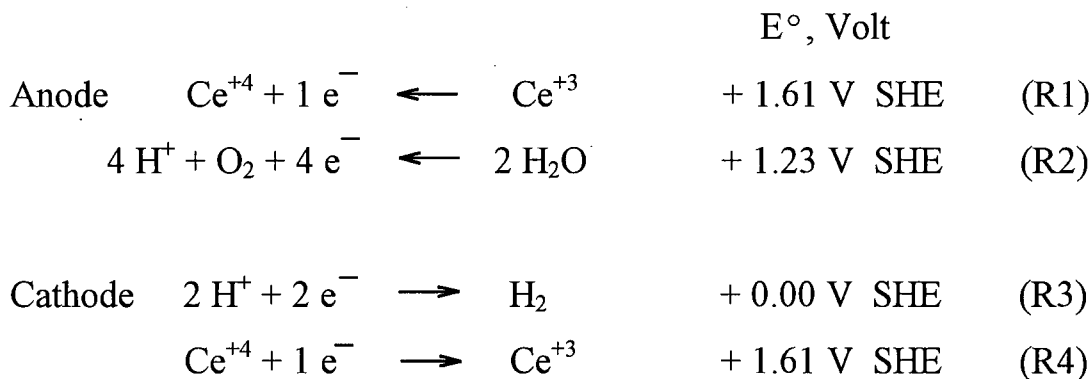


**Figure 3.3** : A typical arrangement of an undivided cell

The glass thermochemical reactor had a nominal volume of two liters with an internal diameter of ten centimeters. This vessel comprised a flat flange lid designed with five sockets used for a condenser (outlet for gases), a thermocouple, and inlets for the electrolyte. Baffles and turbine impellers were designed to achieve vigorous agitation without formation of a vortex in the vessel (see Appendix 4 ).

The units were connected to a magnetic centrifugal pump with one half-inch Teflon tubing. The flow rate of the solution was adjusted with a valve located between the pump and the flowmeter. All parts in contact with the electrolyte (except electrodes and thermochemical reactor) were coated or made of Teflon to avoid any contamination problems. A detailed design of the batch recycle system is given in Appendix 5 .

Considering the electrolyte composition, two reactions can occur on each electrode:



Stainless steel was chosen as the cathode material because of its catalytic properties. This material exhibits a low overpotential for hydrogen evolution which promotes the redox reaction (R3) to occur on the cathode surface. In regards to the anode material, previous works have demonstrated the good performance of an electrode of Pt/ Ti for the oxidation of cerous methanesulfonate solution [16]. Platinum exhibits a high overvoltage for oxygen evolution (R2) and seems to have excellent catalytic properties for the electro-

oxidation of cerous ions (R1). Also, electro-reduction of ceric ions (R4) is suppressed by using a differential area undivided cell, with a mesh anode and a slotted plate cathode.

The preparation of ceric solutions were conducted under the conditions listed in Table 3.2 .

**Table 3.2 : Conditions for the preparation of ceric solutions**

<b>Fixed variables</b>	<b>Conditions</b>
Main flow rate	200 L/ h
Temperature	35 °C
Current applied	20 A

After introducing the cerous solution in the batch recycle system, cold water was fed to the condenser before starting the pump and adjusting the flow rate. Afterwards, the solution was heated and set to the desired temperature. Finally, the electric load was turned on and the number of Coulombs supplied to the electrochemical reactor was counted by the coulometer. The conditions were kept constant until the concentration of Ce(IV) reached a concentration slightly higher than 0.1 M, which was accurately reduced to 0.1 M with a solution of hydrogen peroxide.

### **3.2 Preliminary studies for the indirect in-cell electro-oxidation of PMT in the batch recycle system.**

#### **3.2.1 Objective and apparatus**

Preliminary runs were performed to study the cerium mediated electro-oxidation of PMT in the batch recycle system. The objective of these runs was to determine a satisfactory arrangement for the electrochemical reactor. Electrode fouling is a well-known problem in electrochemical processes involving the contact of electrodes with organic materials. This problem was observed on the cathodic side of the electrochemical

reactor. Consequently, a series of cathode materials and diaphragms was tested to minimise the rate of deposition of organic complexes on the electrode.

### 3.2.2 Conditions of the preliminary studies

The deposition of solids on the cathode acted as a barrier for the current and increased the operating cell voltage which is equal to the absolute value of  $V_{\text{cell}}$  ( $V_{\text{cell}}$  is negative for an electrosynthesis process). Thus, the cell voltage was used to monitor the progression of solids deposition. The runs were stopped when the operating voltage reached 20 volts - well above the initial operating voltage which occurred a few seconds after turning on the power supply. This initial operating voltage was a function of many variables: temperature, composition of the electrolyte, the current applied to the cell and the arrangement of the electrochemical reactor. The first three variables were kept constant to compare the different electrochemical arrangements. The electrolyte was composed of a 2 L aqueous solution of 0.2 M MSA and 1 M Ce(tot) mixed with 100 ml of PMT. The batch recycle system was operated at the conditions listed in the Table 3.3 . Under these conditions, the initial voltage of all the design arrangements studied was in the range of 7 to 10 volts.

**Table 3.3 : Conditions of the preliminary studies**

Fixed variables	Conditions
Main flow rate	200 L/ h
Temperature	40 °C
Current applied	20 A
Agitation	1000 RPM

### 3.2.3 Procedures

Until the desired temperature was obtained, the procedures of these preliminary runs were the same as those followed for the preparation of ceric methanesulfonate solutions

(section 3.1.4). At this point, the agitation was turned on and PMT was poured into the thermochemical reactor. Simultaneously, the electric load was applied and a chronometer was started. The run was shut down by turning off the electric load, the pump and the agitation in that order. The electrochemical reactor was removed by disassembling the apparatus, washed with acetone and with a solution 30% volume MSA, assembled with a new arrangement and restored in the batch recycle system.

### 3.2.4 Cathodes, diaphragms and current density

Stainless steel, graphite and Ebonex coated with platinum were investigated as potential cathode materials for the electro-oxidation of PMT. The cathodes of graphite and platinum were both flat plate electrodes with an area of  $64 \text{ cm}^2$ . The arrangement of the electrochemical reactor was the same as the one described in the preparation of ceric solutions (see Figure 3.3). These cathodes showed poor results for kinetic suppression of the deposition of solids with run times of a few minutes for each electrode.

A diaphragm was placed over the cathode of stainless steel in the hopes of slowing the formation of organic complexes on the electrode. Four diaphragms were investigated:

- a) Celgard 5550 (microporous polypropylene)
- b) Celgard 5511 (microporous polypropylene)
- c) PHDC120 (porous polypropylene)
- d) asbestos cloth

Celgard 5550, Celgard 5511, PHDC120 and asbestos cloth are classed as hydrophilic diaphragms. The wettability in an aqueous environment of the Celgard diaphragms can be achieved by treatment with a cationic/ nonionic surfactant blend. However, no surfactant was used due to the possibility of oxidising the wetting agent by  $\text{Ce(IV)}$  ions. Moreover, formation of foam is a well-known problem related to the presence of surfactant even with



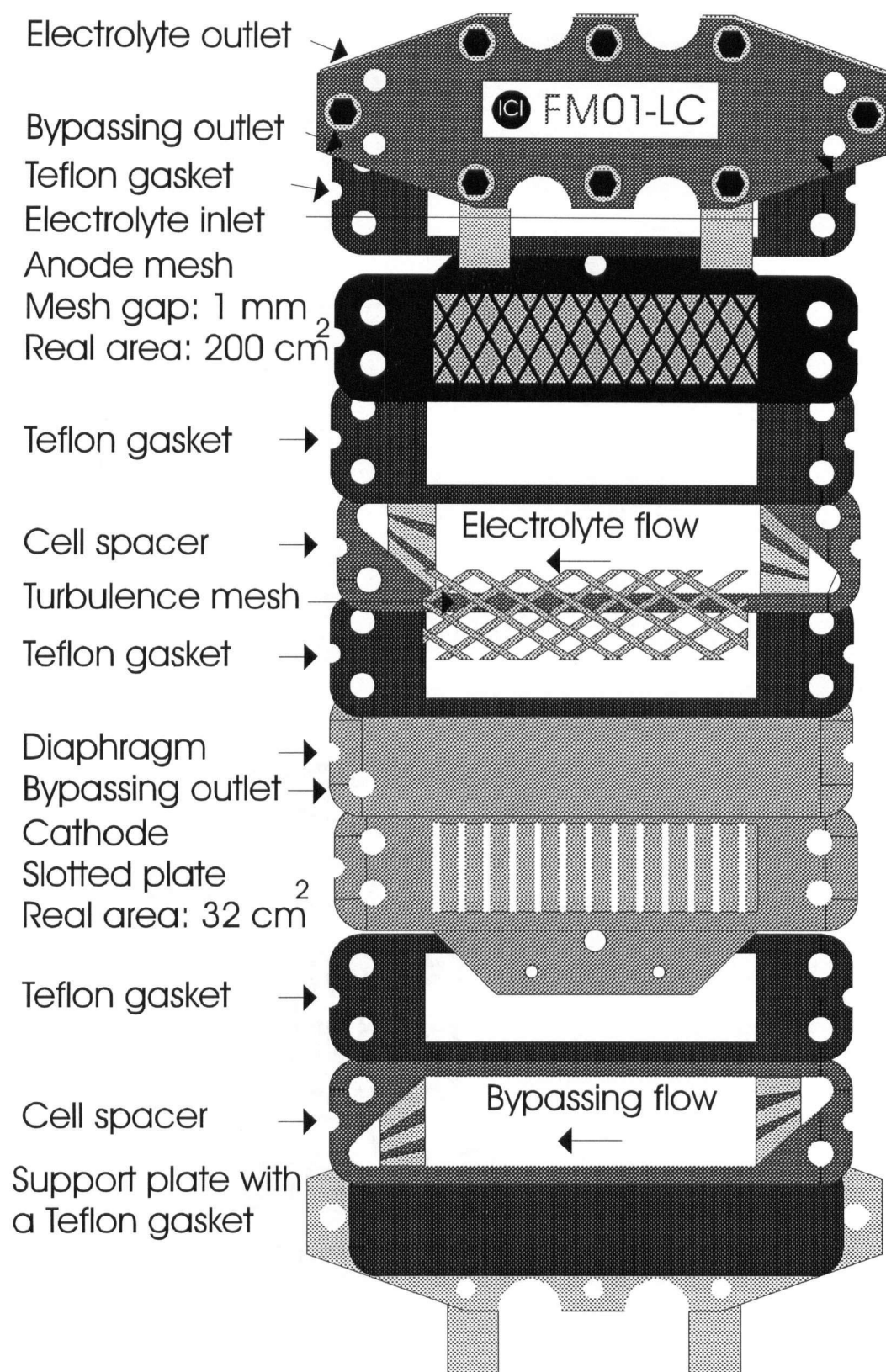
a concentration of few parts per million in the electrolyte. The PHDC120 diaphragm is radiation grafted to make it hydrophilic without using a surfactant.

The formation of bubbles on the cathode surface was problematic in the operation of the cell. The diaphragms studied were not porous enough to permit the bubbles to escape to the electrolyte. Consequently, the arrangement used for the preparation of ceric solutions was not ideal because of the accumulation of gas between the cathode and the diaphragm, generating a high voltage drop for the cell. To overcome this problem, the cell was modified as presented in Figure 3.4 .

A new compartment was formed by adding a spacer behind the cathode. The gas produced on the slotted plate could circulate to this compartment and escape through a process connection port, separate from the two used for the circulation of electrolyte in the cell. However, bypass of liquid to this compartment was the main disadvantage of this arrangement. In order to control the bypassing flow rate of the electrolyte, a valve was installed on the external piping, connecting the new compartment to the thermochemical reactor (see Appendix 5, legend numbers 15,18 and 31). The bypass flow rate was adjusted to 3.6 L/ min.

The total flow rate of electrolyte circulating in the batch recycle system is called the main flow rate (i.e. electrolyte entering by the connection port identified by electrolyte inlet in Figure 3.4 ). The main flow rate should not be confused with the bypassing flow rate which is a portion of the main flow rate (see the connection port, bypassing outlet in Figure 3.4 ).

Celgard diaphragms have shown very poor results, reaching an operating voltage of 20 volts in only few seconds. The results were better, but still mediocre, with the PHD120 and asbestos diaphragm with run times of a few minutes.

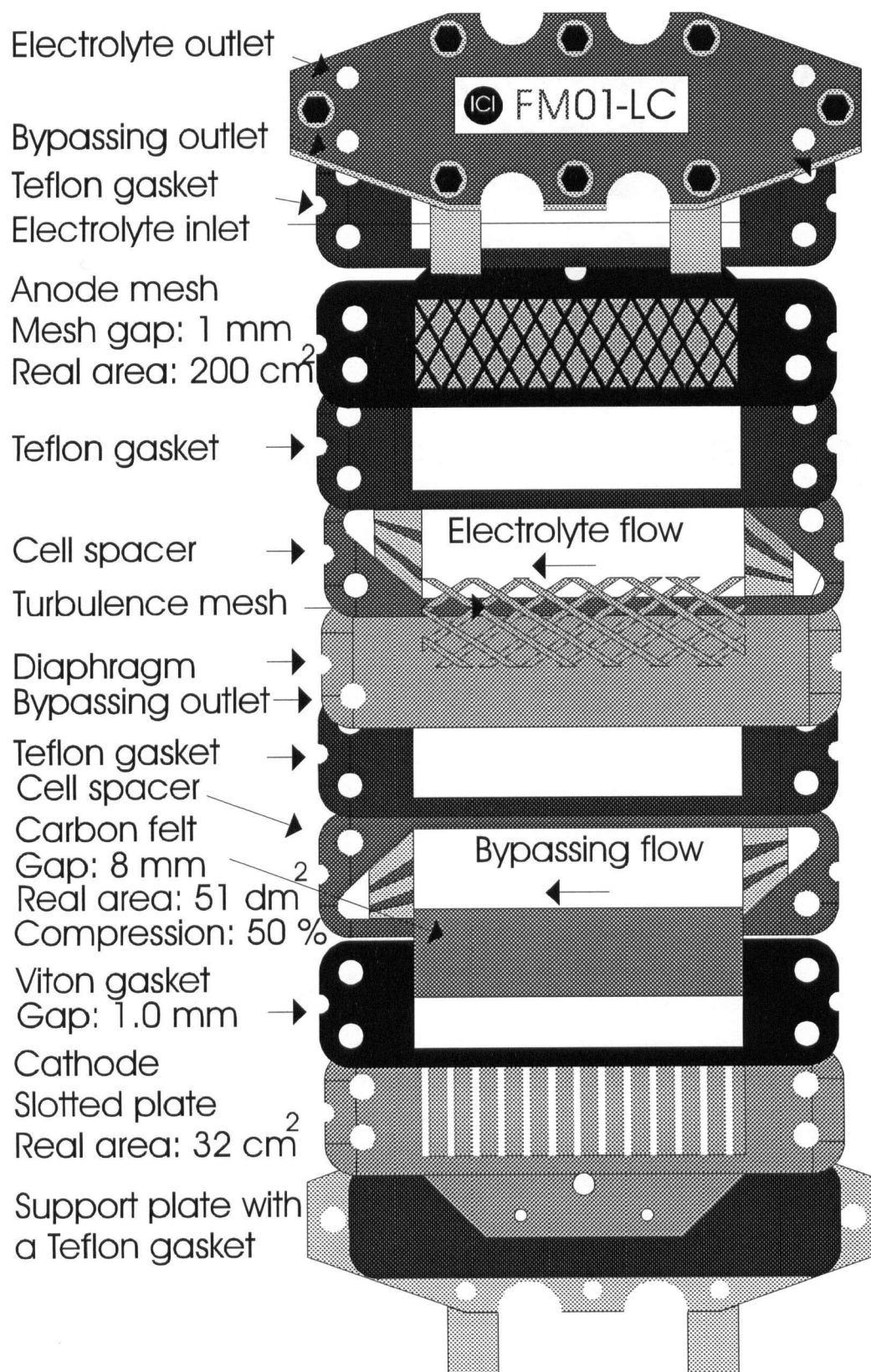


**Figure 3.4:** Arrangement of the cell with a diaphragm

At this point, the intention was to study the effect of the current density on the rate of solid deposition on the cathode. Considering that  $H^+$  ions are far smaller than molecules of PMT, it has been proposed that the current efficiency for hydrogen evolution should be better if the current density is increased. Thus, a slotted sheet of neoprene was used to cover the cathode, reducing the area of the electrode by a factor of eight. The arrangement of the cell was the same as the one used for the preparation of ceric solutions (see Figure 3.3), apart from adding the sheet of neoprene between the cathode and the Teflon gasket.

Unfortunately, after a few minutes of run time, the voltage drop had already reached 20 volts, which was one half the elapsed time for the uncovered cathode. From this observation, a three dimensional porous cathode electrode was made in order to decrease the current density at the cathode, in an effort to obtain better results. The arrangement of the cell is illustrated in Figure 3.5 .

A graphite fiber fixed-bed cathode was designed by compression of a sheet of graphite fiber felt on the slotted plate of stainless steel. A PHDC120 diaphragm was installed on the graphite fiber to slow the flow of electrolyte to the bed. With this arrangement, the electro-oxidation of PMT was run for two hours with an average operating voltage of 11.1 volts. This cell design was chosen to study the electro-oxidation of PMT in the batch recycle system.



**Figure 3.5 :** Arrangement of the cell with a 3-dimensional porous graphite cathode

### 3.3 Electrochemical oxidation of cerous methanesulfonate solutions

#### 3.3.1 Objective and apparatus

Before studying the electro-oxidation of PMT, it was important to verify the performance of the new cell design for the electro-oxidation of cerous methanesulfonate solutions. A few runs were performed to precede the electro-oxidation of cerous methane sulfonate solution in the batch recycle system, which has been described at the beginning of this chapter (section 3.1.4).

#### 3.3.2 Second factorial design

A factorial design was performed to evaluate the current efficiency for Ce(IV), under different experimental conditions. Three variables were investigated: current applied (superficial current densities, 1563-3125 A/ m<sup>2</sup>), temperature and acidity of the cerous methanesulfonate solution. The ranges of the variables studied are listed in the Table 3.4 . These variables were studied at two levels, totalling eight runs for a complete factorial design. Three center point runs were added to determine reproducibility/ linearity. The main flow rate in the batch recycle system was not investigated, in order to have better control of the flow rate of electrolyte bypassing in the graphite fixed-bed electrode.

**Table 3.4 :** Variables investigated in the second factorial design

<b>Variables</b>	<b>Range</b>
Acidity	0.2-0.8 M
Temperature	30-70 °C
Current applied	10-20 A

### 3.3.3 Procedures

Each part of the batch recycle system in contact with the electrolyte was carefully washed with water and acetone before beginning the experiment. Any traces of PMT or its derivatives could be oxidised by ceric ions, affecting the observed overall current efficiency of the cell.

Both the sheet of graphite felt and the PHDC120 diaphragm were changed for each run to limit the influence of uncontrolled variables (modification of the physical and chemical properties of the diaphragm and graphite felt) related to the cell design. Both were wetted in the cerous solution under investigation before assembly in the cell. The cell was arranged as illustrated in Figure 3.5. The graphite felt was compressed uniformly with a compression factor of 50%.

For each run, a precise volume of 2.2 L of the cerous solution was poured in the thermochemical reactor. The runs were halted after passing in the cell, a fixed number of Coulombs, calculated to oxidise the aqueous solution to a ceric concentration of 0.06 M under a hypothetical current efficiency of 100%. A sample of the aqueous solution was taken at the end of each run for the determination of the ceric ion concentration. Three solutions of different acidity were prepared to carry out the factorial design. The ceric solution was carefully reduced with a concentrated solution of hydrogen peroxide in order to be eventually used for another run. The electro-oxidation of the cerous solution was executed under the experimental conditions presented in Table 3.5, according to the procedures mentioned in section 3.1.4. Due to the new cell arrangement, a procedure had to be added concerning the bypassing flow rate in the cathode compartment. This flow rate was adjusted after setting the main flow rate of the batch recycle system.

**Table 3.5 :** Conditions of the electro-oxidation of cerous solutions

<b>Fixed variables</b>	<b>Conditions</b>
Main flow rate	200 L/ h
Bypassing flow rate	3.6 L/ h
Agitation	0 RPM

### 3.4 Indirect in-cell electro-oxidation of PMT in the batch recycle system

#### 3.4.1 Objective and apparatus

The objective of this work was explained in section 2.4 . The apparatus used consists of a batch recycle system as described in section 3.1.4 .

#### 3.4.2 Third factorial design

Four variables were selected and investigated for the electro-oxidation of PMT in the batch recycle system. Acidity of the cerous solution, temperature, initial volume ratio of PMT over the cerous aqueous solution and projected conversion of PMT were studied in the range listed in Table 3.6. Due to the difficulty of sampling during the electro-oxidation of PMT, an accurate analysis of the organic material could be done only at the end of the runs. Consequently, the projected conversion of PMT was investigated rather than the operating time of the runs. It is important to realise that conversion of PMT and operating time are interrelated and are partly determined by the levels of the other independent variables.

**Table 3.6 :** Variables investigated in the third factorial design

Variables	Range
Acidity	0.2-0.8 M
Temperature	30-70 °C
Vol. ratio Org./Aq.	0.029-0.059
Conversion of PMT	10-50 %

For the same reasons specified in the first factorial design, the agitation speed and the initial concentration of Ce(tot) were kept constant at 1000 RPM and 1 M, respectively.

Twelve runs were performed for the electrosynthesis of PMA in the batch recycle system with the same experimental plan used for the oxidation of PMT in a thermochemical batch reactor.

### 3.4.3 Procedures

The first two procedures in section 3.3.3 were applied before each run of the third factorial design.

For each run, the total volume of electrolyte in the batch recycle system was 1.8 L, which contained 50 to 100 ml of PMT depending on the volume ratio used. The time of each run was calculated assuming that all ceric ions produced reacted with PMT for the synthesis of PMA, under an electric load of 20 A and a hypothetical current efficiency for Ce(IV) of 80%. An example calculation is shown in Appendix 6. The electro-oxidation of PMT was conducted using the experimental conditions presented in Table 3.7 and according to the procedures outlined in section 3.2.3.

**Table 3.7 : Conditions of the electro-oxidation of PMT**

<b>Fixed variables</b>	<b>Conditions</b>
Main flow rate	300 L/ h
Bypassing flow rate	4.8 L/ h
Agitation	1000 RPM
Current applied	20 A

After shutting down the batch recycle system, the electrolyte was transferred directly into a funnel. The batch recycle apparatus was washed twice by circulating 500 ml of DCE for 2 minutes. A total of two extractions were done with a decanting time of 15 minutes. During the experiment, a few samples were taken for the determination of ceric ion concentration.



### 3.5 Analytical methods

The acidity of the aqueous solution was determined by volumetric titrations with a standard solution of sodium hydroxide, using methyl orange as indicator. The concentration of Ce(IV) was also determined by volumetric titration in which ceric ions were titrated with a ferrous ammonium sulfate solution (FAS), using ferroin as indicator. This titrant was prepared by dilution of concentrated FAS in distilled water and standardised with a ceric sulfate solution. To determine the concentration of Ce(tot), the aqueous solution was first completely oxidised and then titrated with ferrous ammonium sulfate. Ammonium persulfate was used to oxidise the aqueous solution, using a few drops of silver nitrate solution as catalyst.

The organic chemicals, PMT, PMA and p-anisalcohol, were analysed by gas chromatography using a FID detector. An internal standard method was used to obtain accurate quantification of these compounds. A detailed description of each analytical method is given in Appendix 7.

## Chapter 4

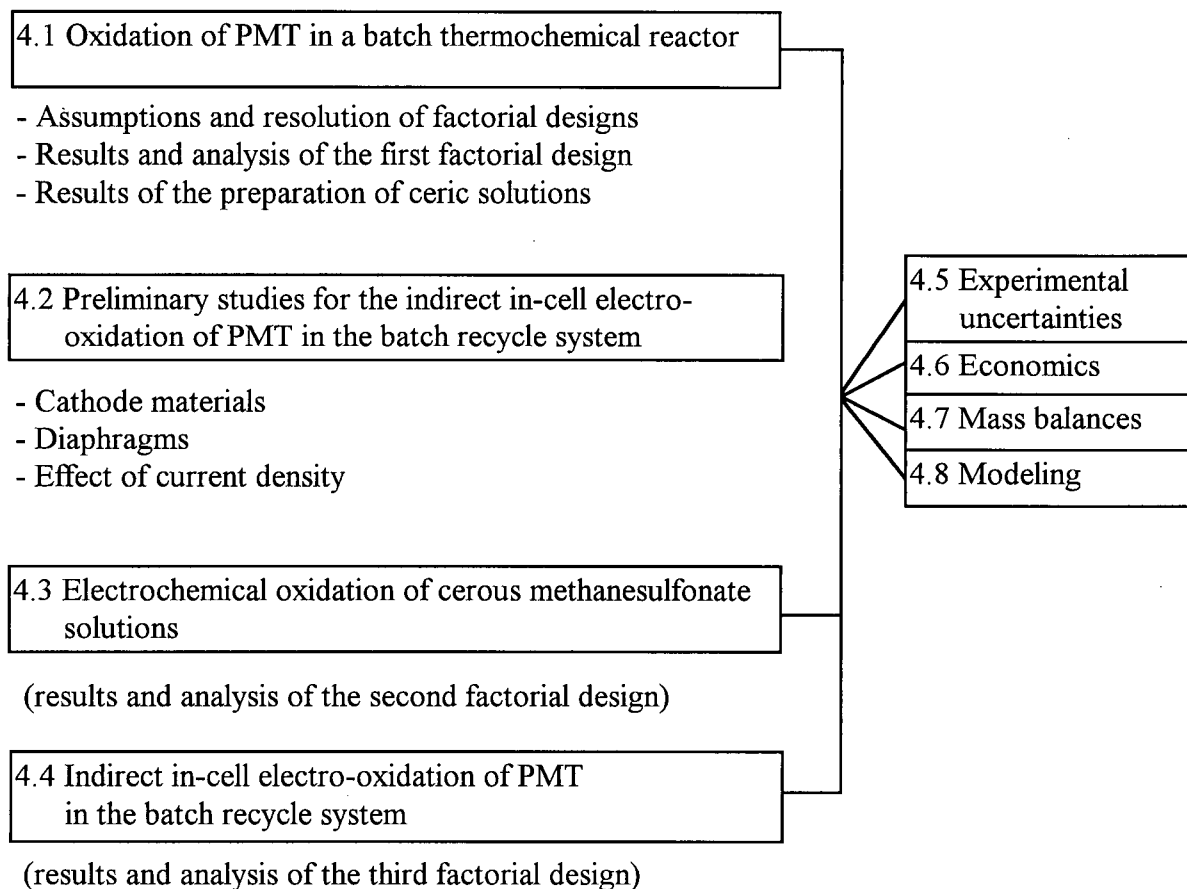
### EXPERIMENTAL RESULTS AND DISCUSSION

Factorial experiments were performed on the thermochemical oxidation of PMT (first factorial design), the electrochemical oxidation of cerous methanesulfonate solutions (second factorial design), and the electro-oxidation of PMT (third factorial design). The data of these factorial designs were fitted via empirical models which were used to analyse the effect of the variables investigated on the yield of PMA and current efficiency for Ce(IV) (the response variables).

The analysis of a factorial design is based on a few assumptions which should be respected to facilitate the interpretation of the results. These assumptions will be summarised at the beginning of this chapter with a brief discussion about the resolution of the first and third factorial design.

A rough economic estimation of the cost of electrosynthesis of PMA via indirect ex-cell and in-cell methods was also done in this work. Comparisons of the two methods were made based on the cost of energy and raw material.

Experimental uncertainties, mass balances, and modeling are other important topics which are discussed in the present chapter. A flowsheet of Chapter 4 is given in Figure 4.1



**Figure 4.1:** Flowsheet of Chapter 4

## 4.1 Oxidation of PMT in a thermochemical batch reactor

### 4.1.1 Assumptions and resolution of factorial designs

For a  $2^k$  factorial design, the following assumptions should be satisfied [26]:

- The order of the runs should be randomised.
- The response variables (yield of PMA, current efficiency for Ce(IV)) should be linear in the range of the variables investigated.
- The difference (called the residual) between the experimental values of response variables and the corresponding values estimated by an empirical model should be normally distributed.

Violation of these assumptions in a factorial design does not mean that the experimental plan is invalid. It implies that the interpretation of the results should be done with more care.

The first and third half factorial designs are classified as resolution (IV) designs. These are designs in which no main effects are aliased with any other main effect or with any two-factor interaction, but two-factor interactions are aliased with each other.

For example in the first factorial design, acidity, temperature, molar ratio Ce(IV)/ PMT and residence time are the main effects and these are represented by the letters A, B, C, D, respectively. The main effect A is aliased with the three-factor interaction effect BCD, B with ACD, C with ABD and D with ABC. Furthermore, every two-factor interaction is aliased with another two-factor interaction. These alias relationships are  $AB=CD$ ,  $AC=BD$  and  $BC=AD$ . It is reasonable to assume that certain high-order interactions are negligible, then information of the main effect A, B, C, D may be still obtained in such half factorial designs.

#### 4.1.2 Results of the first factorial design

The experimental plan for, and results obtained from, the first factorial design are presented in Tables 4.1 and 4.2. To guard against systematic trends in uncontrolled (or unknown) variables during execution of the design, the runs were made in a random order. The plus sign means that the variable is set at the high level whereas the minus sign indicates low level of the range (see Table 4.1). The center point is represented by the notation "CP" and corresponds to an acidity, temperature, residence time and molar ratio set at 1M, 40°C, 5.5 minutes and 4, respectively; the midpoint between the low and high values of the range examined. The yield of p-anis alcohol was less than three percent for each run in this factorial design and has not been investigated as a response variable.

**Table 4.1 :** Plan of the first factorial design

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
	<b>Acidity</b>	<b>Temperature</b>	<b>Residence Time</b>	<b>Molar ratio</b>
<b>Run</b>	<b>0.5 - 1.5 M</b>	<b>20-60 °C</b>	<b>1-10 min</b>	<b>2.0-6.0</b>
1	-	-	-	-
2	+	-	-	+
3	-	+	-	+
4	+	+	-	-
5	-	-	+	+
6	+	-	+	-
7	-	+	+	-
8	+	+	+	+
9	CP	CP	CP	CP
10	CP	CP	CP	CP
11	CP	CP	CP	CP
12	CP	CP	CP	CP

**Table 4.2 :** Results of the first factorial design

Run	Yield	Conversion	Conversion
	PMA %	Ce(IV) %	PMT %
1	39.6	54.7	32.4
2	26.3	44.9	64.2
3	63.3	88.4	93.5
4	33.0	100.0	52.8
5	51.8	67.4	100.0
6	33.9	100.0	62.5
7	78.1	100.0	53.3
8	16.6	100.0	100.0
9	53.4	100.0	100.0
10	56.2	100.0	100.0
11	54.4	100.0	100.0
12	55.1	100.0	100.0

The results obtained for the center points (run 9-12) demonstrate the reproducibility of the factorial design. The interactions of the variables investigated on the yield of PMA are presented in Table 4.3. The analysis of the factorial design was done with ECHIP<sup>®</sup> software, designed specifically for the analysis of factorial designs.

**Table 4.3:** Confidence of effects on the yield of PMA

Effects	Confidence %
A = BCD	98.9
B = ACD	77.1
C = ABD	45.2
D = ABC	60.8
AB = CD	90.6
AC = BD	73.4
AD = BC	51.6

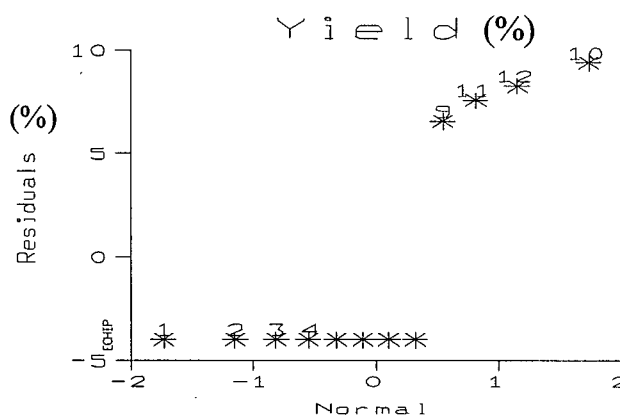
Two strong (confidence of effects higher than 90%) interactive effects can be observed from the analysis of the first factorial design. The main effect A (Acidity) aliased the three factor interaction effect BCD (Temperature-Residence time-Molar ratio) and interaction AB (Acidity-Temperature) aliased CD (Residence time-Molar ratio) were the most important effects with a confidence of 99% and 90%, respectively (see Table 4.3). The main effects C and D were negligible, and thus it was reasonable to assume that the interaction CD and BCD were also insignificant. Thus, only the main effect A and B (because of the strong interaction AB) were analysed in more detail for the oxidation of PMT in the thermochemical batch reactor.

An empirical model was fitted to evaluate the yield of PMA as a function of the main and interactive effects presented in Table 4.3. This model was based on the runs investigated (including center points) in the factorial design and gave a squared correlation coefficient ( $R^2$ ) equal to 0.883.

The residuals of the model are given in Table 4.4 and show that the model underestimated the center points by an average of 8 % whereas the other points were overestimated by 4 %. Of course, the residuals are not normally distributed in such a design because of the influence of the center points in the empirical model. Usually, the normality assumption is respected in factorial design only when center points are excluded from the empirical model, unless the model has a very good linearity ( $R^2 > 0.99$ ). Figure 4.2 shows the distribution of the residuals on a normal axis. For a perfect normal distribution, a linear relation should be obtained for this plot with concentration of points in the middle of the normal axis [26]. The details of the empirical model are presented in Appendix 8 and it showed how the linearity is affected by the center points (via determination of  $B_0$ ).

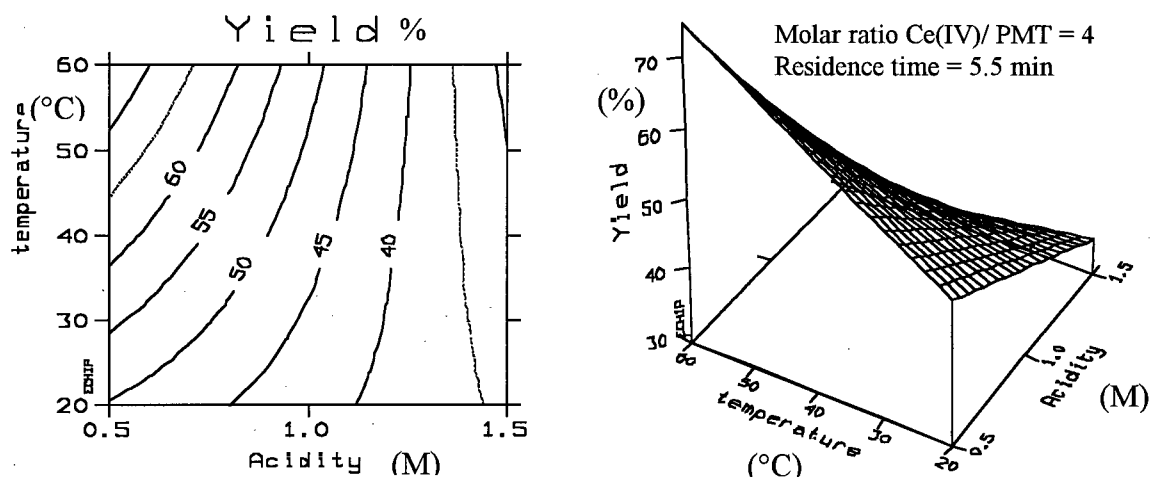
**Table 4.4:** Residuals of the first factorial design

Run	Residuals %
1-8	-4.0
9	6.6
10	9.4
11	7.6
12	8.3



**Figure 4.2:** Distribution of the residuals in the first factorial design

The model was used to show the influence of the temperature and the acidity on the synthesis of PMA (see Figure 4.3). Good yields of PMA were obtained by operating at high temperature and low acidity. It would interesting to do the same work by investigating a range of acidity from 0.2-0.8 M, and temperature from 40-80 °C.



**Figure 4.3 :** Influence of acidity and temperature on the synthesis of PMA

#### 4.1.3 Preparation of ceric solutions

The preparations of ceric solutions (used in the first factorial design) were performed with approximately 85% current efficiency for Ce(IV). During the electrolysis, the cell operating voltage varied roughly from 4.2 to 4.7 volts. The results of the electrolysis for the preparation of three ceric solutions at different acidities are presented in Appendix 9.

### 4.2 Preliminary studies for the indirect in-cell electro-oxidation of PMT in the batch recycle system

#### 4.2.1 Cathode materials

Graphite, platinum on Ebonex and stainless steel were studied as cathode materials for the mediated electro-oxidation of PMT in the batch recycle system. Before attempting to carry out the electrosynthesis of PMA, it was important to verify that the cathodes



selected could provide a good current efficiency for the electro-oxidation of cerous solutions (without organic material in the electrolyte).

A cerous solution 0.2 M MSA, 1 M Ce(tot) was oxidised in the batch recycle system with the cell arrangement presented in Figure 3.3 (section 3.1.4), with different cathode materials. The conditions of the electrolysis and calculation of current efficiencies for Ce (IV) are presented in Appendix 10. Stainless steel and platinum on Ebonex showed 85 % current efficiency, whereas 78% was obtained for a cathode of graphite. The operating voltage under the conditions investigated was around 5.7 volts. No deposition of solids was observed on the electrodes.

Since each of the three electrode materials functioned well for the electro-oxidation of cerous solutions, each of the three electrodes was investigated as potential cathode material for the electro-oxidation of PMT.

During the indirect in-cell electro-oxidation of PMT (experimental conditions, see section 3.2.2), deposition of a brown solid complex was observed on each cathode material investigated. The solid was not identified but it was probably an organic solid complex. The operating voltage reached 20 volts after a run time of 7, 4 and 3 minutes for the cathode constructed from stainless steel, graphite and platinum, respectively.

#### 4.2.2 Diaphragms

Diaphragms constructed of four different materials (asbestos cloth, Celgard 5511, Celgard 5550, and PHDC120) were investigated in this work and none was able to adequately restrict the operating voltage of the cell. A number of problems were discovered in attempting to apply diaphragms in this work and are briefly discussed in the following sections.

Although asbestos cloth is a very hydrophilic material, the thickness of the diaphragm was too high to permit a high bypassing flow rate in the cell design used (see Figure 3.4). Even if the hydraulic pressure in the cell was increased by increasing the main flow rate from 200 to 300 L/ h, the bypassing flow rate remained low (0.6 L/ h). The operating voltage reached 20 volts after a run time of 4 minutes. During the electro-oxidation of PMT, brown deposits were observed on the cathode of stainless steel as well as on the cathodic side of the asbestos cloth diaphragm. The texture of one deposit was similar to

the solid complex observed when different cathode materials were investigated (without diaphragms) during the electro-oxidation of PMT. However, another solid with a different texture (salt) was also observed. This second solid material was mainly located on the diaphragm and was postulated to be a ceric-cerous salt.

In order to explain the appearance of the second, unidentified solid deposition, a hypothesis was formed and some preliminary experiments carried out to test its validity. It was postulated that, during the electro-oxidation process, the rate of electrolyte bypassing was not high enough to replenish the  $H^+$  ions at the cathode surface for hydrogen evolution. Rough calculations were done to evaluate the minimum bypassing flow rate required to supply the cathode of  $H^+$  ions under the conditions investigated. These calculations showed that the minimum bypassing flow rate was six times higher than the flow rate observed under the experimental conditions employed in this investigation. Consequently, a decrease of acidity was probably occurring across the diaphragm from the anodic side to the cathodic side. Figure 2.8 (section 2.3) shows the solubility of ceric and cerous methanesulfonate solutions in function of the concentration of MSA. From this figure, it was reasonably assumed that the salt present on the diaphragm could be a ceric salt due to the low solubility of ceric methanesulfonate solutions at low acidity. At the end of the run, the used asbestos cloth was wetted in a 30 wt % MSA aqueous solution to dissolve the solid. The color of the deposit changed from light brown to yellow, which is the typical color of a ceric salt.

To verify the inorganic nature of the deposit, a run was carried out for the electro-oxidation of a fresh cerous solution (without organic material in the electrolyte) with a new sheet of asbestos cloth. As expected, a light brown solid was observed on the cathodic side of the asbestos cloth. As before, wetting the used diaphragm in an acidic solution of 30 wt% MSA resulted in a colour change from light brown to yellow.

Cerous and/or ceric hydroxide may be also formed on the diaphragm. These compounds have a low solubility in aqueous medium. The solubility product of cerous and ceric hydroxide in water at 25°C is roughly  $10^{-20}$  and  $10^{-48}$ , respectively [9].

Celgard 5511 and Celgard 5550 were investigated as potential separators. The operating voltage reached 20 volts after a run time of only 2 and 20 seconds for Celgard 5511, Celgard 5550, respectively. During the electro-oxidation of PMT, a lot of organic materials were present on the anodic side of these diaphragms, which probably acted as a

filter for organic chemicals. The buildup of organics plugged membrane micropores and effectively reduced the bypassing flow rate to near zero within a few seconds of operating time. It appeared, then, that these diaphragms were too effective at reducing the convection of organic material to the cathode. A second contributing mechanism may have been the fact that these membrane materials were preferentially wetted by PMT, resulting in a decrease in the ionic conductivity of these separators.

PHDC120 was substituted as a separator material with the aim of slowing the convection of organic material to the cathode without reducing the bypassing flow rate of electrolyte. Using this diaphragm, a run time of only 2 minutes was possible before an operating voltage of 20 volts was reached. A brown deposit was observed on the cathode and cathodic side of the diaphragm. A layer of brown material was also observed on the anodic side of the diaphragm though this had not affected the bypassing flowrate in the cell. From these observations, it was concluded that PHDC120 was not adequate to slow the convection of organic material to the cathode.

#### 4.2.3 Effect of current density

As described in the previous chapter (section 3.2.4), a sheet of neoprene was used to uniformly cover the cathode surface, increasing the real cathodic current density. At the higher current density, the operating voltage reached 20 volts after 3 minutes of operating time. This effective operating time was one half of that observed using the uncovered cathode. A brown solid deposit was present on the cathode surface which was exposed to the electrolyte. From these results it seemed that the major effect observed by increasing the cathodic current density was to speed the deposition of organic complex on the electrode.

A three dimensional porous cathode electrode was constructed to decrease the cathodic current density. The electro-oxidation was carried on for two hours with an average operating voltage of 11.1 volts. The results of the electrolysis of the indirect in-cell electro-oxidation of PMT are presented in Appendix 11. The graphite felt bed, the stainless steel cathode and the cathodic side of the PHDC120 diaphragm were clean and without any traces of solid deposits, whereas the anodic side of the separator was covered with a brown layer of chemicals.

To show that the current density was an important variable for the rate of solid deposition on the cathode, a run was done with a non-conductive felt made of polypropylene. In the cell, the graphite felt was simply replaced by a sheet of polypropylene felt. After a run time of 1 minute, the operating voltage was 20 volts.

#### 4.3 Electrochemical oxidation of cerous methanesulfonate solutions

The current efficiencies obtained for the second factorial design are presented in Table 4.5. Runs 1, 8 and 9 showed that the current efficiency was not much influenced by the variables studied. Consequently, it was decided that it would be unnecessary to complete the experimental plan. It was important to adjust carefully the bypassing flow rate for each run due to the side reaction involving the reduction of Ce(IV) ions on the cathode. The details of the experimental conditions for the electro-oxidation of cerous solutions are presented in Appendix 12.

**Table 4.5:** Plan and results of the second factorial design

Run	Acidity 0.2-0.8 M	Temperature 30-70°C	Current applied 10-20 A	Current efficiency % for Ce(IV)
1	-	-	-	74
2	+	-	-	
3	-	+	-	
4	+	+	-	
5	-	-	+	
6	+	-	+	
7	-	+	+	
8	+	+	+	80
9	CP	CP	CP	77
10	CP	CP	CP	78
11	CP	CP	CP	79

#### 4.4 Indirect in-cell electro-oxidation of PMT in the batch recycle system

The experimental plan for, and the results obtained from the third factorial design are presented in Tables 4.6 and 4.7. The details of the experimental conditions for each run are presented in Appendix 17. The range of acidity in the factorial design was selected in accordance with the results obtained in the first factorial design. An acidity of 0.5 M gave good results for the thermochemical batch synthesis of PMA (see section 4.1). Consequently, this concentration was chosen as center point for the range of acidity investigated in the third factorial design.

The times of the experiments were calculated such that 10 to 50 % of the PMT was oxidized to PMA, assuming 100 % yield for the synthesis of PMA. These calculations were done with the assumption that the current efficiency for Ce(IV) was 80% (see section 3.4.3).

**Table 4.6 : Plan of the third factorial design**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
	<b>Acidity</b>	<b>Temperature</b>	<b>Conversion PMT</b>	<b>Vol. ratio</b>
<b>Run</b>	<b>0.2 - 0.8 M</b>	<b>30-70 °C</b>	<b>10-50 %</b>	<b>0.03-0.06</b>
1	-	-	-	-
2	+	-	-	+
3	-	+	-	+
4	+	+	-	-
5	-	-	+	+
6	+	-	+	-
7	-	+	+	-
8	+	+	+	+
9	CP	CP	CP	CP
10	CP	CP	CP	CP
11	CP	CP	CP	CP
12	CP	CP	CP	CP

**Table 4.7 : Results of the third factorial design**

Run	Yield	Yield	Experimental Conversion
	PMA %	p-anisalcohol %	PMT %
1	28.1	7.5	11.4
2	15.2	9.4	11.2
3	11.7	5.8	9.8
4	7.8	7.1	8.8
5	21.7	4.9	38.7
6	13.6	4.6	35.4
7	7.6	5.4	32.8
8	6.5	1.3	32.5
9	15.8	5.7	21.9
10	17.9	6.6	21.6
11	16.2	5.8	24.6
12	15.9	5.9	23.9

From the low yield of PMA obtained in the factorial design, it is not surprising to observe that the experimental conversion of PMT diverges from the theoretical value projected, particularly at high conversion of PMT. The results obtained for the center points (run 9-12) showed the good reproducibility of the third factorial design. It is believed that the geometry of the cell does not affect the reproducibility of the factorial design. However, it is important to operate the cell with a constant bypassing flow rate (see section 4.3).

The main and interaction effects of the examined variables on the yield of PMA are shown in Table 4.8 . From these results, the main effects B (temperature), A (acidity) and C (experimental conversion of PMT) are important variables for the electrosynthesis of PMA. The interaction AB=CD is also significant and probably due to the interaction AB (acidity-temperature) considering the unimportant effect of D and the high confidence obtained for the main effect A and B.

**Table 4.8 :** Confidence of effects on the yield of PMA

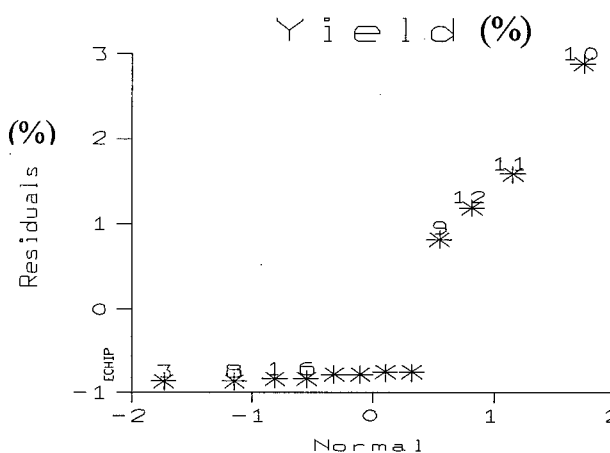
Effects	Confidence %
A = BCD	99.0
B = ACD	99.9
C = ABD	90.4
D = ABC	13.8
AB = CD	95.3
AC = BD	72.3
AD = BC	20.3

As was done for the first factorial design, an empirical model was used to evaluate the yield of PMA as a function of the main and interaction effects of the variables presented in Table 4.8 . The model is based on the results obtained for all the runs in the experimental plan and shows a good linearity with a squared correlation coefficient ( $r^2$ ) of 0.96.

Figure 4.4 shows the distribution of the residuals on a normal axis. As discussed previously, the normality assumption of the residual is not respected in this factorial design because of the influence of the center points in the empirical model. Table 4.9 shows the residuals of the empirical model. The yield of PMA is underestimated by about 1.5 % for all the runs related to the center points (run 9 to 12) whereas it is overestimated for about 0.8 % for the other runs. When there is such a disproportionate relationship between the residuals, it is not unusual to observe a non-normal distribution.

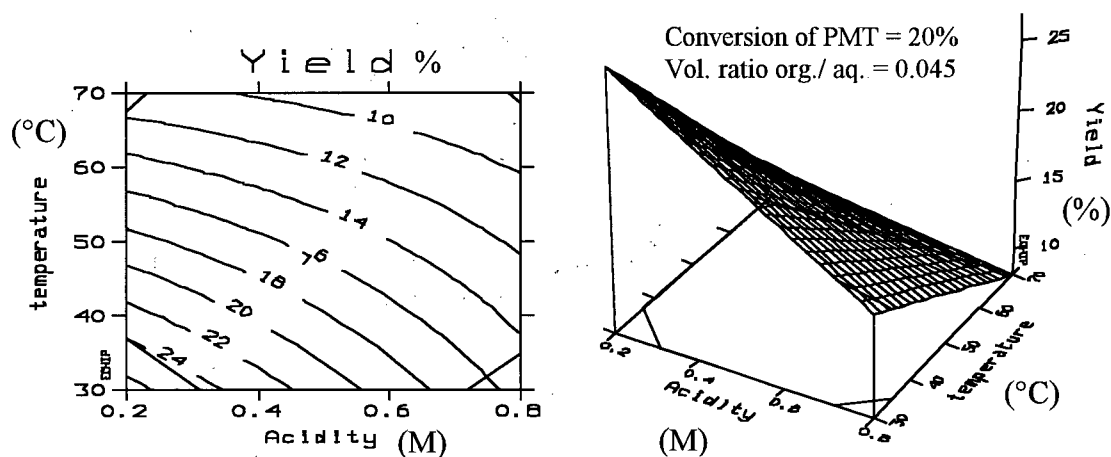
**Table 4.9 :** Residuals of the third factorial design

Run	Residuals %
1-8	-0.8
9	0.8
10	2.9
11	1.6
12	1.2



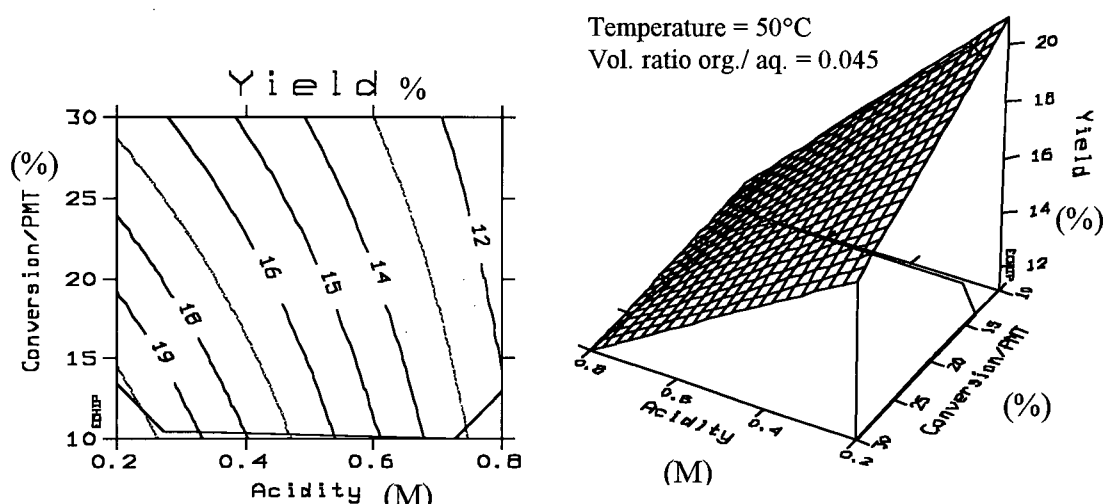
**Figure 4.4 :** Distribution of residuals in the third factorial design

The influence of temperature, acidity, and experimental conversion of PMT on the mediated in-cell electrosynthesis of PMA are presented in Figures 4.5 and 4.6. According to these figures, high yields should be obtained at low temperature, low acidity, and low conversion of PMT.



**Figure 4.5 :** Influence of acidity and temperature on the electrosynthesis of PMA





**Figure 4.6 :** Influence of acidity and conversion of PMT on the electrosynthesis of PMA

#### 4.5 Experimental uncertainties: precision and accuracy

The acidity of the solution, the concentration of Ce(IV) and the concentration of Ce(tot) were calculated at the beginning and at the end of each run. Three volumetric titrations were done for each analysis and the average value of the three determinations is presented for each factorial design in Appendix 13. There are no variations of the acidity and the concentration of Ce(tot) during the runs.

The precision on the yield of PMA, conversion of PMT, and current efficiency for Ce(IV) were evaluated from the center point data. For the first factorial design, it was assumed that the error on the conversion of PMT was the same as the error on the yield of PMA. These errors are presented in Appendix 14. The accuracy and the precision of the analytic methods were also estimated and are presented Appendix 14.

## 4.6 Economics

The operation of a thermochemical batch reactor is analogous to that of a plug flow reactor in a continuous system (assuming the same residence time and similar mixing in both reactors). Thus, the results obtained for thermochemical batch synthesis of PMA and the electrochemical oxidation of cerous solutions (1<sup>st</sup> and 2<sup>nd</sup> factorial design) can be used to give a rough estimation of the economics of the electrosynthesis of PMA in a continuous process using an indirect ex-cell system with a plug flow thermochemical reactor.

The total unit product cost (PC) for an electrochemical process is roughly calculated by the summation of the amortised capital (AC), raw materials (RM), energy (E) and a fixed proportion (5 to 15%) of the capital cost (CC) per year which covers the cost of maintenance and labour. In this work, the calculations are based only on the electrochemical process and do not consider costs associated with other ancillary chemical processes such as preparation of solutions, separation of the organic products, etc. The total product cost is then given by the following equation (assuming 5% of the capital cost for labour and maintenance):

$$PC = AC + RM + E + \frac{0.05 CC}{\theta} \quad (5)$$

where:

$$AC = \frac{CC}{\theta DP} \quad (6)$$

PC - total unit product cost (\$/ kg of PMA)

AC - amortised capital cost (\$/ kg of PMA)

RM - cost of raw materials (\$/ kg of PMA)

E - cost of energy (\$/ kg of PMA)

CC -total capital cost (\$)

$\theta$  - production rate of PMA (kg/ yr), assume 4,000,000 kg of PMA/ yr

DP - depreciation period (years), assume straight line, 5 years

To make profit, the total unit product cost has to be well below the commercial price of PMA (13 \$/ kg). The total unit product cost has been estimated at 3 \$/ kg from a report prepared by Hydro-Québec which states an expected annual profit of \$40 million for a facility producing 4,000 tons of PMA/ year [38]. In the present work, this estimate of the total unit product cost was used to evaluate the capital cost target required for making the process profitable. A lot of information and experience in electrochemical reactor design are required to estimate the capital cost of an electrochemical process. As an alternative approach, the cost of energy and raw materials can be easily calculated and used to project the capital cost target. The amortised capital cost should account for 30 to 60% of the total unit product cost.

The cost of energy (E) for the electrochemical process is calculated using the following equation:

$$E = C_{ac} SE \quad (7)$$

$C_{ac}$  - cost of electricity (\$/ kWh)

SE - specific energy of the electrochemical process (kWh/ kg of PMA)

For these estimates of energy costs, the highest PMA yield obtained in the first factorial design (run 7) was used. The detailed calculations are shown in Appendix 15. Assuming a cost of electricity of 0.06\$/ kWh, the cost of energy was calculated to be 0.32\$/ kg of PMA.

The cost of raw materials is assumed to be the cost of PMT. The acidic aqueous solution is assumed to be unaffected by the accumulation of contaminants in the aqueous phase and capable of being regenerated indefinitely for the electro-oxidation of PMT. The commercial cost of PMT is approximately 1\$/ kg. Considering 80% yield for the electrosynthesis of PMA, the cost of raw material was evaluated to 1.25\$/ kg of PMA. Using the equations 5 and 6, with PC equals to 3\$/ kg of PMA the capital cost target was

estimated to be \$23 million and the amortised capital cost at 1.15 \$/ kg of PMA. This represents 38 % of the total unit product cost, a value which falls close to the lower end of the acceptable range described above.

The capital cost target of the mediated in-cell electrosynthesis of PMA was examined using the results obtained from run 1 of the third factorial design. The cost of energy and raw material were calculated to be 1.8 \$/ kg of PMA and 3.3 \$/ kg of PMA, respectively. The cost of these factors is roughly three times the cost estimated in the indirect ex-cell process. The total of these costs (5.1 \$/ kg of PMA) is higher than the total unit PMA cost (3 \$/ kg of PMA) and consequently no estimation of the capital cost target could be done for the in-cell process to obtain a unit product cost of 3\$/ kg of PMA. Calculations are presented in Appendix 15.

There are a number of qualifications related to this economic analysis which should be discussed. It is expected that the real cost of energy would be much higher than the estimate used in this work. One reason for this is that the distillation unit operation normally used to recover organic materials such as PMA (boiling point 250°C) is energy intensive, particularly for dilute solutions. Addition of such recovery operations would result in a significant additional energy cost. As well, it is likely that the cost of raw material was underestimated. The accumulation of contaminants in the aqueous cerium solution would probably erode process efficiency and necessitate purging of some of the cerium solution.

The purpose of this section was not to investigate in detail the possibility of scaling up a continuous ex-cell organic electrosynthesis of PMA. Rather the economic evaluation provides some reference points which are useful in comparing the in- and ex-cell methods for electrosynthesis of PMA.

#### 4.7 Mass balances

For the runs in which the best yields of PMA were obtained (run 7 and run 1 for the first and third factorial design, respectively) a full organic mole balance performed on PMA and p-anisalcohol showed a loss of 20% and 65% of the converted organic reactant (PMT), respectively. For the latter case, the detailed mole balance is shown in Table 4.10.

**Table 4.10:** Organic material balance; third factorial design, run1

Initial number of moles of PMT (50 ml)	0.392
Final number of moles of PMT (11.4% conversion)	0.347
Moles of PMA produced (28.1% yield)	0.013
Moles of p-anisalcohol produced (7.5% yield)	0.003
Moles of organic matter lost	0.03
Loss of organic matter on PMT converted (%)	65*

In an effort to tighten the mass balance, a method was set up to quantify p-anisic acid by gas chromatography. Unfortunately, after a few injections, it was not possible to detect the organic acid, probably due to the oxidation of the capillary column.

A few samples from run 4 of the third factorial design were analysed at the Hydro-Québec laboratory to quantify p-anisic acid. Only a few ppm were detected by HPLC analysis for the concentration of p-anisic acid in the organic phase. Since there was a possibility that the samples decayed during storage or shipping to Quebec, the stability of the samples was verified by comparing the yield of PMA calculated from the Hydro-Québec analyses (22.6 % yield) and that presented in Table 4.6 (21.7 % yield). These values are in good agreement, and indicate that the samples were stable.

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\* % loss =  $0.03 / (0.392 - 0.347)$  or  $100 - \text{PMA yield} - \text{p-anisalcohol yield}$

Although the concentration of p-anisic acid in the aqueous phase was not analysed, it was suspected that the concentration would be insignificant. Tzedakis [42] showed that the equilibrium distribution coefficient ( $D_{\text{p-anisic acid}}$ ) of p-anisic acid between PMT and a 0.15 M cerous solution in 1 M sulfuric acid at 25°C is 103 (see Appendix 1).

$$D_{\text{p-anisic acid}} = \frac{[\text{p-anisic acid}]_{\text{org.}}}{[\text{p-anisic acid}]_{\text{aq.}}} = 103$$

By-product formation represents an obvious, and largely unquantified contributor to loss of organic matter in this study. It was observed in most runs that the colourless organic phase changed to a reddish brown colour during the indirect oxidation of PMT. The intensity of the final colour of the organic phase varied as a function of the experimental conditions investigated in both half factorial plans. It was observed that the organic phase turned particularly dark at the highest levels of reaction time, experimental conversion of PMT, acidity and temperature examined. A colour change was also observed in the aqueous cerous solution during the mediated in-cell electro-oxidation of PMT. The initially colourless cerous aqueous phase was mild to dark brown at the end of the runs.

Previous workers have also remarked on the colour change in the organic phase during the indirect ex-cell oxidation of PMT via ceric ions in a conventional batch reactor [42]. Since these workers also observed a loss of 20% in the full organic mole balance which was performed on PMA, p-anisalcohol and p-anisic acid, it was postulated that this loss was attributed to reactions leading to the synthesis of dimers (see section 2.1) and higher polymers and that these materials could be responsible for the brown coloring of the organic phase and aqueous phase.

In the present investigation, in addition to the visual observations noted earlier, the presence of secondary products was observed by GC analysis. These products were detected by changing the set temperature of the capillary column. After detection of PMT

and PMA, the temperature was increased to permit the detection of higher molecular weight compounds. At least four secondary chemicals have been detected but not identified or quantified.

Degradation of PMA, due to a long residence time during the electro-oxidation of PMT (up to 2 h and 40 min) could be responsible for the low yield of PMA (7-28%) obtained. For example, the formation of  $\text{CO}_2$  by the direct oxidation of the organic material on the anode is one of several possible degradation reactions.

#### 4.8 Modeling

Empirical models (see Appendix 7) were used to fit the experimental results obtained in the factorial designs and were useful to visualise the effect of variables on response factors. The conclusions obtained for the analysis of the factorial designs are valid strictly over the range of variables investigated, and therefore the response factor should not be extrapolated from the empirical models.

A theoretical model for the electrochemical and chemical steps would be useful to optimise the indirect electrosynthesis of PMA. Previous workers have studied the chemical step via oxidation of PMT with a ceric aqueous solution in sulfuric acid (an ex-cell method). Tzedakis [42, 43] modeled the organic oxidation step with the assumption that the reaction was purely kinetic controlled whereas Kreysa [24] based his model on film theory, assuming that the main mass transfer resistance was located in the aqueous phase. It would be interesting to combine these works to model the chemical reaction. However, a lot of information is required to prepare such a theoretical model. Distribution coefficients, mass transfer coefficients, interfacial area between phases, and kinetic constants are just a few of the parameters which have to be determined before it would be possible to model the chemical step.

Although it seems reasonable to simulate the electrochemical step using an ex-cell method, some difficulties emerge for an in-cell process. Organic by-products exert an unknown degree of influence on the electrochemical step. The current efficiency of the cell would be particularly difficult to evaluate (Ce(IV) ions react with the organic compounds) without a complete balance on the organic material. Although, it is conceivable to construct a model using parameter estimation along with the existing data from the present project, such a theoretical analysis was beyond the scope of this study.



## Chapter 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

The objective of this work was to carry out the electrosynthesis of PMA via the indirect (mediated) in-cell electro-oxidation of PMT. The electrochemical oxidation was performed with cerium methanesulfonate solutions in a batch recycle system. The chemical (oxidation of PMT) and the electrochemical (electro-oxidation of cerous methanesulfonate solutions) steps were separately examined before studying the electro-oxidation of PMT in the batch recycle system.

Four variables were investigated for the synthesis of PMA via oxidation of PMT in a batch thermochemical reactor. Acidity, temperature, molar ratio Ce(IV)/PMT, and residence time were studied in the range of 0.5-1.5 M, 20-60°C, 2-6, and 1-10 minutes, respectively. Over the range of the variables studied, acidity and the interaction acidity-temperature had the greatest influence on the yield of PMA. From an empirical model, it was concluded that the highest yield of PMA (78%) was obtained at high temperature (60°C) and low acidity (0.5 M).

During the indirect in-cell electro-oxidation process, electrode fouling problems were observed on the cathodic side of a undivided cell arrangement. It was also observed that the rate of deposition was increased with the current density applied on the cathode. A 3-dimensional porous graphite cathode (on which a porous diaphragm was installed) was deemed effective to proceed with the indirect in-cell electro-oxidation of PMT.

Three variables were investigated to evaluate the performance of the electrochemical reactor for the electro-oxidation of cerous methanesulfonate solutions. Acidity, temperature, and current applied were studied in the range of 0.2-0.8 M, 20-60°C, and 10-

20 A (superficial current densities, 1563-3125 A/ m<sup>2</sup>), respectively. The current efficiency (78%) for Ce(IV) was not much influenced by these variables.

Four variables were investigated for the electrosynthesis of PMA via oxidation of PMT in a indirect in-cell batch recycle system. Acidity, temperature, volume ratio Org./ Aq., and conversion of PMT were studied in the range of 0.2-0.8 M, 20-60°C, 0.03-0.06, and 10-30 %, respectively. Over the range of the variables studied, three important main effects influence the yield of PMA, namely temperature, acidity and conversion of PMT. The interaction acidity-temperature was also significant. From an empirical model, it was concluded that the highest yield of PMA (28%) was obtained at low temperature (30°C), low acidity (0.2 M) and low conversion of PMT (10%).

A rough economic estimation of the cost of electrosynthesis of PMA via indirect ex-cell and in-cell methods was also studied in this work. These estimates showed that, for an in-cell process, the cost of the energy and raw materials were three times higher than those for an ex-cell process. Higher costs for the in-cell process were primarily due to lower yields of PMA and higher operating voltage in the electrochemical reactor. Moreover, the aqueous methanesulfonate solutions became contaminated during the indirect in-cell electrosynthesis of PMA. This may be problematic from an economic point of view due to the cost of methanesulfonic acid and cerium carbonate.

A mole balance based on the yield of PMA and p-anisalcohol showed 20% and 65% loss of the moles of PMT converted during the preparation of PMA in the first and third factorial design, respectively. This loss was attributed to reactions leading to the synthesis of by-products, such as polymers and other unidentified degradation products. The presence of polymers was indicated by the brown coloring of the organic and aqueous phase. At least four secondary products have been detected but not identified or quantified.

## 5.2 Recommendations

The following recommendations are made for the indirect in-cell electrosynthesis of PMA:

- The rate of the electro-oxidation of PMT was limited by the rate of generation of Ce(IV) in the electrochemical reactor. It would be interesting to attempt to reduce this kinetic limitation by carrying out the same electro-oxidation process with multiple electrochemical reactors.
- The presence of organic material in the electrolyte presented a number of technical challenges for the operation of the electrochemical reactor. Better results for the electrochemical generation of Ce(IV) and the electrosynthesis of PMA could be obtained with a divided cell (separated with an ion exchange membrane). It is expected that such an arrangement would eliminate cathode fouling problems, but membrane fouling and expense may be a concern.
- The batch recycle system could be modified to a continuous process. In such a system, PMT could be injected continuously upstream from the inlet to the electrochemical reactor and removed, along with PMA, in a subsequent separator. By using such an arrangement, the concentration of organic material in aqueous phase in the electrochemical cell would remain low and fouling problems on the cathode may be avoided.
- A method should be developed to quantify the p-anisic acid by HPLC. The GC should be connected in series with a mass spectrometer to identify secondary products.
- Installation of a CO<sub>2</sub> detector to quantify the production of this gas in the process.

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## Appendix 1

### Distribution coefficient of PMA, p-anisic acid, and p-anisalcohol between PMT and an aqueous solution 1 M H<sub>2</sub>SO<sub>4</sub> and 0.15 M Ce<sub>2</sub>SO<sub>4</sub>

The variation of the distribution coefficient of PMA between PMT and an aqueous phase 0.15 M Ce<sub>2</sub>(SO<sub>4</sub>) in 1M H<sub>2</sub>SO<sub>4</sub> has been studied as a function of temperature. For these experiments, a volume of 1 cm<sup>3</sup> of PMA is distributed between 5 cm<sup>3</sup> of PMT and 20 cm<sup>3</sup> of the former aqueous phase [43].

At equilibrium, the distribution coefficient of PMA ( $D_{PMA}$ ) can be calculated by the following relationship:

$$D_{PMA} = 0.55 \exp(15.8 \times 10^3 / RT)$$

R      gas law constant, 8.31 J/((mol) (K))

T      absolute temperature (K)

$D_{PMA}$       distribution coefficient defined as follow:

$$D_{PMA} = \frac{[PMA]_{org.}}{[PMA]_{aq.}}$$

[PMA] org.      concentration of PMA in the organic phase (mol/ L).

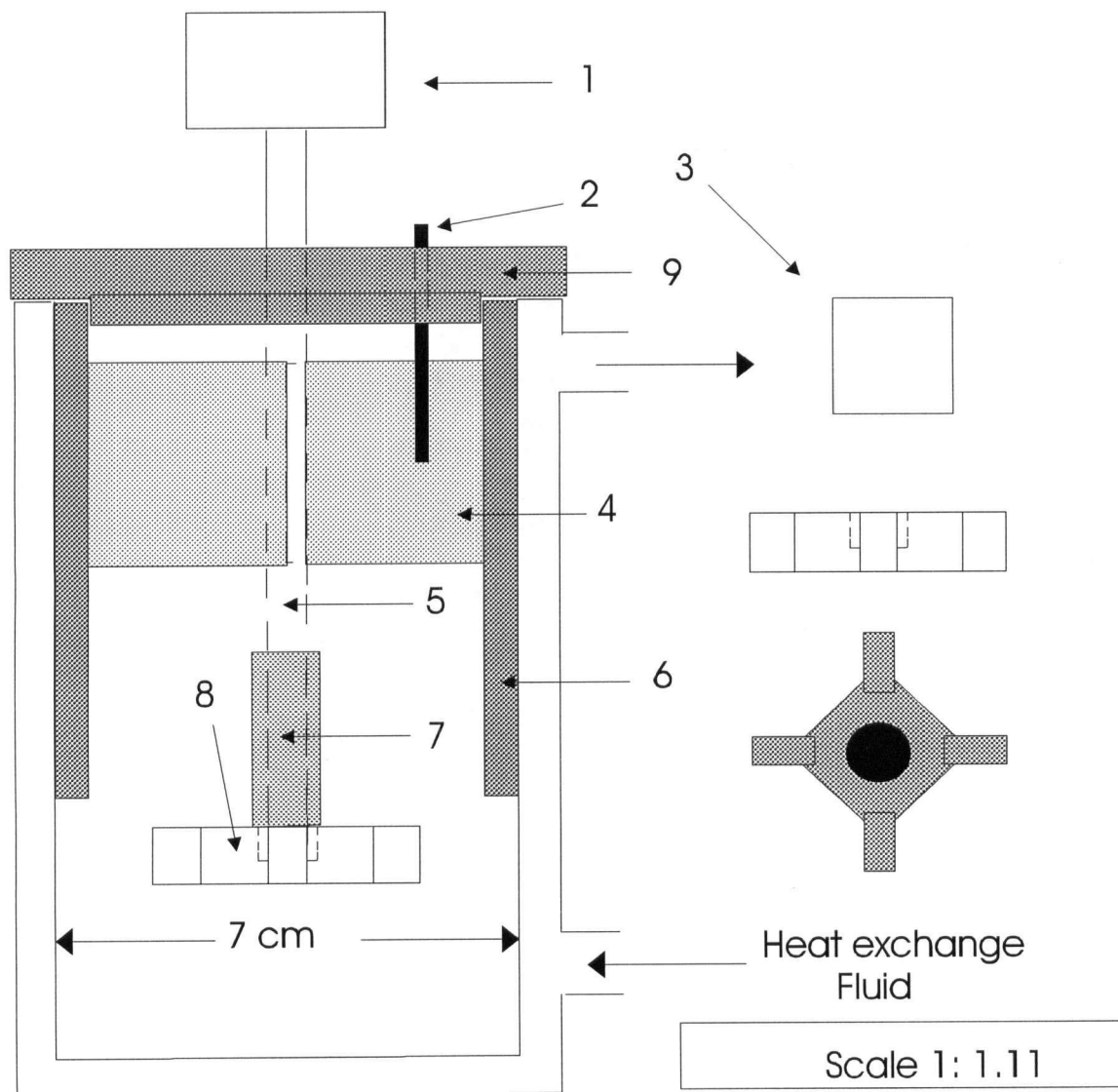
[PMA] aq.      concentration of PMA in the aqueous phase (mol/ L).

At 25 °C,  $D_{PMA}$ ,  $D_{p-anisic\ acid}$ ,  $D_{p-anisalcohol}$  were estimated at 323, 103, and 16 respectively. A second trial operated in the same conditions, with 0.1 cm<sup>3</sup> of PMA gave the same result for the distribution coefficient of PMA.



## Appendix 2

### Design of the thermochemical reactor for the oxidation of PMT



### **Legend**

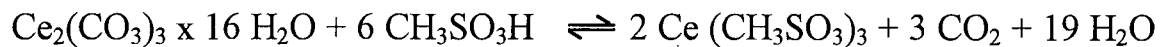
1. G.K. Heller corp. D.C Motor: 1/ 18 H.P, Torq 2.1 lb-in
2. Omega Iron Constantan thermocouple, PFA coated, 1/ 8 " diameter probe
3. Bath and circulator: Laura Thermostat, Type NB-S15
4. Baffles (plane Teflon sheet (30 x 30 x 1.5 mm))
5. Impeller made with 1/ 4 " Teflon PTFE tubing and 1/ 8" stainless rod
6. Baffles (1/ 4" PVDF rods)
7. Teflon PFA male pipe adapter (straight) 1/ 4" x 1/ 4" (OD x NPT)
8. Propeller made in PVDF
9. Teflon flange

### **Ancillary Equipment**

- A. Motor controller G.K. Heller corp: HST20-MD
- B. Omega digital display temperature indicator: model DPH6-JFI

### Appendix 3

#### Preparation of 1 L of solution 0.5 M MSA and 1 M Ce(III)



	0.5 M	3 M	1 M	1.5 M	9.5 M
+					
		0.5 M of free methane sulfonic acid			
<hr/>					
	0.5 M	3.5 M	1 M	1.5 M	9.5 M

- Mass of cerium carbonate (CC)

Advanced Material Ressources, 99% wt., cerium carbonate

1 mole of CC = 748.2 g

0.5 mole of CC = X g

**X = 374.1 g of CC**

- Mass of methanesulfonic acid (MSA)

Atochem ATO 69.5- 70.5% wt., product code 1752-40

1 mole of MSA = 96.1 g

3.5 moles of MSA = Y g

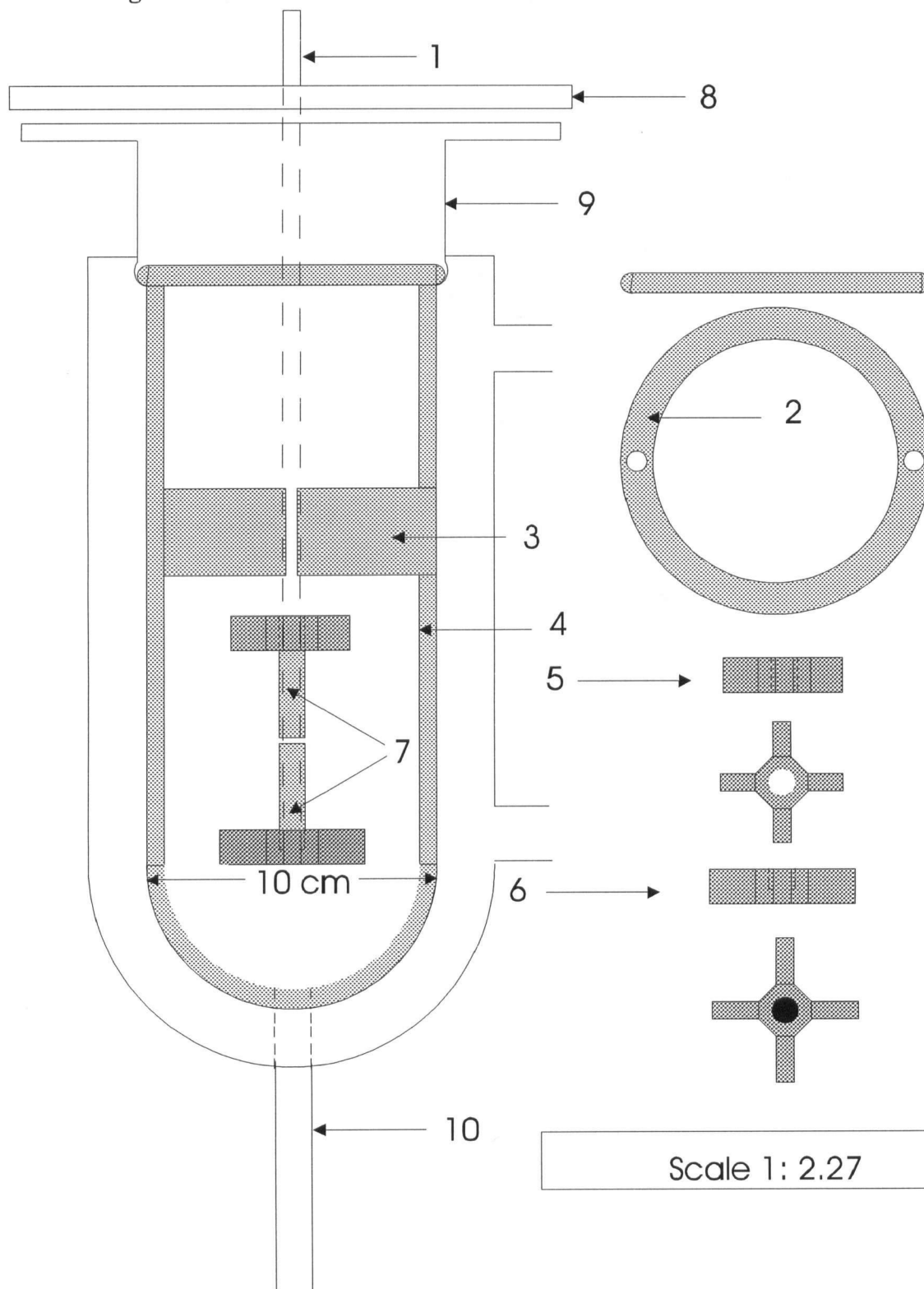
Y = 336.4 g of pure MSA

At 70 wt%

**Y = 480.6 g of MSA, 70% wt**

## Appendix 4

## Design of the thermochemical reactor for the electro-oxidation of PMT

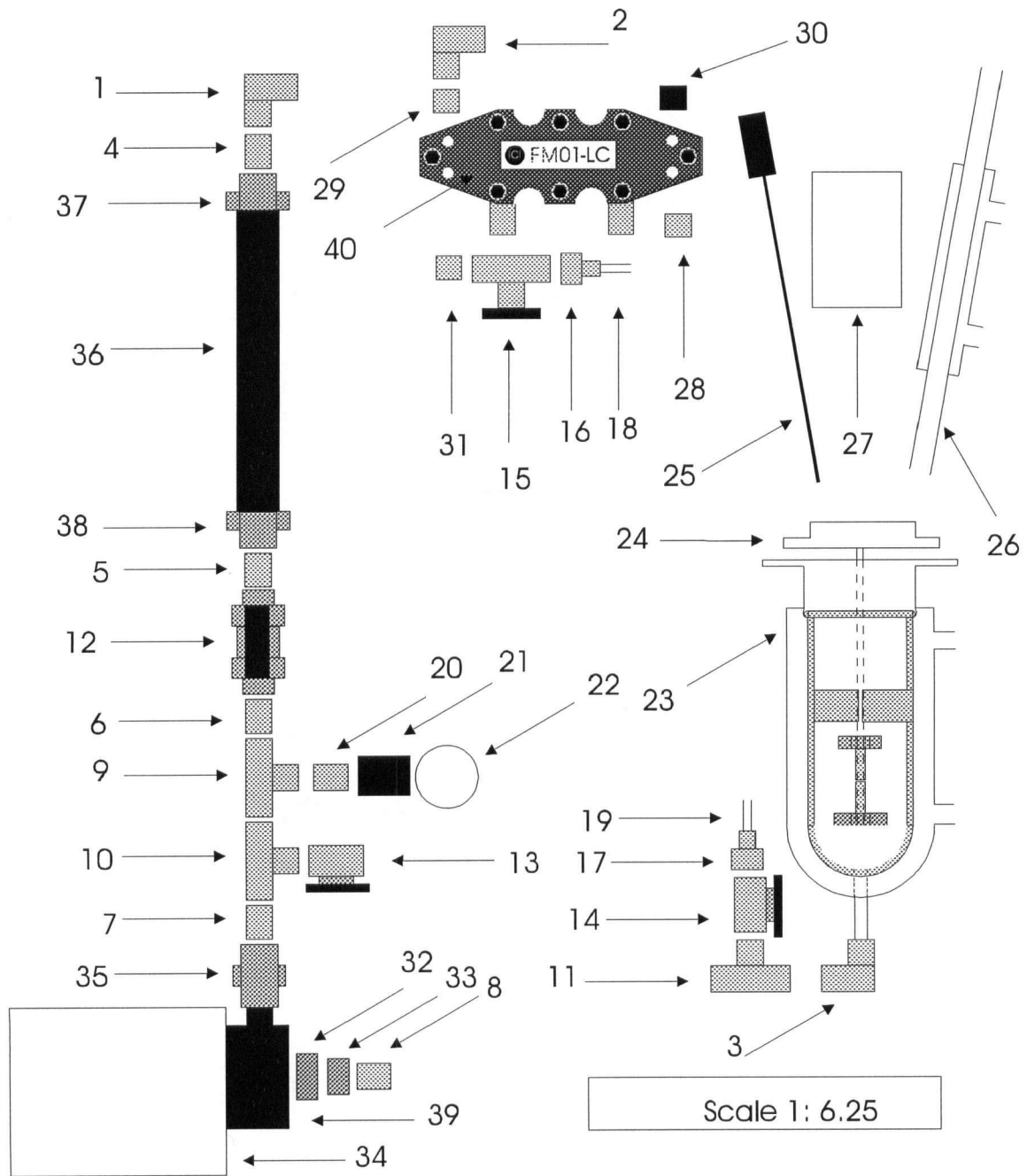


### Legend

1. Impeller made with 1/4 " Teflon PTFE tubing and 1/8" stainless rod
2. Teflon support for baffles
3. Baffles (plane Teflon sheet (30 x 42 x 1.5 mm))
4. Baffles (1/4" Teflon PTFE tubing)
5. Propeller made in PVDF
6. Propeller made in PVDF
7. Teflon PFA male pipe adapter (straight) 1/4" x 1/4" (OD x NPT)
8. Quickfit, Multi socket/ Flat flange lids, model MAF 3/52 (five sockets)
9. Quickfit, Jacketed reaction vessel, model JRV 2 L
10. Exit 1/2" OD glass pipe

## Appendix 5

### Design of the batch recycle system



### Legend

- 1-3. Teflon PFA union elbows, 1/2" x 1/2", Tubing OD
- 4-8. Teflon PFA male pipe adapters (straight), 1/2" x 1/2", Tubing OD x NPT
- 9-11. Teflon PFA union tees, 1/2", Tubing OD
12. PVDF union ball valve, 1/2" NPT connectors
- 13-14. Teflon plug valves with compression fittings, 1/2", Tubing OD
15. Teflon PFA needle valve, 1/2" x 1/2", Tubing OD x OD, for adjustment of the bypassing flow rate
- 16-17. Teflon PTFE compression fittings, 1/2" x 1/4", Tubing OD
18. Teflon PFA tubing, 1/4", Tubing OD, connecting the bypassing flowrate to the CSTR
19. Teflon PFA tubing 1/4", Tubing OD, drain line
20. Teflon PFA male pipe adapters (straight), 1/2" x 1/2", Tubing OD x NPT
21. PVDF Gauge guard, 1/4" x 1/2", NPT(F) x NPT(F)
22. Pressure gauge, 0 to 30 psi, 1/4 NPT
23. Quickfit, Jacketed reaction vessel, model JRV 2 L
24. Quickfit, Multi socket/ Flat flange lids, model MAF 3/ 52 (five sockets)
25. Omega Iron Constantan thermocouple, PFA coated, 1/8" diameter probe
26. Glass condenser, Liebeg, socket size 19/ 26
27. G.K. Heller corp. D.C Motor, 1/18 H.P, Torq 2.1 lb-in
28. Teflon PTFE male pipe adapter elbows (FM01-LC kit), 1/2" x 1/4", Tubing OD x NPT, connection port for the inlet of electrolyte (main flow)
29. Teflon PTFE male pipe adapter elbows (FM01-LC kit), 1/2" x 1/4", Tubing OD x NPT, connection port for the outlet of electrolyte
30. Teflon PTFE male pipe adapter (straight), 1/4" x 1/4", Tubing OD x NPT, plugged with a Viton seal the connection port
31. Teflon PTFE male pipe adapter elbows (FM01-LC kit), 1/2" x 1/4", Tubing OD x NPT, connection port for the outlet of bypassing flow

32. PVDF reducing bushing, 1" x 3/4", NPT x NPT(F)
33. PVDF reducing bushing, 3/4" x 1/2", NPT x NPT(F)
34. Centrifugal magnetic drive pump, Baldor Industrial motor W9-92, 0.2 hp
35. PVDF union pipe, 1/2"
36. Teflon PTFE flowmeter, 50-500 L/h
- 37-38. Teflon union pipe, 1/2", sold with the flowmeter
39. PVDF pump, magnetic drive coupling with ceramic ring magnets, viton o-ring,  
Inlet 1" NPT(F), outlet 1/2" NPT
40. FM01-LC cell from ICI

#### **Ancillary Equipment**

- A. Electric load: Sorensen DC Power Supply DCR40-25B
- B. Digital multimeter: Micronta 22-185A
- C. Digital coulometer: ESC 640, with a 100 amps resistance
- D. Bath and circulator: Laura Thermostat, Type NB-S15 with Electric relay:MGW R10
- E. Motor controller G.K. Heller corp: HST20-MD
- F. Omega digital display temperature indicator: model DPH6-JFI



## Appendix 6

### Determination of a run time for the electro-oxidation of PMT

The time of each run was calculated assuming that all the ceric produced reacted with PMT for the electrosynthesis of PMA, under an electric load of 20 A and a hypothetical current efficiency of 80% for Ce(IV) (100% yield of PMA).

The time is calculated for 10% conversion of PMT, and a Vol. ratio Org./ Aq. equals to 0.059.

#### 1) Volume of organic reactant (PMT)

$$\text{Vol. ratio Org./ Aq.} = \frac{X}{Y} = 0.059$$

$$X + Y = 1800 \text{ ml}$$

$$X = \text{Vol. of Org. (ml)}$$

$$Y = \text{Vol. of Aq. (ml)}$$

$$X = 100 \text{ ml and } Y = 1700 \text{ ml}$$

#### 2) Moles of PMT

$$\text{Molar mass (MM)} = 122.17 \text{ g/ mol of PMT}$$

$$\text{Density } (\rho) = 0.969 \text{ g/ ml of PMT}$$

$$\text{Moles of PMT} = \frac{X \rho}{\text{MM}} = 0.793 \text{ mole of PMT}$$

$$\text{Pure at 99\%} \Rightarrow \mathbf{0.785 \text{ mole of PMT}}$$

## 3) Time of the run

$$CE = \frac{n F R}{I} \quad (\text{see section 2.2.1})$$

where,  $R$  = moles of PMT converted to PMA/ Time of the run

$$T = \frac{n F W}{CE I}$$

$T$  = time of the run (s)

$n$  = 4 moles of electron per mole of PMA

$F$  = 96487 Coulombs/ mole of electron

$W$  = mole of PMT converted to PMA =  $.785 \times 0.10 = 0.0785$  mole of PMA

$CE$  = 0.80

$I$  = 20 (A)

$$\Rightarrow T = 1893 \text{ s} = 32 \text{ min}$$

## Appendix 7

### Analytic methods and reagents

#### 1. Analytic methods of the aqueous phase

##### 1.1 Determination of acidity

The concentration of MSA was determined via volumetric titrations with a standard solution of sodium hydroxide, using methyl orange as indicator.

Procedures:

- A. Depending of the concentration of MSA (0.2-1.5 M), 1 to 10 ml of the aqueous cerium solution was taken with a volumetric pipette or a syringe.
- B. The sample was poured in a 250 ml beaker, containing 100 of distilled water.
- C. Three drops of methyl orange was added to mixture.
- D. The red mixture was stirred and titrated with a standard solution of NaOH certified at 0.499- 0.501 M (using a burette 10 ml). The neutralisation was stopped when the color of the solution changed from red to yellow.

The concentration of MSA is equal to the number of millimeters of NaOH multiplied by the concentration of mol/ L of NaOH and divided by the number of millimeters of the aqueous cerium solution used in step A. The accuracy of the method was estimated at plus of minus 3 % of the exact value.

$$\text{Conc. MSA (mol/ L)} = \frac{\text{Conc. NaOH} \times \text{Vol. NaOH}}{\text{Vol. cerium aqueous solution}}$$

##### 1.2 Determination of Ce(IV) concentration

The concentration of Ce(IV) was determined by volumetric titrations with a ferrous ammonium sulfate solution (FAS), using ferroin as indicator.

Procedures:

- A. Depending on the concentration of Ce(IV) (0-1. M), 0.5 to 1 ml of the aqueous cerium solution was taken with a syringe.
- B. The sample was poured in a 250 ml beaker, containing 100 ml of a dilute sulfuric acid solution (5 vol.%).
- C. Three drops of ferroin were added to mixture.
- D. The mixture was stirred and titrated with a standard solution of FAS at 0.015 M (with a burette 10 ml). The titration was stopped when the color of the solution changed from blue to red.

The concentration of Ce(IV) is equal to the number of millimeters of FAS multiplied by the concentration of mol/ L of FAS and divided by the number of millimeters of the aqueous cerium solution used in step A. The accuracy of this method was estimated at plus or minus 3% of the exact value.

$$\text{Conc. Ce(IV) (mol/L)} = \frac{\text{Conc. FAS} \times \text{Vol. FAS}}{\text{Vol. cerium aqueous solution}}$$

The FAS solution was prepared by dissolving FAS<sub>(s)</sub> in distilled water. The FAS solution was standardised before every experiments due to the instability of the solution. The precise concentration of the titrant was determined via titration with a standard 0.1 normal ceric sulfate solution. Three titrations were done for each analyse to standardise the titrant according to the procedures used for the determination of Ce(IV) concentration. The accuracy of this method was estimated at plus or minus 2%.

### 1.3 Determination of Ce(tot) concentration

To determine the concentration of Ce(tot), the aqueous solution was first completely oxidise and then titrated with the solution FAS 0.015 M. Ammonium persulfate was used to oxidise the aqueous solution, using a few drops of silver nitrate as catalyst.

Procedures:

- A. A 0.5 ml sample of the cerium solution was taken with a syringe.
- B. The sample was poured in a 250 ml beaker, containing 100 ml of a dilute sulfuric acid solution (5 vol.%).

- C. Fifteen drops of silver nitrate 0.1 N and 3 grams of ammonium persulfate were added to mixture
- D. The mixture was stirred and boiled for 15 minutes. The solution was cooled to room temperature, and then was ready for titration according to the procedures given for the determination of Ce(IV) concentration (with a burette 50 ml).  
The accuracy of the method for the determination of Ce(tot) was estimated at plus or minus 4% of the exact value.

## 2. Analytic methods for the organic phase

PMT, PMA and p-anisalcohol were analysed by gas chromatography, using a FID detector.

**Instrument:** Gas chromatograph, Varian model 6000 with a Vista 401 Chromatograph Data System

**Column:** DB-5-15N, 15m x 0.25mm

**Detector:** FID detector, 300 °C

**Oven temperature:** 55°C to 85°C

**Injector:** 200°C

**Injection volume :** 0.5 µl

**Analysis time :** 15 minutes

### **Preparation of standards:**

Five standard solutions were prepared for each organic compound (PMT, PMA, p-anisalcohol). A factor of dilution of 150 was chosen to prepare these solutions using 1-2 dichloroethane (DCE) as solvent and n-nonane as internal standard. For instance, pure PMT has a concentration of 7.93 M. Thus, with a factor of dilution of 150, five standards were prepared with a concentration of PMT varying between 0.006 M to 0.053 M. A concentration of 0.044 M was used for the internal standard for each standard solution prepared.

Example calculations for the preparation of a standard solution 0.053 M of PMT.

First, a primary internal standard solution was prepared with a concentration of 0.554 M for n-nonane. The primary internal solution was used for the preparation of the fifteen standard solutions used for the calibration curve of PMT, PMA, and p-anisalcohol. The preparation of the primary internal standard solution was proceeded as follow:

- Put 40 ml of DCE in a 50 ml volumetric flask.
- Pipette 5 ml of n-nonane 99% and put this amount in the 50 ml volumetric flask.
- Fill up the flask with DCE (keep the temperature of the flask at 20°C).

The preparation of the standard solution 0.053 M PMT was proceeded as follow:

- Put 5 ml of DCE in a 10 ml volumetric flask.
- Pipette 0.8 ml of the primary internal standard solution and put this amount in the 10 ml volumetric flask.
- Put 68  $\mu$ l of PMT 99% and put this amount in the 10 ml flask.
- Fill up the 10 ml flask with DCE.

Each standard solution was done with a concentration of n-nonane at 0.044 M.

#### **Sample preparation:**

- Put 1 ml of DCE in a 25 ml volumetric flask.
- Pipette 2 ml of the primary internal standard solution and put this amount in a 25 ml volumetric flask.
- Put between 1 to 22 ml of the extracting solvent and put this amount in the 25 ml flask.
- Fill up the 25 ml flask with DCE.

Two samples were prepared for each extraction in the first and third factorial design. One sample for the analysis of PMT and an another for the analysis of PMA and p-anisalcohol.

Three injections were done for each sample. The accuracy was estimated at plus or minus 5 % for the determination of the concentration of PMA, 4.5 % for PMT, and 13 % for p-anisalcohol.

The GC was calibrated before each experiment. At least nine points was used for the calibration curve of each compound. The correlation coefficients for linear regressions were always higher than 0.995 for each calibration curve.

### **3. Reagents**

- Cerium carbonate 99%, ADVANCED MATERIAL RESSOURCES
- Methanesulfonic acid 69.5-70.5%, ATOCHEM (ATO)
- p-Methoxytoluene 99%, PENTA MANUFACTURING

- 1,2-Dichloroethane 99.9%, Sodium hydroxide N/ 2; Silver Nitrate 1/ 10 N, Hydrogen peroxide 30-35%, Ammonium persulfate 99.8%, Ferroin 0.025 M, FISHER
- n-Nonane 99%, SIGMA
- p-Anisaldehyde 98%, p-Anisic acid 99%, ALDRICH
- p-Anisalcohol 98% (4-Methoxybenzylalcohol), p-Methoxytoluene 99%, p-Anisic acid 99%, ALDRICH
- Ceric sulfate 1/ 10 N, ANACHEMIA
- Ammonium ferrous sulfate 98.5%, BDH

## Appendix 8

### Empirical model of the first factorial design

#### 1. First factorial plan

Run	A	B	C	D	AB CD	AC BD	AD BC	Yield % PMA
1	-	-	-	-	+	+	+	39.6
2	+	-	-	+	-	-	+	26.3
3	-	+	-	+	-	+	-	63.3
4	+	+	-	-	+	-	-	33.0
5	-	-	+	+	+	-	-	51.8
6	+	-	+	-	-	+	-	33.9
7	-	+	+	-	-	-	+	78.1
8	+	+	+	+	+	+	+	16.6
9								53.4
10								56.2
11								54.4
12								55.1

The sign of the interaction effects in the factorial design is determined by the product of the sign of the main effects involved in the interaction. For instance in run 1, the sign of the interaction AB (+) is determined by the multiplication of the sign of the main effect A (-) by the sign of the interaction B (-).

#### 2. Empirical model for a half factorial plan

$$Y = B_0 + (B_1 X_1 + B_2 X_2 + B_3 X_3 + B_4 X_4 + B_{12} X_{12} + B_{13} X_{13} + B_{14} X_{14}) / 8$$

Y = estimate of the yield of PMA

$B_0$  = Grand average of the yield of PMA obtained in the half factorial design (including center points)

$B_1, B_2, B_3, B_4, B_{12}, B_{13}, B_{14}$  = regression coefficients

$X_1, X_2, X_3, X_4, X_{12}, X_{13}, X_{14}$  = parameters equal to (1) or (-1) and related to the signs in the experimental plan for the run 1 to 8. These parameters are equal to zero for the runs 9-12.

The subscript 1,2,3,4, 12, 13, 14, represent the main and interactive effects A,B,C,D, AB or CD, AC or BD, AD or BC, respectively.

- Determination of  $B_0$

$$B_0 = \frac{(39.6 + 26.3 + 33.9 + 51.8 + 33.0 + 63.3 + 78.1 + 16.6 + 53.4 + 56.2 + 54.4 + 55.1)}{12}$$

12

$$B_0 = 46.8$$



### - Determination of $B_1$

The parameter  $B_1$  is determined by the addition of PMA yield of the runs 1 to 8, in which the yield of each run is multiplied, prior addition, by the sign of the column related to the subscript of the parameter (subscript 1  $\Rightarrow$  Column A, see the experimental plan in section 1 of this Appendix)

$$B_1 = (-)39.6 + (+)26.3 + (-)63.3 + (+)33.0 + (-)51.8 + (+)33.9 + (-)78.1 + (+)16.6 = -123$$

The parameters  $B_2, B_3, B_4, B_{12}, B_{13}, B_{14}$  are similarly determined with the sign values in the columns B, C, D, AB or CD, AC or BD, AD or BC, respectively

$$\begin{aligned} B_2 &= 39.4 \\ B_3 &= 18.2 \\ B_4 &= -26.6 \\ B_{12} &= -60.6 \\ B_{13} &= -35.8 \\ B_{14} &= -21.4 \end{aligned}$$

### - Determination of the yield of PMA in run 1 ( $Y_1$ ) via the empirical model.

$$Y = B_0 + (B_1 X_1 + B_2 X_2 + B_3 X_3 + B_4 X_4 + B_{12} X_{12} + B_{13} X_{13} + B_{14} X_{14}) / 8$$

$$Y = 46.8 + (-123 X_1 + 39.4 X_2 + 18.2 X_3 - 26.6 X_4 - 60.6 X_{12} - 35.8 X_{13} - 21.4 X_{14}) / 8$$

The sign of the parameters  $X_1, X_2, X_3, X_4, X_{12}, X_{13}, X_{14}$  are determined by the sign related to the column A, B, C, D, AB, AC, AD, in run 1.

$$\begin{aligned} X_1 &= (-1) \\ X_2 &= (-1) \\ X_3 &= (-1) \\ X_4 &= (-1) \\ X_{12} &= (+1) \\ X_{13} &= (+1) \\ X_{14} &= (+1) \end{aligned}$$

Thus,

$$Y_1 = 46.8 + \frac{[-123 (-1) + 39.4 (-1) + 18.2 (-1) - 26.6 (-1) - 60.6 (+1) - 35.8 (+1) - 21.4 (+1)]}{8}$$

$$Y_1 = 43.6$$

In the present case, the residual is equal to -4 (39.6- 43.6), as presented in Table 4.4 .

## Appendix 9

### Detailed results for the preparation of ceric solutions at different acidities

Electrolyte	Arrangement of the cell
Concentration of Ce(tot): 1.03 M	See Figure 3.3
Acidity: <b>1.52 M</b>	Anode material/ real area: Pt/ Ti 200 cm <sup>2</sup>
Initial/ final volume: 1755/ 1729 ml	Cathode material/ real area: S.S 32 cm <sup>2</sup>
Initial/ final Ce(IV) conc.: 0./ 0.10 M	
Current efficiency	Conditions
84%	Main flow rate: 200 L/ h
	Current applied: 20 A
	Temperature: 30 °C

Time min:s	Coulometer Coulombs x 10 <sup>2</sup>	Operating voltage V	Temperature °C
0	0	4.25	30
5:5	61.0	4.45	31
10:7	121.5	4.52	30
15:10	182.0	4.68	30
16:46	201.3	4.71	30

### Calculation of the current efficiency

$$CE = \frac{n F R}{I}$$

n = 1 mole of electron/ mole of Ce(IV)

F = 96487 Coulombs/ mole of electron

R = Final concentration of Ce(IV) x Initial volume of electrolyte/ time of the run

R = 0.1 M x 1.755 L/ 1006 s = 1.74 mol x 10<sup>-4</sup> of Ce(IV)/ s

I = 20 Coulombs/ s

**Electrolyte**

Concentration of Ce(tot): 1.03 M  
 Acidity: **1.00 M**  
 Initial/ final volume: 1770/ 1763 ml  
 Initial/ final Ce(IV) conc.: 0./ 0.12 M

**Arrangement of the cell**

See Figure 3.3  
 Anode material/ real area: Pt/ Ti 200 cm<sup>2</sup>  
 Cathode material/ real area: S.S 32 cm<sup>2</sup>

**Conditions****Current efficiency**

86%

Main flow rate: 200 L/ h  
 Current applied: 20 A  
 Temperature: 35 °C

Time min:s	Coulometer Coulombs x 10 <sup>2</sup>	Operating voltage V	Temperature °C
0	0	4.25	35
5:1	60.3	4.44	34
10:5	121.1	4.42	34
15:9	181.8	4.38	35
20:14	242.8	4.40	35
20:41	248.2	4.39	35

**Electrolyte**

Concentration of Ce(tot): 1.05 M  
 Acidity: **0.50 M**  
 Initial/ final volume: 1745/ 1741 ml  
 Initial/ final Ce(IV) conc.: 0./ 0.11 M

**Arrangement of the cell**

See Figure 3.3  
 Anode material/ real area: Pt/ Ti 200 cm<sup>2</sup>  
 Cathode material/ real area: S.S 32 cm<sup>2</sup>

**Conditions****Current efficiency**

86%

Main flow rate: 200 L/ h  
 Current applied: 20 A  
 Temperature: 35 °C

Time min:s	Coulometer Coulombs x 10 <sup>2</sup>	Operating voltage V	Temperature °C
0	0	4.83	35
5:2	60.4	4.92	36
10:5	121.2	4.89	34
15:10	182.1	4.85	34
18:43	224.5	4.81	34

## Appendix 10

### Detailed results of the electro-oxidation of cerous solutions with different cathode materials

Electrolyte		Arrangement of the cell	
Concentration of Ce(tot): 1.05 M		See Figure 3.3	
Acidity: 0.20 M		Anode/ real area: Pt/ Ti 200 cm <sup>2</sup>	
Initial/ final volume: 2200/ 2170 ml		Cathode/ real area: S.S 32 cm <sup>2</sup>	
Initial/ final Ce(IV) conc.: 0./ 0.053 M			
Current efficiency		Conditions	
85%		Main flow rate: 200 L/ h	
		Current applied: 20 A	
		Temperature: 40 °C	
Time min:s	Coulometer Coulombs x 10 <sup>2</sup>	Operating voltage V	Temperature °C
0	0	5.9	40
2:0	24.0	6.0	40
4:0	48.1	5.9	39
6:0	72.2	5.8	39
8:1	96.3	5.8	39
10:2	120.4	5.7	39
11:2	132.4	5.7	39

#### Calculation of the current efficiency

$$CE = \frac{n F R}{I}$$

n = 1 mole of electron/ mole of Ce(IV)

F = 96487 Coulombs/ mole of electron

R = Final concentration of Ce(IV) x Initial volume of electrolyte/ time of the run

R = 0.053 M x 2.2 L/ 662 s = 1.76 mol x 10<sup>-4</sup> of Ce(IV)/ s

I = 20 Coulombs/ s

**Electrolyte**

Concentration of Ce(tot): 1.00 M  
 Acidity: 0.19 M  
 Initial/ final volume: 2000/ 1972 ml  
 Initial/ final Ce(IV) conc.: 0./ 0.049 M

**Arrangement of the cell**

See Figure 3.3  
 Anode/ real area: Pt/ Ti 200 cm<sup>2</sup>  
 Cathode/ real area: **Graphite** 64 cm<sup>2</sup>

**Conditions****Current efficiency**

78%

Main flow rate: 200 L/ h  
 Current applied: 20 A  
 Temperature: 40 °C

Time min:s	Coulometer Coulombs x 10 <sup>2</sup>	Operating voltage V	Temperature °C
0	0	6.6	40
4:58	59.6	6.0	40
7:27	89.4	5.9	40
9:26	113.3	5.8	40
9:55	119.1	5.8	41

**Electrolyte**

Concentration of Ce(tot): 1.00 M  
 Acidity: 0.19 M  
 Initial/ final volume: 2000/ 1970 ml  
 Initial/ final Ce(IV) conc.: 0./ 0.052 M

**Arrangement of the cell**

See Figure 3.3  
 Anode/ real area: Pt/ Ti 200 cm<sup>2</sup>  
 Cathode/ real area: **Pt/ Ebonex** 64 cm<sup>2</sup>

**Conditions****Current efficiency**

84%

Main flow rate: 200 L/ h  
 Current applied: 20 A  
 Temperature: 40 °C

Time min:s	Coulometer Coulombs x 10 <sup>2</sup>	Operating voltage V	Temperature °C
0	0	5.4	40
2:29	29.9	5.6	40
5:0	60.0	5.6	41
7:30	90.0	5.5	42
9:0	108.0	5.5	41
	119.1	5.5	41

## Appendix 11

### Preliminary results for the electro-oxidation of PMT with a 3-dimensional porous graphite cathode

Electrolyte	Arrangement of the cell
<b>Aqueous phase</b>	See Figure 3.5
Initial/ final Ce(tot) conc.: 0.99/ 0.98 M	Anode/ real area: Pt/ Ti 200 cm <sup>2</sup>
Initial/ final MSA conc.: 0.20/ 0.19	Cathode: graphite felt 51 dm <sup>2</sup>
Initial/ final volume: 2100/ # ml	Uncompressed felt thickness: 8 mm
	Compression factor: 50%
	Diaphragm: PHDC120

#### Organic phase

#### Conditions

Initial volume of PMT: 100 ml

Main flow rate: 200 L/ h  
 Bypassing flow rate: 3.6 L/ h  
 Current applied: 20 A  
 Temperature: 40 °C  
 Agitation: 1000 RPM

Time min:s	Coulometer Coulombs x 10 <sup>2</sup>	Operating voltage V	Temperature °C
0	0	8.8	40
0:54	10.8	9.3	39
1:59	23.8	9.4	39
2:58	35.7	9.5	39
3:58	47.6	9.5	40
4:57	59.4	9.6	40
5:57	71.3	9.5	40
6:56	83.2	9.1	40
7:56	95.1	9.1	40
8:55	107.0	9.1	41
10:0	120.0	9.1	41
14:57	179.4	9.2	41
20:0	240.0	9.5	40
24:57	299.4	9.9	40
30:0	360.0	9.9	39
35:2	420.5	10.0	41
40:0	480.0	10.4	41
45:8	541.6	10.6	40
50:16	603.2	10.8	41
56:36	675.6	11.1	39

60:22	724.3	11.1	40
76:40	919.9	11.6	42
90:59	1091.8	12.6	39
106:34	1278.8	13.0	41
122:4	1464.8	13.4	40

---

## Appendix 12

### Detailed results for the electro-oxidation of cerous solutions in the second factorial design

**Run number:** 1

**Acidity/ Temperature/ Current applied:** 0.2 M/ 30°C/ 10 A (-,-,-)

#### Electrolyte

Initial/ final Ce(tot) conc.: 1.03/ 1.00 M  
Initial/ final MSA conc.: 0.20/ 0.20 M  
Initial/ final volume: 2150/ 2115 ml  
Initial/ final conc. Ce(IV): 0.0/ 0.049 M

#### Arrangement of the cell

See Figure 3.5  
Anode/ real area: Pt/ Ti 200 cm<sup>2</sup>  
Cathode: graphite felt 51 dm<sup>2</sup>  
Uncompressed felt thickness: 8 mm  
Compression factor: 50%  
Diaphragm: PHDC120

#### Current efficiency

74%

#### Conditions

Main flow rate: 200 L/ h  
Bypassing flow rate: 3.6 L/ h  
Current applied: 10 A  
Temperature: 30°C

Time min/ s	Coulombs	Operating voltage V	Temperature °C	Bypassing flow rate L/ h
0	0	5.1	30	
2:0	12.1	5.4	31	2.7
4:0	24.0	5.4	31	3.6
8:0	48.1	5.4	30	4.1
12:2	72.2	5.5	30	
16:4	96.3	5.4	30	3.8
20:4	120.4	5.3	30	3.6
22:4	132.4	5.2	30	
22:55	137.5	5.2	30	



**Run number: 8**

**Acidity/ Temperature/ Current applied: 0.8 M/ 70°C/ 20 A** (+,+,+)

### Electrolyte

Initial/ final Ce(tot) conc.: 1.02/ 1.00 M  
 Initial/ final MSA conc.: 0.79/ 0.76 M  
 Initial/ final volume: 2200/ 2170 ml  
 Initial/ final conc. Ce(IV): 0.0/ 0.052 M

### Arrangement of the cell

See Figure 3.5  
 Anode/ real area: Pt/ Ti 200 cm<sup>2</sup>  
 Cathode: graphite felt 51 dm<sup>2</sup>  
 Uncompressed felt thickness: 8 mm  
 Compression factor: 50%  
 Diaphragm: PHDC120

### Current efficiency

80%

### Conditions

Main flow rate: 200 L/ h  
 Bypassing flow rate: 3.6 L/ h  
 Current applied: 20 A  
 Temperature: 70 °C

Time min/ s	Coulombs	Operating voltage V	Temperature °C	Bypassing flow rate L/ h
0	0	4.3	70	
2	24.0	4.9	71	4.1
4	48.0	5.0	71	3.6
5:58	71.7	5.1	71	
7:58	95.7	5.2	69	3.9
9:58	119.5	5.3	68	
10:58	131.6	5.2	68	3.5
11:27	137.5	5.2	69	

**Run number: 11****Acidity/ Temperature/ Current applied: 0.5 M/ 50°C/ 15 A (CP,CP,CP)****Electrolyte****Arrangement of the cell**

Initial/ final Ce(tot) conc.: 1.02/ 1.02 M

See Figure 3.5

Initial/ final MSA conc.: 0.50/ 0.49 M

Anode/ real area: Pt/ Ti 200 cm<sup>2</sup>

Initial/ final volume: 2200/ 2165 ml

Cathode: graphite felt 51 dm<sup>2</sup>

Initial/ final conc. Ce(IV): 0.0/ 0.051 M

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

**Current efficiency****Conditions**

79%

Main flow rate: 200 L/ h

Bypassing flow rate: 3.6 L/ h

Current applied: 15 A

Temperature: 50 °C

Time min/ s	Coulombs	Operating voltage V	Temperature °C	Bypassing flow rate L/ h
0	0	4.3	49	
2:28	22.3	4.9	50	3.6
3:59	34.0	5.0	50	4.1
6:0	53.9	5.1	50	
8:0	72.0	5.1	50	3.6
10:0	90.0	5.2	50	
12:1	108.1	5.2	51	
14:1	126.1	5.1	50	4.2
15:1	135.1	5.1	50	
15:17	137.5	5.1	50	

**Run number:** 10

**Acidity/ Temperature/ Current applied:** 0.5 M/ 50°C/ 15 A (CP,CP,CP)

### Electrolyte

Initial/ final Ce(tot) conc.: 1.03/ 1.02 M  
Initial/ final MSA conc.: 0.51/ 0.50 M  
Initial/ final volume: 2200/ 2170 ml  
Initial/ final conc. Ce(IV): 0.0/ 0.051 M

### Arrangement of the cell

See Figure 3.5  
Anode/ real area: Pt/ Ti 200 cm<sup>2</sup>  
Cathode: graphite felt 51 dm<sup>2</sup>  
Uncompressed felt thickness: 8 mm  
Compression factor: 50%  
Diaphragm: PHDC120

### Current efficiency

78 %

### Conditions

Main flow rate: 200 L/ h  
Bypassing flow rate: 3.6 L/ h  
Current applied: 15 A  
Temperature: 50 °C

Time min/ s	Coulombs	Operating voltage V	Temperature °C	Bypassing flow rate L/ h
0	0	4.4	50	
2:0	17.9	4.7	49	4.1
3:59	35.8	4.9	49	
5:58	53.6	5.0	49	3.6
7:56	71.3	5.1	50	
9:53	89.0	5.2	49	3.8
11:52	106.9	5.4	49	
13:52	124.9	5.4	50	4.1
14:52	133.8	5.4	50	
15:17	137.5	5.4	50	

**Run number: 9****Acidity/ Temperature/ Current applied: 0.5 M/ 50°C/ 15 A** (CP,CP,CP)**Electrolyte****Arrangement of the cell**

Initial/ final Ce(tot) conc.: 1.02/ 1.01 M

See Figure 3.5

Initial/ final MSA conc.: 0.50/ 0.50 M

Anode/ real area: Pt/ Ti 200 cm<sup>2</sup>

Initial/ final volume: 2200/ 2165 ml

Cathode: graphite felt 51 dm<sup>2</sup>

Initial/ final conc. Ce(IV): 0.0/ 0.050 M

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

**Current efficiency****Conditions**

77%

Main flow rate: 200 L/ h

Bypassing flow rate: 3.6 L/ h

Current applied: 15 A

Temperature: 50 °C

Time min/ s	Coulombs	Operating voltage V	Temperature °C	Bypassing flow rate L/ h
0	0	5.4	49	
1:58	17.7	5.8	50	4.1
3:59	36.0	5.8	50	
6:0	53.9	5.8	50	
8:0	72.0	5.7	50	4.6
10:0	90.0	5.7	50	3.6
12:0	108.1	5.7	50	
14:1	126.1	5.7	50	4.1
15:1	135.1	5.6	49	
15:17	137.5	5.6	49	

### Appendix 13

Initial and final concentrations of MSA, Ce(tot), Ce(IV) for each factorial design

#### First factorial design

Run	Concentration Ce(IV) mol/ L		Concentration Ce (tot) mol/ L		Concentration MSA mol/ L	
	Initial/	Final	Initial/	Final	Initial/	Final
1	0.101	0.0453	1.05	1.04	0.50	0.50
2	0.100	0.0551	1.04	1.03	1.50	1.49
3	0.100	0.116	1.03	1.04	0.50	0.50
4	0.100	0	1.07	1.06	1.50	1.50
5	0.100	0.0326	1.04	1.04	0.51	0.50
6	0.099	0	1.03	1.04	1.53	1.50
7	0.100	0	1.04	1.05	0.50	0.50
8	0.100	0	1.03	1.03	1.52	1.48
9	0.101	0	1.03	1.02	1.01	0.99
10	0.100	0	1.04	1.04	1.01	1.00
11	0.100	0	1.04	1.05	1.01	1.00
12	0.100	0	1.04	1.04	1.00	1.00

#### Second factorial design

1	0	0.049	1.03	1.00	0.20	0.20
8	0	0.052	1.02	1.00	0.79	0.76
9	0	0.050	1.02	1.01	0.50	0.50
10	0	0.051	1.03	1.02	0.51	0.50
11	0	0.051	1.02	1.02	0.50	0.49

#### Third factorial design

1	0	0	1.05	1.03	0.20	0.20
2	0	0	1.03	1.01	0.80	0.80
3	0	0	1.02	1.02	0.20	0.20
4	0	0	1.04	1.02	0.80	0.79
5	0	0	1.02	1.01	0.20	0.22
6	0	0	1.04	1.03	0.80	0.80
7	0	0	1.04	1.03	0.20	0.20
8	0	0	0.98	0.97	0.80	0.81
9	0	0	1.01	0.99	0.50	0.50
10	0	0	1.04	1.03	0.50	0.50
11	0	0	1.03	1.03	0.50	0.50
12	0	0	1.03	1.01	0.50	0.50

## Appendix 14

### Accuracy and precision of analytic methods and factorial designs

#### 1. Analytic methods

##### Aqueous phase

	Conc. Ce(IV) mol/ L	Conc. Ce(tot) mol/ L	Conc. MSA mol/ L
Accuracy	3 %	4 %	3 %
Precision	1.5 %	1 %	1 %

##### Organic phase

	Conc. PMT mol/ L	Conc. PMA mol/ L	Conc. p-anisalcohol mol/ L
Accuracy	4.5 %	5 %	13 %
Precision	2.5 %	2.5 %	8 %

The accuracy is the difference between the experimental concentration obtained and the true or exact value. The accuracy of a method is related to the errors involved during the preparation of the samples. These errors are based on a careful specification of the uncertainties in the various primary experimental measurements. For example during the determination of Ce(tot) concentration, these errors includes the uncertainties of the burette ( $\pm 0.05$  ml), syringe ( $\pm 0.012$  ml), standard concentration of FAS ( $\pm$  mol/ L), etc.

The precision is related to the reproducibility of a analytic result. The evaluation of this kind of error is based on statistical analysis of experimental data. Three experimental titrations were done for each analysis of Ce(IV), Ce(tot), MSA concentrations. Three experimental concentrations were also obtained for each analysis of PMA, PMT, and p-anisalcohol. It has been assumed that these errors follow a normal distribution with a confidence of 95%.

#### 2. Precision of the factorial designs

Factorial plan	Conversion PMT	Yield PMA	Yield p-anasalcohol	Current efficiency for Ce(IV)
First	4.5 %	4.5 %	-	-
Second	-	-	-	2.5 %
Third	12 %	6 %	7 %	

The precision of the factorial designs has been calculated with the center points data. It has been assumed that these errors follow a normal distribution. A confidence of 95% has been respected for the precision of the results obtained in each factorial design.

## Appendix 15

### Economics

#### 1. Indirect ex-cell electrosynthesis of PMA

- Determination of the cost of energy

$$E = C_{ac} SE$$

$C_{ac}$  - cost of electricity ( 0.06\$/ kwh)

SE - specific energy of the electrochemical process (kwh/ kg of PMA)

$$\text{specific energy} \quad SE = \frac{n F V_{cell}}{3600 CE MM} \quad (1A)$$

$n$  = 4 mole of electron/ mole of PMA

$F$  = 96487 Coulombs/ mole of electron

$V_{cell}$  = operating voltage estimated from the results obtained for the preparation of ceric solutions. The electro-oxidation of a cerous solution 0.5 M MSA, 1 M Ce (tot) was carried out at 40 °C under an applied current of 20A, giving 86 % current efficiency for Ce(IV) (see Appendix 9).

$V_{cell}$  = 4.85 volts

CE = 0.86 for the production of Ce(IV)

MM = 136.2 g/ mol of PMA

To get the the specific energy in kWh/ kg of PMA, the equation (1A) has to be divided by the number of moles PMA produced by mole of Ce(IV) converted (selectivity of Ce(IV) for the production of PMA). From, the results obtained in Table 4.1, 4.2, and the information in section 3.1.3, the selectivity of PMA can be calculated as follow:

$$\text{Selectivity of PMA} = \frac{(\text{Final moles of PMA}) (4)}{\text{Initial moles of Ce(IV)} - \text{Final moles of Ce(IV)}}$$



The selectivity of PMA is multiplied by a factor 4, because 4 moles of electron react with 1 mole of PMT to synthesise one mole of PMA (see section 2.1).

Initial moles of Ce(IV) in the batch thermochemical reactor :

Initial moles of Ce(IV) = Initial Conc. Ce(IV) x Vol. of the aqueous solution

Initial moles of Ce(IV) = 0.10 M x 0.4 L = 0.040 mole

Final moles of Ce(IV) in the thermochemical reactor:

100 conversion of Ce(IV)  $\Rightarrow$  0.0 mole of Ce(IV)

Initial moles of PMT in the batch thermochemical reactor:

Molar ratio Ce(IV)/ PMT = 2.0

Initial moles of PMT = 0.04/ 2 = 0.02

Final moles of PMT in the batch thermochemical reactor:

Moles of PMT consumed = Initial moles of PMT x Conversion of PMT

Moles of PMT consumed = 0.02 x 0.533 = 0.0107

Final moles of PMT: 0.02 - 0.0107 = 0.0093

Final number PMA moles in the batch thermochemical reactor:

Final number PMA moles = (Initial PMT moles - Final number PMT moles) x Yield PMA

Final number PMA moles = (0.02 - 0.0093) x 0.78 = 0.0083

Selectivity of PMA = 0.0083 x 4/ (0.04) = 0.83

Specific energy  $SE = \frac{n F V_{\text{cell}}}{3600 CE MM} \text{ (kWh/ kg of PMA)}$

$$SE = \frac{(4) (96487) (4.85)}{(3600) (0.86) (136.2) (0.83)}$$

$$SE = 5.3 \text{ kWh/ kg of PMA}$$

The specific energy may also evaluated with the following equation:

$$SE = \frac{V_{\text{cell}} I}{3600 \text{ MM P}}$$

$$I = 20 \text{ A}$$

P = production rate of PMA (mol/ s)

The production rate of PMA is evaluated by the following equation.

$$P = \text{Production rate of Ce (IV)} \times \frac{\text{mole of PMA formed}}{\text{mole of Ce(IV) consumed}}$$

$$P = \frac{I \text{ CE}}{n F} \times \frac{\text{mole of PMA formed}}{\text{mole of Ce(IV) consumed}}$$

$$P = \frac{(20) (0.86)}{(1) (96487)} \times \frac{0.0083}{0.04} = 3.7 \times 10^{-5} \text{ mol of PMA/ s}$$

$$SE = \frac{(4.85) (20)}{(3600) (136.2) (3.7 \times 10^{-5})} = 5.3 \text{ kWh/ kg of PMA}$$

Both methods for the evaluation of the specific energy give the same result.

$$E = C_{\text{ac}} SE$$

$$E = (0.06\$/ \text{ kWh}) (5.3 \text{ kWh/ kg of PMA})$$

$$E = 0.32\$/ \text{ kg of PMA}$$

- Determination of the cost of raw material (RM)

$$RM = \frac{\text{Cost of PMT/ kg}}{\text{Yield of PMT}}$$

The yield of PMT is around 80% for the run 7 in the first factorial design. The cost of PMT is around 1\$/ kg. Thus, the cost of raw material is estimated as follow:

$$RM = 1\$ / 0.80 = 1.25 \$ / \text{kg of PMA}$$

- Determination of the capital cost

$$CP = AC + RM + E + \frac{0.05 \text{ CC}}{\theta}$$

where:

$$AC = \frac{CC}{\theta \text{ DP}}$$

CP - 3.0\$/ kg of PMA

RM - 1.25\$/ kg of PMA

E - 0.32\$/ kg of PMA

AC - amortised capital cost (\$/ kg of PMA)

CC - total capital cost (\$)

$\theta$  - 4,000,000 kg of PMA/ yr

DP - 5 years

$$CC = \frac{CP - RM - E}{\frac{1}{\theta \text{ DP}} + \frac{0.05}{\theta}}$$

$$CC = \frac{(3) - (1.25) - (0.32)}{\frac{1}{(4,000,000) (5)} + \frac{0.05}{4,000,000}}$$

$$CC = 23,000,000 \$$$

- Determination of amortised capital cost

$$AC = \frac{CC}{\theta \text{ DP}}$$

$$AC = \frac{21,600,000}{(4,000,000) (5)}$$

$$AC = 1.15 \$ / \text{kg of PMA}$$

The amortised capital cost represent 38% of the total unit product cost.

$$AC/CP = 1.15/3.0 = 0.38$$

## 2. Indirect in-cell electrosynthesis of PMA

- Determination of the cost of energy

$$\text{Specific energy} \quad SE = \frac{V_{\text{cell}} I}{3600 MM P} \quad (\text{kWh/ kg of PMA})$$

$$I = 20 \text{ A}$$

$V_{\text{cell}}$  = operating voltage during the electro-oxidation of PMT in run 1 of the third factorial design (see Appendix 17).

$$V_{\text{cell}} = 9.3 \text{ V}$$

$$MM = 136.2 \text{ g/ mol of PMA}$$

$$P = \text{production rate of PMA (mol/ s)}$$

The production rate of PMA can be evaluated with the results obtained in Table 4.7, and the experimental conditions presented in Appendix 17 for the run 1 of the third factorial design.

$$P = (\text{Initial moles of PMT} \times \text{Conversion of PMT} \times \text{Yield of PMA}) / (\text{time of the run})$$

$$\text{Conversion of PMT} = 0.11$$

$$\text{Yield of PMA} = 0.28$$

$$\text{Time of the run} = 16.0 \text{ min} = 960 \text{ s}$$

$$\text{Initial moles of PMT} = (\text{Vol. of PMT} \times \rho_{\text{PMT}}) \times 0.99 / MM_{\text{PMT}}$$

$$\text{Vol. of PMT} = 50 \text{ ml}$$

$$\rho_{\text{PMT}} = 0.969 \text{ g/ ml}$$

$$MM_{\text{PMT}} = 122.2 \text{ g/ mol of PMT}$$

$$\text{Production rate of PMT} = \frac{(50) (0.969) (.99) (0.11) (0.28)}{(122.2) (960)}$$

$$\text{Production rate of PMT} = 1.3 \times 10^{-5} \text{ mol/ s}$$

$$\text{SE} = \frac{(9.3) (20)}{(3600) (136.2) (1.3 \times 10^{-5})}$$

$$\text{SE} = 29.2 \text{ kWh/ kg of PMA}$$

Cost of energy

$$E = C_{ac} \text{ SE}$$

$$E = (0.06\$/ \text{ kWh}) (29.2 \text{ kWh/ kg of PMA})$$

$$E = 1.75\$/ \text{ kg of PMA}$$

- Determination of the cost of raw material (RM)

The yield of PMT is around 30% for the run 1 in the third factorial design. The cost of PMT is around 1\$/ kg. Thus, the cost of raw material is estimated as follow:

$$\text{RM} = 1\$/ 0.30 = 3.3 \text{ \$/ kg of PMA}$$

The addition of the cost of energy (E) and raw material (RM) of the in-cell process is higher than the total acceptable unit product cost (PC). Thus, no estimation of the total capital cost (CC) has been done for this process.

## Appendix 16

### Determination of the limit current density

The theoretical determination of  $i_L$  is evaluated by the following equation:

$$i_L = n F K_m C_{\text{Ce(III)}}$$

$C_{\text{Ce(III)}} = 1000 \text{ mol/ m}^3$  (concentration of Ce(III) in the bulk electrolyte)

$n = 1$  mole of electron/ mole of Ce(III)

$F = 96487$  Coulombs/ mole of electron

$K_m$  - mass transfer coefficient (m/ s)

- Determination of the mass transfert coefficient

$$K_m = \frac{\text{Sh } D}{d_E}$$

where; the coefficient of diffusion of Ce(III) has been estimated at  $1 \times 10^{-9} \text{ m}^2/\text{s}$  for a solution 1 M Ce(III), 3.5 M MSA at  $60^\circ\text{C}$  [15].

where;

$$d_E = \frac{2 B S}{B + S}$$

$$B = 4 \times 10^{-2} \text{ m}$$

$$S = 5 \times 10^{-3} \text{ m}$$

$$d_E = \frac{(2) (4 \times 10^{-2}) (5 \times 10^{-3})}{4 \times 10^{-2} + 5 \times 10^{-3}} = 0.00888 \text{ m}$$

where;

$$\text{Sh} = 0.82 \text{ Re}^{0.61} \text{ Sc}^{0.33}$$

$$\text{valid for } 10^2 < \text{Re} < 2 \times 10^3$$

Re - Reynolds number

$$\text{Re} = \frac{U d_E \rho}{\mu}$$

$U$  - linear velocity of fluid in the cell (m/ s)

$$U = \frac{Q}{A}$$

$Q$  - main flow rate of electrolyte in the cell ( $\text{m}^3/\text{s}$ )

$$Q = 200 \text{ L/h} \Rightarrow 5.6 \times 10^{-5} \text{ m}^3/\text{s}$$

$A$  = cross section area for main flow ( $\text{m}^2$ ) =  $B \cdot S$

$$A = (4 \times 10^{-2}) (5 \times 10^{-3}) = 0.0002$$

$$U = 0.28 \text{ m/s}$$

$\rho$  - density of the solution ( $\text{kg}/\text{m}^3$ )

$\mu$  - viscosity of the solution ( $\text{kg}/(\text{m s})$ )

The ratio ( $\mu/\rho$ ) has been estimated at  $1.51 \times 10^{-6} \text{ m}^2/\text{s}$  for a solution 1 M Ce(tot) 3.5 M MSA at 60 °C [15].

$$\text{Re} = \frac{(0.28) (0.00888)}{1.51 \times 10^{-6}}$$

$$\text{Re} = 1600$$

$Sc$  - Schimdt number

$$Sc = \frac{\mu}{\rho D}$$

$$Sc = \frac{1.51 \times 10^{-6}}{1 \times 10^{-9}}$$

$$Sc = 1500$$

$$Sh = 0.82 Re^{0.61} Sc^{0.33}$$

$$Sh = 0.82 (1600)^{0.61} (1500)^{0.33}$$

$$Sh = 825$$

Thus,

$$K_m = \frac{Sh D}{d_E}$$

$$K_m = \frac{(825) (1 \times 10^{-9})}{0.00888}$$

$$K_m = 9.3 \times 10^{-5} \text{ m/s}$$

- Determination of  $i_L$

$$i_L = n F K_m C_{Ce(III)}$$

$$i_L = (1) (96487) (9.3 \times 10^{-5}) (1000)$$

$$i_L = 8900 \text{ A/m}^2$$



## Appendix 17

### Detailed results for the electro-oxidation of PMT in the third factorial design

**Run number:** 1

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.2 M/ 30°C/ 10 %/ 0.03 (-,-,-)

#### Electrolyte

#### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.05/ 1.03 M

Initial/ final MSA conc.: 0.20/ 0.20 M

Initial/ final volume: 1750/ 1720 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

Initial volume of PMT: 50 ml

#### Conditions

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 30 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0.0	6.6	30	300	
2:0	24.0	9.9	29	300	4.6
4:0	48.0	9.7	29	300	5.0
6:0	72.0	9.5	30	300	
8:0	96.0	9.8	30	300	4.7
10:0	120.0	9.6	30	300	5.3
12:0	144.0	9.5	30	300	4.9
14:0	168.0	9.4	31	300	5.3
16:0	192.0	9.5	30	300	

**Run number: 2**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.8 M/ 30°C/ 10 %/ 0.06 (+, -, -, +)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.03/ 1.01 M

Initial/ final MSA conc.: 0.80/ 0.80 M

Initial/ final volume: 1700/ 1670 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

#### Conditions

Initial volume of PMT: 100 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 30 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	5.6	30	300	
1:59	23.8	6.0	30	300	4.4
3:59	47.8	6.2	29	300	4.2
6:0	71.9	6.3	29	320	
7:59	95.8	6.4	30	335	4.4
9:54	118.9	6.5	31	340	4.7
11:53	142.7	6.7	30	340	4.8
13:57	167.5	6.7	29	350	4.6
16:02	192.4	6.9	28	350	4.3
17:59	215.9	6.9	28	370	5.0
19:59	239.9	6.9	29	370	4.8
21:59	263.9	7.0	30	370	4.8
23:59	287.9	7.0	30	370	4.7
26:0	312.0	7.1	29	370	4.6
28:0	336.0	7.1	29	370	4.3
30:0	360.0	7.1	29	370	4.3
32:0	384.0	7.1	30	370	

**Run number: 3**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.2 M/ 70°C/ 10 %/ 0.06 (-,+, -, +)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.02/ 1.02 M

Initial/ final MSA conc.: 0.20/ 0.20 M

Initial/ final volume: 1700/ 1680 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

#### Conditions

Initial volume of PMT: 100 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 70 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0.0	5.4	70	300	
2:0	24.0	6.8	69	300	5.3
4:0	48.0	7.5	70	300	4.3
6:0	72.0	8.2	71	300	4.8
8:0	96.0	8.8	72	300	4.7
10:0	120.0	8.9	71	300	4.7
12:0	144.0	9.0	71	300	4.6
14:0	168.0	9.3	70	300	4.6
16:0	192.0	9.3	70	300	4.7
18:0	216.0	9.4	70	300	
20:0	240.0	9.5	69	300	4.8
22:1	264.2	9.7	69	300	4.7
24:1	288.2	10.0	70	300	4.8
26:2	312.3	10.1	69	300	4.6
27:56	335.1	10.2	70	300	4.7
30:2	360.3	10.5	70	300	4.8
32:1	384.3	10.5	70	300	

**Run number: 4**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.8 M/ 70°C/ 10 %/ 0.03      (+,+,,-,-)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.04/ 1.02 M

Initial/ final MSA conc.: 0.80/ 0.79 M

Initial/ final volume: 1750/ 1730 ml

See Figure 3.5

Anode: mesh Pt/ Ti      200 cm<sup>2</sup>

Cathode: graphite felt      51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

### Conditions

Initial volume of PMT: 50 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 70 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0.0	4.5	70	300	
2:0	24.0	5.3	70	300	5.4
3:59	47.8	6.0	70	300	4.8
6:0	71.9	6.5	71	300	4.7
8:59	95.9	6.6	71	300	4.6
9:59	119.9	6.6	71	300	4.7
11:59	143.8	6.6	70	300	4.7
13:59	167.9	6.7	69	300	5.0
16:0	192.0	6.7	70	300	

**Run number: 5**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.2 M/ 30°C/ 30 %/ 0.06 (-,-,+,+)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.02/ 1.01 M

Initial/ final MSA conc.: 0.20/ 0.22 M

Initial/ final volume: 1700/ 1665 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

### Conditions

Initial volume of PMT: 50 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 70 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	6.7	30	300	
2:0	24	7.3	30	300	4.6
4:0	48	7.7	29	300	4.7
6:0	72	8.1	30	300	3.8
8:0	96	8.2	30	300	5.0
10:0	120	8.3	30	300	4.6
15:0	180	8.7	30	300	5.0
20:0	240	8.7	29	300	4.4
25:0	300	8.9	30	310	4.2
30:0	360	8.8	31	310	4.7
35:0	420	8.8	30	310	4.8
40:0	480	9.0	29	310	4.8
45:0	540	9.2	30	310	4.6
50:0	600	9.1	32	310	4.9
55:0	660	9.2	28	310	4.8
60:0	720	9.4	30	310	4.8
70:0	840	9.7	31	310	4.4
80:0	960	9.9	29	320	4.7
90:0	1080	10.2	30	320	4.6
100:0	1200	10.3	32	310	5.0
110:0	1320	10.8	32	310	4.6

120:0	1440	11.0	31	310	4.8
130:0	1560	11.4	32	310	4.7
140:0	1680	11.7	28	310	4.8
150:0	1800	11.7	30	310	4.7
155:0	1860	11.8	30	310	4.6
160:0	1920	11.8	30	310	

---

**Run number: 6**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.8 M/ 30°C/ 30 %/ 0.03 (+,-,+, -)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.04/ 1.03 M

Initial/ final MSA conc.: 0.80/ 0.80 M

Initial/ final volume: 1750/ 1730 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

### Conditions

Initial volume of PMT: 50 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 30 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	5.4	30	300	
2:0	24	6.2	30	300	4.8
4:0	48	6.7	30	300	4.4
6:0	72	7.1	30	300	4.8
8:0	96	7.2	30	300	4.4
10:0	120	7.2	30	300	4.8
15:0	180	7.5	31	300	4.8
20:0	240	7.3	30	320	4.4
25:0	300	7.7	30	320	4.7
30:0	360	7.7	30	320	4.7
35:0	420	7.8	30	320	4.4
40:0	480	7.8	30	330	4.7
45:0	540	7.7	30	330	4.9
50:0	600	7.8	30	330	4.4
55:0	660	7.9	29	330	4.4
60:0	720	7.9	30	340	4.7
65:0	780	7.9	30	340	4.7
70:0	840	8.0	30	340	4.8
75:0	900	8.0	31	340	4.6
80:0	960	8.0	31	340	

**Run number: 7**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.2 M/ 70°C/ 30 %/ 0.03 (-,+,+,-)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.04/ 1.03 M

Initial/ final MSA conc.: 0.20/ 0.20 M

Initial/ final volume: 1750/ 1730 ml

See Figure 3.5

Anode: mesh Pt/ Ti

200 cm<sup>2</sup>

Cathode: graphite felt

51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

### Conditions

Initial volume of PMT: 50 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 30 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	5.4	30	300	
2:0	24	6.2	30	300	4.8
4:0	48	6.7	30	300	4.4
6:0	72	7.1	30	300	4.8
8:0	96	7.2	30	300	4.4
10:0	120	7.2	30	300	4.8
15:0	180	7.5	31	300	4.8
20:0	240	7.3	30	320	4.4
25:0	300	7.7	30	320	4.7
30:0	360	7.7	30	320	4.7
35:0	420	7.8	30	320	4.4
40:0	480	7.8	30	330	4.7
45:0	540	7.7	30	330	4.9
50:0	600	7.8	30	330	4.4
55:0	660	7.9	29	330	4.4
60:0	720	7.9	30	340	4.7
65:0	780	7.9	30	340	4.7
70:0	840	8.0	30	340	4.8
75:0	900	8.0	31	340	4.6
80:0	960	8.0	31	340	



**Run number: 8**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.8M/ 70°C/ 30/ 0.06 (+,+,+,+)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 0.98/ 0.97 M

Initial/ final MSA conc.: 0.80/ 0.81 M

Initial/ final volume: 1700/ 1675 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

#### Conditions

Initial volume of PMT: 100 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 70 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	4.8	70	300	
2:0	24	5.4	70	300	4.6
4:0	48	5.7	71	300	4.2
6:0	72	6.0	71	300	
8:0	96	6.3	70	300	5.4
10:0	120	5.6	70	300	4.9
20:0	240	6.7	70	300	4.8
30:0	360	6.9	70	300	5.4
40:0	480	7.0	70	300	5.0
50:0	600	7.1	70	300	4.8
60:0	720	7.2	68	300	4.6
70:0	840	7.5	70	300	4.8
80:0	960	7.3	71	300	
90:0	1080	7.5	68	300	4.8
100:0	1200	7.6	69	300	
110:0	1320	7.7	70	300	4.8
120:0	1440	7.7	69	300	4.6
130:0	1560	7.7	74	300	
140:0	1680	7.7	70	300	4.8
150:0	1800	7.8	70	300	4.8
160:0	1920	7.8	70	300	

**Run number:** 9

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.5 M/ 50°C/ 20 %/ 0.045 (CP,CP,CP,CP)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.01/ 0.99 M

Initial/ final MSA conc.: 0.50/ 0.50 M

Initial/ final volume: 1725/ 1700 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

#### Conditions

Initial volume of PMT: 75 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 50 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	4.6	50	300	
2:0	24	6.0	50	300	5.0
4:0	48	6.6	50	300	4.2
8:0	96	7.6	51	300	5.0
10:0	120	8.0	50	300	4.7
15:0	180	8.1	50	300	4.8
20:0	240	8.2	50	300	4.6
25:0	300	8.2	50	300	4.6
30:0	360	8.2	50	300	5.0
35:0	420	8.1	51	300	4.8
40:0	480	8.2	50	300	4.8
45:0	540	8.3	50	300	
50:0	600	8.2	49	300	
55:0	660	8.2	50	300	4.8
60:0	720	8.2	51	300	
65:0	780	8.1	51	300	4.7
70:0	840	8.2	51	300	4.7
71.45	861	8.2	51	300	

**Run number:** 10

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.5 M/ 50°C/ 20 %/ 0.045 (CP,CP,CP,CP)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.04/ 1.03 M

Initial/ final MSA conc.: 0.50/ 0.50 M

Initial/ final volume: 1725/ 1710 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

#### Conditions

Initial volume of PMT: 75 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 50 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	5.6	50	300	
2:0	24	6.0	50	300	4.8
4:0	48	6.3	50	300	5.4
8:0	96	7.1	51	300	4.6
10:0	120	7.3	50	300	4.8
15:0	180	7.5	50	300	4.6
20:0	240	7.5	50	300	4.9
25:0	300	7.6	50	300	4.9
30:0	360	7.7	51	300	4.9
35:0	420	7.9	50	300	4.9
40:0	480	8.0	50	300	4.9
45:0	540	8.1	50	300	4.9
50:0	600	8.1	50	300	4.9
55:0	660	8.3	50	300	4.9
60:0	720	8.3	50	300	4.9
65:0	780	8.4	50	300	
70:0	840	8.5	50	300	4.8
71.45	861	8.5	50	300	

**Run number: 11**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.5 M/ 50°C/ 20 %/ 0.045 (CP,CP,CP,CP)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.03/ 1.03 M

Initial/ final MSA conc.: 0.50/ 0.50 M

Initial/ final volume: 1725/ 1720 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

Initial volume of PMT: 75 ml

### Conditions

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 50 °C

Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	5.4	50	300	
2:0	24	5.7	50	300	5.4
4:0	48	5.8	50	300	4.7
6:0	72	6.0	50	300	4.4
8:0	96	6.3	50	300	4.8
10:0	120	6.6	50	300	4.8
15:0	180	7.2	50	300	4.6
20:0	240	7.2	50	300	4.9
25:0	300	7.3	50	300	4.9
30:0	360	7.4	50	300	4.9
35:0	420	7.5	50	300	4.9
40:0	480	7.5	50	300	4.8
45:0	540	7.6	50	300	4.9
50:0	600	7.6	50	300	5.0
55:0	660	7.6	50	300	5.2
60:0	720	7.7	50	300	4.6
65:0	780	7.8	50	300	4.7
70:0	840	7.8	50	300	
71.45	861	7.8	50	300	

**Run number: 12**

**Acidity/ Temperature/ Conversion of PMT/ Vol. phase ratio Org./ Aq.:**

0.5 M/ 50°C/ 20 %/ 0.045 (CP,CP,CP,CP)

### Electrolyte

### Arrangement of the cell

#### Aqueous phase

Initial/ final Ce(tot) conc.: 1.03/ 1.01 M

Initial/ final MSA conc.: 0.50/ 0.50 M

Initial/ final volume: 1725/ 1730 ml

See Figure 3.5

Anode: mesh Pt/ Ti 200 cm<sup>2</sup>

Cathode: graphite felt 51 dm<sup>2</sup>

Uncompressed felt thickness: 8 mm

Compression factor: 50%

Diaphragm: PHDC120

#### Organic phase

#### Conditions

Initial volume of PMT: 75 ml

Main flow rate: 300 L/ h

Bypassing flow rate: 4.8 L/ h

Current applied: 20 A

Temperature: 50 °C

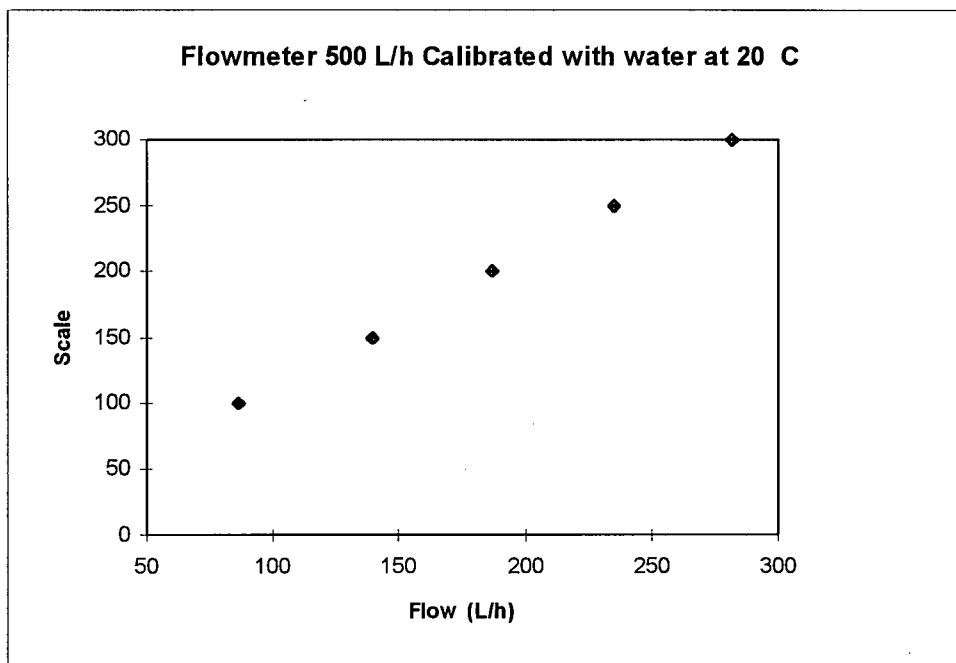
Agitation: 1000 RPM

Time min:s	Coulometer C x 10 <sup>2</sup>	Voltage V	Temperature °C	Main flow L/ h	Bypassing Flow L/ h
0:0	0	5.6	50	300	
2:0	24	6.0	50	300	5.3
4:0	48	6.3	50	300	4.9
6:0	72	6.6	50	300	5.0
8:0	96	7.1	50	300	4.6
10:0	120	7.3	51	300	4.2
15:0	180	7.6	50	300	4.8
20:0	240	7.8	49	300	4.7
25:0	300	7.8	51	300	4.7
30:0	360	8.0	49	300	4.7
35:0	420	8.1	50	300	4.8
40:0	480	8.2	51	300	4.8
45:0	540	8.2	50	300	5.0
50:0	600	8.3	50	300	5.2
55:0	660	8.4	50	300	4.8
60:0	720	8.5	51	300	4.7
65:0	780	8.6	50	300	4.7
70:0	840	8.6	50	300	4.8
71.45	861	8.6	50	300	

## Appendix 18

### Rotameter calibration

The rotameter (see Appendix 5, legend number 36) has been calibrated with water at 20°C.



Flow (L/ h)	Scale
86.2	100
139.2	150
186.9	200
185.8	200
184.2	200
235.2	250
282.0	300

$$\text{Scale} = (B) (\text{Flow}) + A$$

$$A = 9.80$$

$$B = 1.0$$

$$\text{Correlation linear coefficient: } 0.999$$