# THE DEVELOPMENT OF AN ELECTROCHEMICAL PROCESS FOR THE PRODUCTION OF PARA-SUBSTITUTED DI-HYDROXY BENZENES

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# SUMMARY

The project was concerned with the investigation of the electrochemical oxidation of various phenols, and to develop a viable reaction system for the production of the respective hydroquinones. Current production routes utilizing phenol as starting material have the limitations of using large amounts of acids, having to be stopped at low conversions and producing a mixture of the hydroguinones and catechols. Of the possible routes to the respective hydroquinones from the various phenols, the electrochemical oxidation of these phenols offers commercial and environmental advantages and hence formed the theme of the investigation. The synthetic possibilities proved to be more prevalent in a system when the electrochemical oxidation of these phenols was performed in an aqueous medium utilizing an organic co-solvent. Results obtained during this investigation made it possible to make certain predictions about the mechanism taking place. This was found to depend on the anode material used for the oxidation. The results showed that the process developed for the electrochemical oxidation of these phenols, yields mainly the para-isomers of the respective hydroquinones and benzoquinones in good yields and selectivities, with fair current efficiencies and good mass balances at high conversions. For example:

- Phenol (batch) 8 F: 34 % current efficiency, 70 % hydroquinone, 6 % catechol, 9 % benzoquinone, 9 % phenol and 94 % mass balance.
- 2-T*ert*-butylphenol (flow) 10 F: 37 % current efficiency, 65 % hydroquinone,
   33 % benzoquinone, 2 % phenol and 100 % mass balance.
- 2,6-Di-*tert*-butylphenol (flow) 11 F: 23 % current efficiency, 92 % hydroquinone, 6 % benzoquinone, 1 % phenol and 99 % mass balance.

The developed electrochemical oxidation system offers the following advantages over previous and current methods: simplified isolation and extraction procedures, smaller amounts of acid usage, reasonably selective synthesis of the *para*-isomer and a less corrosive system all at high conversions.

**KEYWORDS**:

Electrochemical oxidation, Flow cell, Batch cell, Phenol, 2-T*ert*-butylphenol, Hydroquinone, 2-*Tert*-butylhydroquinone, Benzoquinone, 2-*Tert*butylbenzoquinone

# **CHAPTER 1**

## Introduction

### 1.1 Importance of the chemical industry

In some or other form chemicals have been used since the origin of civilization. Dyes, fragrances and medicinal products were extracted from plants, and animal fats were used for the production of soap and the treatment of leather. These activities were very localized, only serving the needs of the immediate population. But as the world developed and the industrial revolution began, it was realized that there was a need for better products and more effective production procedures. This resulted in the establishment of the chemical industry.<sup>1</sup>

The first widespread commercial application of organic chemistry was the production of synthetic dyestuffs in the late 1850's. This stimulated the industry over the following 30 - 40 years to such an extent as to have side industries develop, which did not necessarily specialize in dye-related technologies. By 1900 the interest in organic synthesis, generated by the dyestuff industry, was so pronounced that a number of organic products became commercially available.<sup>2</sup>

During the past century the organic chemical industry has developed rapidly. The major reason for this was competition. Companies tried to outwit each other so as to have larger profit margins, and countries waging war on each other needed to better equip their troops to ensure victory, for example the need for rubber for gas masks and vehicles.<sup>3</sup>

During the twentieth century chemistry penetrated into everyday life and made a major improvement on both our standard of living and life expectancy. Common chemicals are polymers (plastics, synthetic rubbers and fibres), pharmaceuticals and dyes. The world as we know it, would not have been possible if it were not for the rapid development and progress made in the field of chemistry.

The chemical industry is of special importance to developing countries. When comparing the share the chemical industry has in the manufacturing industrial output, the output of a developing country like South Africa is twice that of a developed country like the UK, in fact 20  $\%^4$  compared to the 9 % of the UK.<sup>2</sup>

As mentioned previously in this section, competition had a great effect on the development of the chemical industry, due to companies producing similar products competing with each other. Since the market value of the product is fixed, the company, which has the most cost-effective production procedure, using more efficient technologies, will prosper financially over the competitor. Thus the need exists to continually improve present technologies. In this way technologies are developed which are simpler and cheaper, so as to obtain higher profit margins. Thus research is constantly performed in order to improve yields and selectivities of reactions used in industry.<sup>5</sup>

# 1.2 Development of the South African chemical industry

The South African chemical industry has a long history. Since the latter part of the nineteenth century, chemicals have been produced for a variety of industries, the main one being the mining industry.<sup>1</sup> As the country developed, the requirements of other industries such as the farming industry resulted in a diversification of the South African chemical industry.<sup>5</sup>

The chemical industry in South Africa stems from the mining industry and its need for chemicals. The discovery of diamonds (Kimberly, 1868), gold (Witwatersrand, 1886) and coalfields (Witbank and Vryheid), led to a rapid growth in the demand for explosives.<sup>1</sup> By 1911 there were three separate companies making explosives using similar feedstocks and technologies in the production of similar explosives. The only factor that kept the companies running was the export market that

resulted from the need for explosives during the First World War. Following the war, two of the companies diversified into fertilizer production. This was due to the fierce competition in the explosives industry and the need for fertilizers expressed by the agricultural industry. More diversification followed, leading to the true start of the South African chemical industry.<sup>6</sup> This diversification resulted in the production of both inorganic and organic chemicals:<sup>7</sup>

- Inorganic: acids, fertilizers and a wide variety of mining chemicals such as calcium cyanide.
- Organic chemicals: ethanol, petrol, DDT and CFC's.

Since there is no oil and little natural gas reserves in South Africa, emphasis was placed on the coal reserves in order to supply organic feedstock and fuel. This resulted in research being done in order to gasify coal. The interest in the gasification and carbonisation of coal can be traced back to 1927, when a Government White Paper recommending the development of such processes was published.<sup>8</sup>

The first process relating to this was when SATMAR (South African Torbanite Mining and Refining Company) was established in the early 1930's. This was to mine oil shale and distil and refine the resulting oil in order to produce petrol. The interest in this field was extended and rights to the German Fischer-Tropsch process were acquired. As a result of this, the Government-sponsored South African Coal, Oil and Gas Corporation Ltd. (later to become known as South African Synthetic Oil Limited, SASOL), was established on 26 September 1950. The plant SASOL One produced medium octane petrol, LPG and a range of chemicals (higher boiling waxes and oils including diesel). Due to the increased isolation of South Africa as a result of sanctions imposed by the international community during the apartheid years, the focus of this industry shifted. The shift was from the production of fuel to the establishment of a local chemical industry that could primarily be sustained from locally available raw materials derived from the oil from coal process, which was only achieved in the sixties. Further research

was done and feedstock for rubber, fertilizer and secondary chemicals were produced. This development was further driven by the establishment of plants that could aid in the achievement of this goal.<sup>8</sup> Examples of these were:<sup>8</sup>

- The establishment of the NATREF refinery in 1960, thought to be a collaboration of Total SA and the National Iranian Oil Company. The aim was to refine and crack imported petroleum to produce ethylene for plastics and pipeline gas.
- The establishment of two large oil-from-coal plants in Secunda during the early 1980's to allow self-sufficiency in fuels.

The synfuel sector serves not only the local petroleum industry as fuel source but also became the major source of chemical feedstock and intermediates.<sup>9</sup>

Since the 1990's the largest South African chemical company proved to be SASOL. Since its inception it has been innovating and diversifying itself by placing high priority on research and development. By continuous improvement to the Fisher – Tropsch process, SASOL first developed their Synthol and later the SASOL Advanced Synthol process. The primary organic products obtained from the Advanced Synthol process are almost exclusively aliphatic and include olefins (ethylene, propylene, 1-pentene, 1-hexene and 1-octene) and oxygenates (alcohols, ketones and carboxylic acids). Aromatic compounds such a phenols, cresols and xylenols are obtained in small amounts as by-products from the gasification of coal. <sup>8</sup>

#### 1.2.1 Recent Trends

More recently the South African chemical industry has been shaped by a variety of factors. Among these are changing environmental, legislative and labour conditions. All the above conditions can in some or other way be related to the changes that occurred in the country since 1994. The new government is more representative of the workers and reflects the needs and wishes of a broader society. This has affected the legislative, environmental and labour conditions

under which companies have to operate, resulting in increased production costs but better environmental and occupational safety.<sup>10,11</sup>

The adoption by the chemical community of Responsible Care,<sup>12</sup> which affects the way in which a company operates, has also shaped it to a great extent.

The admission of South Africa back into the world market also exposed the local chemical companies to competition from international chemical companies. This exposed the South African chemical industry to a variety of problems, most of these resulting from the isolation which the South African chemical industry underwent in the past. During the isolation, the South African chemical industry made an effort to protect the industry and to manufacture products geared for local use. This inward focus resulted in the construction of small-scale plants situated close to available raw material sources (oil-from-coal) and the largest domestic market (Gauteng). The size of a plant was geared to local demands and thus too small to competently compete economically with larger companies. The inland location of the plants increased costs due to raw material and product transportation costs to and from sea ports.<sup>9</sup>

The above-mentioned factors forced the South African chemical industry to look closely at its available and viable options. The SASOL-AECI joint venture Polifin (1993) is an example of this investigation. The aim of this venture was the production of monomers, polymers, cyanide, peroxide and chlor-alkali products, thus allowing the companies to compete economically in the world market.<sup>6</sup>

The resulting exposure of the South African chemical industry to the world markets was both beneficial and detrimental, in that it forced companies to either "cut their losses" and concentrate on the more economical processes in their arsenal or to go under. Examples of the rationalization and mergers carried out by some South African chemical companies are:

- SASOL:<sup>8</sup> Has at great expense undergone a variety of changes in order to improve their range of products as well as the quantity and quality of said products.
- AECI:<sup>6</sup> Has moved away from ammonia and urea production by the sale of their interests in Polfin to SASOL (1999), and the disposal of 50% of Kynoch. They are also in the process of developing a Dulux technical paints business together with PPG Industries of Pittsburg.
- Sentrachem:<sup>13</sup> Has during the 1990's been affected adversely by factors such as a prolonged drought, high interest rates, increasing international competition and devaluation in the Rand. This produced a vulnerable company, which in 1997 was successfully acquired by the Dow chemical company. Dow then carried out the following steps:
  - > The acquisition of Hoechst SA's interest in Safripol.
  - Restructuring of Agrihold into Dow Agrosciences, and moving its Middle-East-Africa headquarters from London to Johannesburg, thus showing a marked interest in the possibilities of the South African chemical industry.

The South African chemical industry is the largest of its kind in Africa. It is of substantial economic importance to the country, contributing 5% to GDP and approximately 25% of its manufacturing sales.<sup>14</sup> Whilst the industry is complex and diversified, the end products can be divided into the following:<sup>9</sup>

- Base chemicals: these include petrochemical building blocks such as ethylene, propylene, benzene, toluene and methanol. The production of these products is mainly centred on SASOL and their Sasol 1 and 2 installations.
- Intermediate chemicals: these include a variety of compounds such as solvents, phenols, plastics and rubber.
- Chemical end-products: these include processed plastics, paints, explosives and fertilizers.

Speciality chemical end products: These products tend to be lower volume but higher added-value chemicals. These include pharmaceuticals, agrochemicals, food-, fuel-, and plastics additives.

The first three categories are dominated by Sasol Chemical industries, AECI and Dow Sentrachem. There are however, a number of other companies which are active in these three sectors; they are Hoechst SA, Afrox, Bayer, Smithchem, Shell Chemicals, BASF, African Products, Engen Petroleum, ICI, Rohm and Haas and finally Omnia.<sup>9</sup>

The speciality chemical end-products field has a variety of producers and importers of these chemicals. These are: Chemserve, Fine Chemicals Corp, Noricel, Henkel, Revertex, CH Chemicals and various companies in the Protea group.<sup>9</sup>

## **1.3 Industrial electrochemical processes**

### 1.3.1 World-wide trends<sup>15</sup>

During the last few decades the chemical industry has shown an increasing interest in electrochemistry to develop electron-driven processes. Electrochemical processes are considered to be environmentally friendly and economical and a much greater selectivity over the reaction pathway can be introduced due to the control of electrochemical factors, such as current density and potential. In the field of organic electro-chemical processes, there has been tremendous growth over recent years, as can be seen by consulting the pages of specialized journals. Electrochemical processes are found frequently for the development of pharmaceuticals, perfumes, agricultural chemicals etc. The electrochemical preparation of ingredients or precursors of certain pharmaceuticals and perfumes has been of commercial interest for a number of years. However, production of organic chemicals at multi-thousand ton per year rates is only relatively recent, for example, Monsanto's adiponitrile process , the Nalco tetra-alkyl lead facility in

Texas and the Atlas Powder Company's manufacture of sorbitol and mannitol by cathodic reduction of glucose.

Electro-organic processes covering a wide range of reaction types have been investigated on a pilot plant or semi-commercial scale. For example, more than 40 electrochemical processes have been developed by the Central Electrochemical Research Institute (CECRI) in India and many of these have been commercialized on a relatively small scale.<sup>16</sup> Otsuka Chemical Company in Japan has operated several different electro-organic processes on a semi-commercial scale, using plate and frame cells at operating currents of 4500 – 6000 A.<sup>73</sup>

A summary of current electro-organic processes will be given in Section 1.3.5 but before this is dealt with, it is informative to look at electrochemical processes taking place in South Africa.

### **1.3.2 The South African situation**

In South Africa, virtually all electrochemical processes taking place centre around the electrowinning of metals, like AI, Cu, Zn etc, and the chlor alkali manufacturing industry, for producing NaOH, Cl<sub>2</sub> and H<sub>2</sub>. At present no organic electrochemical process is running in the country.<sup>18</sup>

The largest facility in South Africa is the Alusaf aluminium smelter in Richards Bay, using the Hall-Heroult process with current production figures being 636 kilotons per annum (ktpa).<sup>19</sup> In 1983 Alusaf cast its first million tons of aluminium. In 1992 Alusaf produced about 1 % of the world production of Aluminium, one third of which was exported.<sup>20</sup> In 1998 Alusaf was renamed Bayside Aluminum.<sup>21</sup>

There are 3 local producers of caustic soda, namely SASOL Polymers, NCP Chlorchem and Mondi Paper Company. Sasol Polymer has the largest production capacity followed by NCP Chlorchem and Mondi Richards Bay.<sup>18</sup>

SASOL Polymers has one diaphragm cell plant that produces about 95 ktpa of caustic soda. It also has two membrane cell plants that together produce about 72 ktpa of caustic soda. These plants, both in Sasolburg, are operated on a continuous basis. NCP Chlorchem has a single membrane cell plant at Chloorkop in Johannesburg which produces a maximum of about 84 ktpa. Mondi produces approximately 19 ktpa at their Richards Bay site, which is used internally for making paper. The total South African production capacity is therefore about 270 ktpa. By contrast the world consumption of NaOH is about 58 million tpa, which shows that the South African production is less than 0.5 % of the worlds supply. The small size of the South African industry is also reflected in individual cell room size, with South Africa's largest cell room size of 95 ktpa competing with world scale plants of 500 ktpa. In addition SASOL produces 145 ktpa Cl<sub>2</sub> and 4 ktpa H<sub>2</sub> as by-products from the electrochemical process.<sup>18</sup>

SAPPI, Mondi also produces sodium chlorate via electrolysis of brine under certain conditions in an undivided cell for production of chlorine dioxide as a bleaching agent.<sup>22</sup>

CISA (Chromium International South Africa), originally a joint venture between Bayer and Sentrachem, and later between Bayer and Dow, has a plant located in Newcastle, which produces sodium chromate, sodium dichromate (used for leather tanning chemicals) and chromic acid. The electrochemical process involves the electrolysis of a dichromate solution in a unique way and is based on the electrolysis of water to form chromic acid.<sup>22</sup>

Finally there are a number of metal winning, metal refining and recovery processes.

# 1.3.3 Organic versus inorganic electrochemical processes

In comparison with inorganic electro-synthesis, organic electrochemical work suffers from the following limitations:<sup>23</sup>

- Conductivity of solution: It is normally an order of magnitude smaller for organic solutions. This results in the need for new cell designs in order to cope with this low conductivity.
- Solvent supporting electrolyte: In inorganic work the solvent-supporting electrolyte system is normally an inorganic salt dissolved in water. For organic solutions the solvent-supporting electrolyte system is normally an organic or inorganic supporting electrolyte dissolved in an organic solvent.
- Product selectivity: The number of reactive sites on an organic molecule or ion is usually larger than for an inorganic molecule or ion, so the tendency to form by-products is more extensive in organic electro synthesis. This, along with the factors mentioned above results in more complicated product separation procedures.

The field of organic electrochemical synthesis appears more complex than inorganic synthesis; in addition few students in South Africa are exposed to the principles and possibilities of electro-organic chemistry. The electrochemical terminology is complex and often confusing, and the type of equipment used is very specialized. These reasons may account for the non-existence of electroorganic processes in South Africa.

### 1.3.4 Brief history of organic electrochemistry

Electro-organic chemistry has been known since the 1800's, when it was first found that a potential difference between two electrodes could result in a chemical reaction. Achim Von Arnim discovered that when he dipped a voltaic pile into an alcoholic beverage (either wine or beer) he observed the formation of a sour smelling product, acetic acid.<sup>24</sup>

Later, researchers like Michael Faraday, Hermann Kolbe and Otto Haber founded the field of electro-organic synthesis. Faraday was the first to determine the amount of charge necessary to convert a mole of substrate to a mole of product. This was, however, done with an inorganic copper salt. To Faraday's disappointment, the discovery did not hold true when he changed to an organic substrate namely an acetate salt; with this substrate he only formed carbon dioxide and ethane.<sup>25</sup> In 1849 Kolbe used Faraday's results as a basis for the work he did with long chain fatty acids, which resulted in carbon-carbon bond formation.<sup>26</sup> Countries like Russia, India, Japan and Germany still use this technology.<sup>27,28</sup> Kolbe's work was also used as a basis for other researchers. In 1891 they modified the Kolbe reaction and used the electrolysis of hemi-esters of dicarboxylic acids to produce di-esters having twice as many CH<sub>2</sub> groups as the parent acid. This was the first real synthetic organic electrochemical reaction.

In the period between 1920 and 1940 a number of electrochemical reactions were adopted by industry. These included the reduction of nitrobenzene to benzidine and pyridine to piperidine.<sup>29</sup> The first large-scale industrial application of electro-organic synthesis was introduced by the Atlas Powder Co. (now ICI USA Inc.) in 1937. It was the cathodic reduction of glucose to manitol and sorbitol and this process produced 1400 metric tons per year. The process was used until 1948 when it was replaced by a more economically viable catalytic hydrogenation process.<sup>29,30</sup> The next large electro-organic process adopted by industry was in 1964, when the small start-up company Nalco, based in Freeport Texas, adopted a process where tetra-alkyl lead was produced at 1500 to 1800 t per year.<sup>29,31</sup> Shortly after this, in 1965, Monsanto at Decator Alabama adopted a process for the electro-reductive coupling of acrylonitrile to adiponitrile.<sup>32,33</sup>

The above-mentioned industrial electro-organic processes were made possible by advances in a number of electrochemistry fields. Two such fields were:<sup>25</sup>

- Electrochemical analysis: techniques such as potentiostatic measurements, cyclic voltammetry and rotating disk electrodes made the understanding of reaction mechanisms possible.
- Electrochemical engineering: advances in cell design, electrode material and many other components used for electrochemical cells made it possible to develop and design better electrochemical reactors.

When considering the history of organic electrochemical processes, it can be seen that only reductive processes made it to an industrial scale; this was due to the highly corrosive environments involved during electrochemical oxidations. However, the advances mentioned above made this now also possible. Examples of these advances are shown in Table 1.4. The publication of a comprehensive literature also helped in the understanding of the field. These publications included books like Organische Elektrochemie by F.R. Fichter,<sup>34</sup> Electro-organic Synthesis, 1800-1975 by Sherlock Swann JR<sup>35</sup> and Organic Electrochemistry by Manuel M. Baizer.<sup>36</sup>

# 1.3.5 Survey of current industrial electro-organic processes

The scale of electro-organic processes varies widely, with one very large one and about a hundred smaller ones. The Monsanto process for the production of adiponitrile is running at a total capacity of more than 200000 t per year. Generally the production of a commercial electrochemical process is around 100t per year or lower. There are currently more than a 100 processes running at this scale over the world. It is expected that advances in the field of electrochemical engineering, such as minimization in cell cost, electricity consumption and optimisation of product selectivity, will pave the way for further expansion of the smaller electrochemical processes.<sup>37,38</sup>

Tables 1.1 to 1.4 illustrate the most important industrial electrochemical processes in operation, classified according to reaction type. All the information in these Tables is extracted from Robert Jansson Chemical Engineering News.<sup>39</sup>

Table1.1: Cathodic co	upling
-----------------------	--------

Туре	No	Starting material	Product	Status <sup>a</sup>	Developer
C=C	1	Acrylonitrile	Adiponitrile	С	Monsanto
C=O	2	Formaldehyde	Ethylene glycol	B/P	Electrosyn
	3	Acetone	Pinacol	Р	BASF, Bayer
	4	Acetylpyridine	A pinacol	B/P	Ciba

a : B – bench-scale development of significance, P – pilot-plant development, C – Commercial process

#### Table1.2: Anodic coupling

Туре	No	Starting material	Product	Status <sup>a</sup>	Developer
Kolbe	1	Adipic hemiesters	Sebacic diesters	P/C	BASF, USSR,
					Asahi Chemical
	2	Monomethyl	Tetradecanedioic	С	Soda Aromatic
		suberate	ester		(Japan)

a : P – pilot-plant development, C – Commercial process

Туре	No	Starting material	Product	Status <sup>a</sup>	Developer
C=C	1	Maleic acid	Succinic acid	С	CERCI
C=C	2	Benzene	1,2-	Р	Exxon,
			Dihydrobenzene		Monsanto
C≡N	3	Tetra-	Carbazoline	С	BASF
		hydrocarbazole			
C=O	4	Glucose	Sorbitol/manitol	С	Atlas
					Powder
	5	Carbon dioxide	Oxalic acid	В	DECHEMA
	6	Oxalic acid	Glyoxylic acid	С	Rhone
					Poulenc,
					Steeley
					Chemicals
COOH	7	Anthranilic acid	o-Aminobenzyl	P/C	BASF
			alcohol		
	8	salicylic acid	Salicylaldehyde	F	USSR,
					CERCI
NO <sub>2</sub>	9	Nitrobenzene	Aniline	С	CERCI
	10	o-Nitrotoluene	o-Toluidine	С	CERCI

Table1.3: Cathodic hydrogenation of carbon containing multiple bonds

a : B – bench-scale development of significance, P – pilot-plant development, C – Commercial process, F – former processes

Molecules can be coupled to synthesize products. The most important industrial example of this type of reaction is the Monsanto process mentioned above and shown as number 1 in Table 1.1. Cathodic coupling is summarized in Table 1.1 and anodic coupling in Table 1.2.

Туре	No	Starting	Product	Status <sup>a</sup>	Developer
		material			
Oxidation	1	Butane	Methyl ethyl	Р	Exxon
(2 F)			ketone		
	2	Ethyl oxalate	Ethyl	В	Royal Dutch
			isocyanate		Shell
Oxidation	3	Isobutanol	Isobutyric acid	P/C	USSR
(4 F)					
	4	Toluene	Benzaldehyde	Р	CERCI
			(redox e.g.		
			Ce <sup>4+</sup> )		
	5	p-Xylene	Tolualdehyde	Р	CERCI
			(redox e.g.		
			Ce <sup>4+</sup> )		
	6	p-Methoxy	p-Methoxy	С	BASF
		toluene	benzaldehyde		
			(via		
			methoxylation)		
Oxidation	7	p-Nitrotoluene	p-Nitrobenzoic	С	CERCI
(6 F)			acid		
	8	Benzene	Quinone	Р	Braunkohlen
					, ECRC
Hydroxylation	9	Benzene	Hydroquinone	Р	Union
					Rheinisch
	10	Naphthalene	∞-Naphthol	P/C	BASF
			(via		
			acetoxylation)		

Table1.4: Anodic functionalization (oxidation)

a : B – bench-scale development of significance, P – pilot-plant development, C – Commercial process

Reduction reactions, involving cathodic hydrogenation of carbon compounds, containing multiple bonds, are shown in Table 1.3. Oxidation reactions, describing anodic conversion of functional groups, are shown in Table 1.4., and some of these reactions are represented in equations 1.1 to 1.4, the number preceding the reaction number refers to the table no of the appropriate example in Table 1.4



In Equations 1.1 to 1.4 the F value is the amount of faradays per mole for the particular reaction, which is the same as the number of electrons per molecule required.

## **1.4 The practice of electrochemical synthesis**

In this section the practical aspects of electrochemistry over conventional chemical methods will be discussed, along with the various approaches to perform electrochemical reactions.

# 1.4.1 Electrochemical versus conventional chemical methods

Every successful chemical reaction involving oxidation or reduction, should have an electrochemical equivalent, whilst the opposite of this statement should also be true. At present this is not the case, the reason being that in many cases suitable chemical redox reagents have not yet been discovered. In electrochemistry, the conditions can be as forcing or as mild as required; this is normally governed by the potential at which the working electrode operates.<sup>40</sup>

Electrochemistry has several advantages and disadvantages when compared to conventional chemical techniques. These are as follows: <sup>,23,29,41,42,40</sup>

- Reactor setup: Electrochemical reactors are more expensive than stirred tank reactors. On the other hand electrochemical reactors lend themselves better to automation; this is due to easier control of the electrical parameters.
- Utilities: a large amount of electricity is used in electrochemical operations; generally one uses complex cells, especially for continues-flow work.
- Environmentally: Electrochemistry is viewed as a clean method. This is because there is improved management of potential pollutants, as well as possible minimization of toxic and hazardous reagents. This is achieved by the regeneration of redox reagents, (as in indirect oxidation using Ce<sup>4+</sup>) resulting in minimization of waste.
- Safety: Electrochemistry affords the ability to localise the generation of extreme conditions to only the cell, thus minimizing the risks involved in plant operations. Examples of this are the in-situ generation of hydrogen peroxide

and lithium aluminium hydride. The reactions are also operated under milder conditions (temperature and pressure).

- Reaction: Electrochemistry affords better control over reaction rate. In many cases it also reduces the number of reaction steps and allows novel chemical transformations to be performed. The electrochemical production of quinone from benzene is an example of a decrease in the number of reaction steps required when compared to conventional methods. The reactions are shown in Equations 1.5 to 1.8 below.
  - Electrochemical process

$$+ 2H_2O \longrightarrow 0 + 6H^+ + 6e^-$$
(1.5)

- Conventional process
  - The oxidation and nitration of benzene to nitrobenzene (Equation 1.6):



Reduction of nitrobenzene to aniline (Equation 1.7):



• Oxidation of aniline to quinone with chromic acid (Equation 1.8):



- Product quality: There is normally an improvement in product quality. This is due to the fact that the selectivity of electrochemical reactions is normally high and there is less and, more specifically, a smaller variety of impurities present in electrochemical processes as compared to conventional methods.
- Convenience in work-up: The reactions generally yield fewer and less varied impurities due to improved selectivity. Separation of chemical oxidants or reductants is also eliminated from the work-up procedure if allowance is made for the supporting electrolyte. All these factors contribute to processes which are more convenient to work up.
- Cost: Neglecting the initial cost of equipment, it is normally cheaper to run a electrochemical process than a conventional one. This is possible since the reagents used are electrons and electrons are normally considerably cheaper than chemical reagents, especially in a country where electricity is very cheap.

Considering these factors it is possible to conceive a process where it will be more economical to perform the reaction electrochemically than it will be to perform it using conventional methods.

### 1.4.2 Industrial considerations

For an industrial electrochemical process to be developed, the following guidelines should be followed:

General:42

- Processes that have effective catalytic procedures should be avoided.
- Processes that result in products which are currently being phased out in industry, should not be considered.
- There is a definite advantage to manufacturing products with high molecular mass.
- Processes where more than 8 electrons are transferred per molecule should be avoided.
- The process being considered should yield high current efficiencies, yields and selectivities.

Along with the above, BASF, a large German company, also recommends the following:<sup>43</sup>

- Electrode service life  $\geq$  4000hr.
- Membrane service life  $\geq$  8000hr.
- Current efficiency  $\geq$  75%.
- Concentration of product in final electrolyte  $\ge 8\%$ .
- Simple product isolation.

### **1.4.3 Direct versus Indirect Electron transfer**

The main difference between these two electrochemical procedures is with regards to the mechanism of electron transfer. <sup>25,29,42,44</sup>

- Direct electrochemistry: The transfer of the electrons takes place heterogeneously across the electrode / solution interface.
- Indirect electrochemistry: The electron transfer takes place between a mediator and a substrate. The electron transfer can be either hetero- or homogeneous, since the nature of the mediator can differ.

#### 1.4.3.1 Direct electron transfer<sup>45</sup>

Since the electron transfer takes place heterogeneously across the electrode solution interface, it is easy to determine the potential at which the substrate undergoes an electrochemical reaction. This is determined through electrochemical analysis such as cyclic voltammetry.

The mechanism of direct electron transfer is explained below:

- Migration of the substrate to the electrode surface.
- Adsorption of the substrate on the electrode surface.
- Electron transfer between the electrode and the substrate, forming a radical.
- Either, reaction of the generated radical followed by desorption of the product or desorption of the radical followed by further reaction to a product.

Tables 1.1 – 1.4 gives many examples of direct electron transfer processes.

#### 1.4.3.2 Indirect electron transfer

In this process a mediator is used which selectively oxidises or reduces the substrate to the target compound. This mediator is then regenerated electrochemically either in-cell, or ex-cell after separation of the organic phase.

An example is the conversion of anthracene to anthraquinone via electrogenerated chromic acid.<sup>46,47,48</sup> A concentrated solution of chromium(III) in aqueous sulphuric acid is partly oxidized to chromic acid at a PbO<sub>2</sub> anode (Equation 1.9):

$$2 \operatorname{Cr}^{+3} + 7 \operatorname{H}_2 O \longrightarrow \operatorname{Cr}_2 O_7^{-2} + 14 \operatorname{H}^+ + 6 \operatorname{e}^-$$
(1.9)

and the dichromate is then reacted with anthracene (Equation 1.10):



This reaction takes place in a separate reactor, and the above process has been carried out for over 50 years. Recent improvements have been introduced where the electrolysis is performed in a membrane cell and the chemical step is carried out by allowing the chromic acid to trickle through a column of solid anthracene.

Another example is the use of  $Ce^{4+}$  as mediator in the selective oxidation of various toluenes to the respective benzaldehyde, as shown in Table 1.4 (entries 4, 5). Here the  $Ce^{3+}$ , formed upon oxidation of the toluene, is regenerated electrochemically to form  $Ce^{4+}$  and recycled to the reactor.<sup>49</sup>

Mediators can be either inorganic or organic in nature, and operate homogeneously ( $Ce^{4+}$ ) or heterogeneously, when the mediator is bound to the electrode (MnO<sub>2</sub>, PbO<sub>2</sub>).<sup>50</sup>

There are several advantages of indirect electron transfer:

- The redox catalyst can have a high solubility in water, allowing electrochemistry to be carried out at high current densities in an aqueous electrolyte.
- Multiphase procedures can lead to straightforward product isolation.
- Since the redox reagent is recycled, the problems of using toxic reagents are reduced and large volumes of unwanted solid or solution effluent are not produced.

### **1.4.4 Constant current and constant potential electrolysis**

Electrochemical reactions can be carried out using one of two procedures: constant current and constant potential electrolysis.<sup>23,51</sup>

- Constant potential electrolysis: This reaction is carried out as the name suggests. The potential of the working electrode is kept constant with respect to a reference electrode. As the reaction proceeds the cell current gradually decreases, since the amount of electro-active species at the potential decreases.
- Constant current electrolysis: The current is kept constant throughout the reaction, whilst the potential of the electrolysis system increases gradually as the reaction proceeds, as the concentration of species with lower oxidation potentials decrease.

In constant potential and constant current electrolysis the amount of charge sent through the reaction mixture can be determined using Equation 1.11 and 1.12 respectively.<sup>51</sup>

$$Q = \int_0^\infty I dt = nFN \tag{1.11}$$

$$Q = \int_0^\infty I dt = It = nFN \tag{1.12}$$

Referring to Equations 1.11 and 1.12 the symbols can be explained as follows:

- Q is the quantity of electricity (in coulombs passed through the cell).
- I is the current (Ampere).
- n is the total number of electrons involved per molecule.
- t is time (seconds).
- F is the Faraday constant; it is the charge needed (96500 coulombs) per mole of substrate to effect the electrochemical reaction, assuming there is a one electron change.
- N is the number of moles of substrate initially present.

These two processes have several advantages and disadvantages when compared to each other. These are as follows:<sup>23</sup>

- Complexity of equipment: The electronic equipment to both effect and monitor the electrolysis in constant current electrolysis is much less complicated and cheaper than that needed for constant potential electrolysis.
- Selectivity: Constant potential electrolysis is much more selective than constant current electrolysis. With proper understanding of the specific reaction being investigated, the selectivity of constant current electrolysis can approach that of constant potential electrolysis.

Taking the above into account, it is not difficult to see why most of the electrolysis procedures carried out in industry today are done using constant current electrolysis.

### 1.4.5 Divided versus undivided

Electrolysis procedures, whether direct or indirect, can be carried out in the simplest way using one of two methods: undivided (one compartment) or divided (two compartments). These are explained below:<sup>23,25</sup>

- Undivided: Here there is no separation between the anode (oxidation) and the cathode (reduction), i.e. the two electrodes are immersed in the same solution.
- Divided: Here there is a physical separation (micro-porous divider) between the anolyte and the catholyte. This prevents products, formed at one electrode, from migrating to the other where it can undergo additional reactions.

There are several advantages and disadvantages of using divided and undivided processes in electrochemical synthesis. These are mentioned below:<sup>23,25</sup>

 Cell design: This is much less complicated in undivided processes than it is in divided processes. The separator used in the divided cell can also cause problems: the cell resistance is increased and this problem could be magnified if fouling of the separator occurs. When scaling-up, it is known that an undivided reactor is cheaper than a divided reactor by an order of magnitude.

Reactions: Divided cells prevent the occurrence of side reactions, which can occur at the counter electrode, and which can interfere with the reaction in question. The divided cell does, however, facilitate the possibility of performing paired synthesis, where two distinctly separate reactions could be carried in the same reactor at the same time.<sup>52</sup>

The separators used in divided electrolysis can be of two kinds: <sup>23,25</sup>

- Inert physical separation: These separators normally consist of sintered glass or micro-porous polypropylene and only prevent substantial mixing of the anolyte and the catholyte.
- Ion exchange separators: These separators consist of polymers, which have functional groups bonded to the polymer itself; an example of this is Nafion. These separators prevent the mixing of the anolyte and the catholyte solutions. The flow of charge is facilitated by ion exchange reactions, which take place between the solution and the membranes.

As mentioned above, it is known that industry would prefer the construction of undivided cells above that of divided cells, purely because of financial reasoning.

## 1.4.6 Reactor design<sup>53</sup>

Classification of reactor designs is done using the following divisions:

- Number of phases present.
- Mode of operation:
  - Batch.
  - Continuous.
  - Intermediate (semi-batch).
- Flow conditions within the reactor:

- Simple batch reactor (SBR).
- Plug flow reactor (PFR).
- Continuous stirred tank reactor (CSTR).
- Temperature.

The different types of reactors will now be discussed:

- Simple batch reactor: In this reactor setup the reactants and supporting electrolyte are added to the reactor and the reaction commenced. After reaction the reactor is discharged, cleaned if necessary and charged again in order to repeat the reaction. This process is what makes this type of reactor labour intensive and uneconomical to operate in anything but small scale. During electrolysis the concentration of products and reactants change depending on the reaction kinetics, electrode geometry, mass transport conditions and electrolyte volume. At any instant the composition within the reactor is uniform throughout the reactor. The mean residence time of electrolyte in the reactor is equal to the reaction time.
- Plug flow reactor (continuous flow reactor, piston flow): In this process the reactants and supporting electrolyte mixture continuously flow through the reactor and the products and unreacted starting material containing electrolyte flows out of the reactor. Due to the continuous production and the lower down time compared to the batch reactor, this process is more attractive than the batch reactor. Within this reactor it is assumed that there is no mixing of reagents and products in the direction of flow. The reactant and product concentrations are a function of distance between the inlet and the outlet, and the residence times are the same for all the species.
- Continuous stirred tank reactor: In this process the reactants are added continually to the reactor and the products continually extracted. This results in an intermediate process between the batch and flow cell. Due to the continuous (assumed perfect) mixing within the reactor the concentration of species in the outlet is the same as the concentration of species within the
reactor. So the concentration change effectively takes place between the inlet manifold and the reactor.

In this study use was made of batch reactors in two different configurations. The one configuration was a normal batch reactor setup and the second configuration was a batch recirculation setup using a flow cell (filter press cell) for electrolysis. In this second process the flow cell is connected to a well stirred external reservoir, with continuous recirculation from the reservoir to the flow cell. The batch recirculation setup affords the following advantages:

- Electrolyte capacity is significantly increased.
- pH and composition of the supporting electrolyte may be corrected by addition.
- Reagent preparation and mixing can be conveniently carried out in the reservoir.
- The reservoir tank acts as a gas disengagement vessel or even a solid liquid separator.
- The flow circuit or reservoir can be equipped with a heat exchanger in order to afford temperature control.
- The residence times in the system are much longer compared to single pass reactors but the mass transfer conditions are the same.
- The longer residence times allow for further chemical reactions to occur.

An important fact to note is that with the plug flow reactor and to a certain extent with the continuous stirred tank reactor, the ratio of electrode surface area to volume of electrolyte is much higher than with the batch reactor.

# 1.5 Reaction types occurring during electrolysis of aromatic hydrocarbons and phenols

A variety of reactions can take place upon electrolysis of a solution containing aromatic substrates. These reactions are facilitated through electron transfer and are possible if there is a potential difference between the two electrodes. Two types of reactions can take place, which can be explained using molecular orbital theory:<sup>25</sup>

- Oxidation (anodic): the loss of electrons from the highest occupied molecular orbital (HOMO).
- Reduction (cathodic): Acceptance of electrons into the lowest unoccupied molecular orbital (LUMO).

This section will concentrate on electrochemical oxidation. This is because the majority of work done in this investigation covers electrochemical oxidation. The most common reactions encountered during the electrochemical oxidation of aromatic substrates will now be presented.

# 1.5.1 Reaction types for aromatic hydrocarbons

In these reactions R represents any organic constituent, and Nu stands for a suitable nucleophile such as a hydroxide (<sup>-</sup>OH).

## 1.5.1.1 Side chain substitution (Equation 1.13):<sup>54</sup>



In this process a radical cation is formed which then undergoes rearrangement so that the side chain is the active site; the resulting nucleophilic attack then results in the loss of an  $\alpha$ -hydrogen and the addition of the nucleophile to the side chain.

# 1.5.1.2 Ring substitution (Equation 1.14):<sup>55</sup>



In this process the radical cation is again formed but the active site remains on the ring structure; the resulting nucleophilic attack then causes the loss of a aromatic hydrogen and the addition of the nucleophile to the ring.

1.5.1.3 Ring addition (Equation 1.15):<sup>56</sup>



This process proceeds just as a normal ring substitution, but in this case the hydrogen or other substituent on the ring that is normally substituted has difficulty leaving the ring, resulting in different compounds to those attained for the ring substitution.

# 1.5.1.4 Dimerization:<sup>57</sup>

Ring dimerization (Equation 1.16)



Side chain dimerization (Equation 1.17)



This process can occur by one of two ways:

- The formation of radicals followed by the coupling of these radicals in order to produce the dimer.
- The formation of a radical cation followed by nucleophilic attack of an additional substrate molecule, resulting in the dimer.

# 1.5.2 Factors influencing the reactions of aromatic substrates<sup>23,25,29,57,58,59,60</sup>

- Structure and nature of the substrate which produces the radical ion: The substituents on the molecule will affect the route the reaction follows; substituents which are electron donating (-OH) will make the molecule more susceptible to oxidation whereas electron withdrawing substituents (-NO<sub>2</sub>) will have the opposite effect. Substituents which are conjugated with the ring or possess non-bonded electron pairs will aid in the stabilization of charges formed on the molecule. The reason for this is resonance stabilization.
- Environment in which the substrate and resulting radical ion finds itself: This includes variables such as:

- Electrodes: The type of electrode affects both the formation of the radical and the follow-up reactions of the radical. This is done through adsorption of the substrate onto the electrode surface in a specific orientation. This orientation can then affect factors such as the regeoselectivity of the reaction, resulting in the promotion of one reaction above another on the surface of the electrodes.
- Solvent and supporting electrolyte: These factors affect the reaction to a great extent. They can either take part in the reaction (nucleophile or electrophile) or they can aid in both the chemical and electrochemical steps of the reaction. The following properties of solvents and electrolytes are important in affecting the reaction mechanism:
  - Proton availability: This is an important factor in governing the route and rate of the reaction, since most electrochemical reactions are affected by either the gain or loss of protons. This results in the classification of solvents according to the proton availability:
    - Protic: Proton rich (water).
    - Aprotic: Lack of protons (acetonitrile).
    - Semi-protic: Availability of protons to an extent (mixture of water and acetonitrile in varying ratios).
  - Conductivity and dielectric constant: These two factors are closely related. The dielectric constant is a measure of the ability of the solvent to dissolve compounds and the dissolved compounds can conduct electricity. The conductivity of the reaction mixture can affect the reaction.
  - Viscosity: This influences the mass transport mechanism in the reaction mixture, thus possibly affecting the route of the reaction, since electrochemical reactions take place between the radical and other constituents of the solution. If these components cannot reach each other, the radical formed during the electrolysis will

react with itself or the substrate so producing dimers and polymers.

Temperature: The temperature of the reaction mixture can also have an effect on the reaction, since it affects the stabilities of the different participants in the reaction as well as the conductivity and the mass transport characteristics of the solution.

# 1.5.3 General reactions of radical cations

Radical cations are formed upon oxidation of aromatic substrates as shown in Equation 1.17.<sup>54,55,56,59</sup>

$$(1.17)$$

As mentioned in Section 1.5.2, the factors influencing the stability of this radical cation will govern the route the reaction follows.

The reactions shown in Section 1.5.1 are possible because of the reactivity of this radical cation in different situations.<sup>61</sup>

Radical cations derived from saturated systems will preferentially lose a proton to yield a radical as shown in Equation 1.18:

 $RH_{+}^{\bullet} + B^{-} \longrightarrow R^{\bullet} + BH$  (1.18)

 Radical cations derived from unsaturated systems can react via Equations 1.19, 1.20 and 1.21.

RH <b>:</b>	+	Nu-	>	H <sup>•</sup> R — Nu	(1.1
кп <del>+</del>	Ŧ	nu		H K — NU	(

RH <b>:</b>	+	B⁻		R•	+	BH	(1.20)
-------------	---	----	--	----	---	----	--------

+ RH HR+ HR+ (1.21)

 Radical cations can be oxidised further to di-cations at the anode as shown in Equation 1.22.

 $RH^{-} - e^{-} RH^{2+}$  (1.22)

The reaction with the nucleophile (Equation 1.19) and the base (Equation 1.20) predominate over the coupling reaction (Equation 1.21), which is relatively rare.<sup>61</sup>

Deprotonation of the radical cation depends on the reaction mechanism, but normally occurs just after the first oxidation step.

Due to the wide variety of reactions which radical cations can undergo, there is the possibility of forming complex mixtures of products during anodic reactions.

# 1.5.4 Reaction types applied to the electrochemical oxidation of phenol

One of the main products SASOL makes through MERISOL is phenol, an aromatic alcohol. It would be of interest to investigate the type of reactions possible during electrolysis of a phenol solution, in order to possibly transform this compound to higher value added products.

The reactions and mechanisms shown below illustrate the effect of the OH group, in the structure, on the pathway of the electrochemical oxidation of phenolic compounds.



It is generally accepted that the first step in the electrochemical oxidation of aromatic compounds involves the removal of an electron from the substrate in order to produce a radical cation as shown in Equation 1.23. The formation of this radical cation is important to explain the electrochemical behaviour of phenol because phenol will not react with water, but the radical cation of phenol will.<sup>59</sup>

Phenolic compounds are easily oxidised.<sup>59</sup> This is because the hydroxyl group is electron donating and the loss of electrons can be stabilized. The hydroxyl group has non-bonded electron pairs on the oxygen, which can take part in the resonance stabilization of the molecule.<sup>60</sup> Using these resonance forms, predictions can be made on possible reaction pathways the molecule might undergo.

The stabilization of the radical cation is achieved through the delocalisation of both the positive charge and radical through the conjugated system.

### 1.5.4.1 Side chain substitution <sup>54</sup>

The most important prerequisite for the side chain substitution of the aromatic substrate is the presence of  $\alpha$ -hydrogens. Since none of these hydrogens are present on phenol, side chain substitution cannot take place.

### 1.5.4.2 Ring substitution <sup>56</sup>

This reaction normally takes place when:

Strong nucleophiles are present.

(1.23)

The ring is not highly alkylated.

The process is shown in Scheme 1.1 and can be explained as follows <sup>57</sup>:

- i The substrate loses an electron in order to produce a radical cation.
- ii The radical cation then loses a proton in order to produce a radical.
- iii The radical then loses an additional electron in order to produce a cation.
- iv This cation then undergoes attack by a nucleophile in order to produce the nucleophilic-substituted product.

Scheme 1.1: Ring substitution



An example of this is the anodic oxidation of phenol to hydroquinone.<sup>62</sup>

# 1.5.4.3 Ring addition<sup>57</sup>

This reaction takes place under the same conditions as nuclear substitution, but can predominate under certain conditions mentioned below:

- In an environment where protons are not easily lost.
- Very strong nucleophiles are present .
- The ring is not sterically hindered .

The process is shown in Scheme 1.2 and can be explained as follows:

v The substrate loses an electron in order to produce a radical cation.

- vi The radical cation is attacked by a nucleophile.
- vii The radical loses an additional electron in order to produce a cation.
- viii This cation is then again attacked by a nucleophile in order to produce the product.





An example of this is the anodic methoxylation of phenols to the paramethoxylated dienones.<sup>63</sup>

# 1.5.4.4 Dimerization<sup>57</sup>

This type of reaction takes place when:

- There is no nucleophile present in the reaction medium.
- The mass transfer of the reaction mixture is not good enough to replenish the depleted concentration of the nucleophile present in the vicinity of the radical cation.

Under these conditions the substrate itself can act as a nucleophile towards the cationic radicals, resulting in the formation of dimers and polymers.

Two possibilities exist in the case of phenolic compounds:

Ring dimerization as shown in Scheme 1.3.





An example of this is the dimerization of 2,6-di-*tert*-butylphenol to 2,2',6,6'tetra-*tert*-butyldiphenoquinone at a platinum anode in a lithium perchlorate acetonitrile medium.<sup>64</sup>

Side chain dimerization as shown in Schemes 1.4 and 1.5.

Scheme 1.4: Side chain dimerization (side chain, nuclear)



Scheme 1.5: Side chain dimerization (side chain, side chain)



A variety of dimers can be formed when phenolic compounds are electrolysed. An indication of the identity of the dimers formed can be gained when looking at the

possible resonance structures attainable for the radical and radical cation. The oxygen bridged dimers are however unstable and are seldom identified. An example where the oxygen bridged dimer can be isolated is the dimerization of 2,4,6-tri-*tert*-butylphenol to the corresponding 3-(cyclohexa-2,5-dien-1-ylperoxy)cyclohexa-1,4-diene.<sup>65</sup>

# 1.6 Possible electrochemical pathways towards hydroxylated phenols

Hydroxylated phenols, like hydroquinone, resorcinol and catechol are compounds that can be obtained using electrochemical oxidation. The structures of these three hydroxylated phenol isomers are shown in Scheme 1.6. A literature survey pointed to a variety of technologies which can be used to do this. These methods will be briefly mentioned below. More emphasis will be placed on the technologies thought to be viable and possible using the equipment available.

#### Scheme 1.6: Structures of the three hydroxylated phenols

# 1.6.1 Indirect procedures using inorganic ions

The following technologies, based on the electrochemistry of inorganic ions, could be used to hydroxylate phenols and other aromatic substrates:

Inorganic peroxides: Among these are potassium peroxydiphosphate,<sup>66,67</sup> sodium perborate,<sup>68</sup> potassium peroxydisulphate<sup>69,70</sup> and hydrogen peroxide.<sup>71</sup> To organic chemists they are well known as stoichiometric

oxidants but the fact that they can be regenerated using electrochemical means is relatively unknown. The most important example here is the electrogenerated Fentons reagent.<sup>72</sup>

- $\div$ Stoichiometric reagent regeneration: Acetoxylation can be carried out using catalysis. An example of this is the use of cobalt(III)acetate in order to aromatic substrates; acetoxylate subsequent hydrolysis vields the products.<sup>73</sup> hydroxylated This catalyst can be regenerated electrochemically.74
- Inorganic metal mediators: Metal ions such as V(II) and Cr(II) were found to be able to hydroxylate phenol in the presence of oxygen. These processes do, however, suffer from low current efficiencies, and poor product outputs.<sup>75</sup>

These indirect processes were not investigated as it was felt that inorganic ions such as metals would contaminate the product stream.

# 1.6.2 Indirect procedures based on acetoxylation

This is a broad classification for processes in which the nucleophiles are acetate anions. The reaction proceeds through the oxidation (anodic) of the aromatic substrate, followed by nucleophilic attack to form the aromatic acetate. Two reactions were investigated during preliminary work: acetoxylation, where the nucleophile is an acetate,<sup>76,77</sup> and trifluoro-acetoxylation,<sup>78</sup> where the nucleophile is a trifluoro-acetate. The reaction is shown in Scheme 1.7.

Scheme 1.7: Acetoxylation



Acetoxylation:  $R_1$  = OH and  $R_2$  = CH<sub>3</sub> Trifluoro-acetoxylation:  $R_1$  = OH and  $R_2$  = CF<sub>3</sub>

The reaction sequences (Scheme 1.7) for the production of the acetate correspond to an ECEC mechanism. In this notation E stands for an electron transfer step, while C stands for a chemical step.

- i E: The anodic oxidation of the aromatic substrate at the electrode surface in order to produce the radical cation, followed by resonance stabilization of this radical. The extent to which the oxidation occurs depends on the oxidation potential of the substrate. The lower the oxidation potential the greater the extent of the reaction.
- ii C: The loss of a proton from the cationic radical in order to produce a radical, followed by resonance stabilization. The location and the rate at which this proton is lost depend on the acidity of the reaction environment in which the cationic radical finds itself.
- iii E: The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- iv C: Nucleophilic attack of the ester anion on the cation in order to form the neutral aromatic ester.

Once the ester has been produced electrochemically, it is hydrolyzed to yield the hydroxylated product as shown in Equation 1.24.

$$\begin{array}{c} & & R_1 \\ & & + H_2O \\ & & & \\ & &$$

 $R_1 = OH and R_2 = CH_3 or CF_3$ 

The major difference between acetoxylation and trifluoroacetoxylation is that acetoxylation proceeds well on activated aromatic rings whereas well deactivated trifluoroacetoxylation proceeds on aromatic rings. Trifluoroacetoxylation generally yields better results. This is due to the higher oxidation potential of the trifluoroacetates and the trifluoroacetoxylated compounds compared to the normal acetates. This implies that the trifluoroacetoxylated compounds are more stable to further oxidation, hence fewer side reactions. Also, due to the increased stability of the trifluoro acetate to oxidation, the interference of the Kolbe reaction (discussed in Section 1.6.2.1) is minimized.

# 1.6.2.1 Kolbe reaction<sup>79</sup>

This is an anodic process in which an acetate anion is oxidised to carbon dioxide and a radical. This process is shown in Equation 1.25. The radical produced can then take part in a variety of reactions.

$$2 \xrightarrow{O} O^{-} \xrightarrow{-e^{-}} 2 CO_{2} + 2 R^{-} \longrightarrow R^{-}R$$
 (1.25)

During acetoxylation reactions, the Kolbe process is an unwanted side reaction, which results in by-product formation, decreased current efficiency and material accountabilities.

The problems encountered during the preliminary study were so severe that the acetoxylation studies on phenol and phenyl acetate were discontinued. The reasons for this were:

- Phenol yield: Very small amounts of products at low current efficiencies.
- Phenyl acetate: Yielded better results than phenol, but these results were still unacceptable. The best results obtained were 81 % accountability, and 10% acetoxylated products and the best current efficiency was 20%.
- Toxicity of reagents.
- High cost of reagents.
- Corrosive media.

# **1.6.3 Direct electrochemical oxidation mechanism**<sup>71,72,80</sup>

Here the hydroxylated products are produced directly from the substrate. This is achieved through reaction of the substrate, in a conductive medium at the electrode surface to a radical cation, which then undergoes nucleophilic attack. The proposed reaction sequence, involving the direct electrochemical oxidation of the phenolic substrate, is shown in Scheme 1.8 and the reduction of the benzoquinone to the hydroquinone in Scheme 1.9 below. When considering the mechanism it can be seen that it is an ECEC mechanism.

#### Scheme 1.8: Direct electrochemical oxidation of phenol



The mechanism can be broken down into the following steps:

- i E: Anodic oxidation of the aromatic substrate at the electrode surface in order to produce the radical cation, followed by resonance stabilization of this radical. The extent to which this occurs depends on the oxidation potential of the phenolic compound. The lower the oxidation potential the greater the extent of the reaction.
- ii C: The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical. The location from which this proton is lost depends on the acidity of the phenolic group and the reaction medium. This is a rapid reaction due to the acidity of the phenolic radical cation, since the pKa value is in the range of 9.98 for unsubstituted phenol.<sup>79</sup>
- iii E: The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- iv C: Nucleophilic attack of water on the cation, resulting in a highly unstable structure, which is then rapidly rearranged, with the loss of a proton.
- v C: Rearrangement of the compound to hydroquinone.
- vi E: Anodic oxidation of the hydroquinone at the electrode surface in order to produce the radical cation, followed by resonance stabilization of this radical.
- vii C: The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical.
- viii E: The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- ix C: Nucleophilic attack of water on the cation, resulting in an unstable structure, which is then rapidly rearranged, with the loss of a proton in order to produce the cyclohexadienyl compound.
- x This cyclohexadienyl compound then loses water in order to produce the benzoquinone.

p-Benzoquinone is the predominating isomer. This can be explained through the relative stabilities of the isomeric benzoquinones, as well as the directing effect of the hydroxyl group already present on the ring.

This reaction can also take place in a basic solution; when this is the case, the mechanism follows a CECE mechanism, where the initial C reaction is the loss of the acidic proton on the hydroxyl group.<sup>71, 72</sup>

Since the *p*-benzoquinone can readily be reduced at the cathode of the electrochemical cell, it is important to look at the mechanism of this reaction. This is shown in Scheme 1.9 and it can be seen that this is also a ECEC mechanism.

Scheme 1. 9: Reduction to hydroquinone<sup>75,76</sup>



R<sub>1</sub> and R<sub>2</sub> in this investigation was H or C(CH<sub>3</sub>)<sub>3</sub>

The mechanism takes place in the following steps:

xi E: A one electron reduction of the benzoquinone at the cathode in order to produce the radical anion. This radical can then be resonance stabilized. The

ease with which this occurs depends on the reduction potential of the molecule.

- xii C: The addition of a proton to the radical anion followed by electron rearrangement within the molecule in order to produce the aromatic radical.
- xiii E: The gain of an additional electron to the molecule so as to form an anion, which is resonance stabilized. In a protic media, this species will be short lived, due to the high proton affinity of the anion.
- xiv C: The anion will then rapidly accept a proton from almost any source in order to produce the hydroquinone.

### 1.6.4 Lead dioxide as an anode

Of the three proposed routes for the electrochemical oxidation of phenol to hydroxylated products, the last one shown in Section 1.6.3 seems to be the most attractive, since it offers the widest scope with reference to types of electrodes, solvent conditions and experimental parameters (current density, voltage, temperature).

Preliminary work with a number of different electrodes (C, Pt, PbO<sub>2</sub>) showed that the lead dioxide electrode gave the most promising results for the anodic oxidation of phenol towards hydroxylated products.

Consulting the literature, it was found that anodic oxidation of phenol using lead dioxide has been studied widely, but mainly for the electrochemical destruction of phenol in waste streams<sup>83,84,85,86,87</sup>. Although the objective in such studies was to oxidize the phenol present in the waste water stream completely to carbon dioxide, it was felt that under milder oxidizing conditions, lead dioxide as an anode, should be able to selectively oxidize the substrate phenol to the specific benzoquinones, catechols and hydroquinones.<sup>88</sup>

Initial investigations into the mechanistic pathway of phenol oxidation in an aqueous solution indicated that the particular mechanism depends on the type of

anode material used. With carbon and platinum as anode, the proposed mechanism set out in Section 1.6.3 seems to be valid; with lead dioxide as anode, however, an entirely different mechanism seems to apply, involving adsorption of the substrate onto the electrode surface, formation of hydroxyl radicals from water oxidation on the surface and combination of the hydroxyl radical with the substrate on the surface to form the hydroxylated product.<sup>84,85,86,87,89</sup> This latter mechanism can be termed an indirect pathway through oxidation of water. This mechanism is shown below in Scheme 1.10 and each step is described in detail.

It is well known that peroxides and hydrogen peroxide can hydroxylate phenols to hydroquinones. The use of hydrogen peroxide in the presence of catalysts is currently the only route from phenol to hydroquinone used in industry. Through the electrochemical generation of a hydroxyl radical, the rate of hydroxyl generation and the nature of reaction undergone by the radical is potentially more easily controlled.

In this process water adsorbed on the lead dioxide anode is oxidised to hydroxyl radicals which remain bonded to the electrode. These adsorbed hydroxyl radicals then react with adsorbed phenol in order to afford hydroxylated products.

Scheme 1.10: Indirect oxidation of phenols at a lead dioxide electrode

$$R_{sol} \xrightarrow{i} R_{elec}$$

$$R_{elec} + MO_{x}[] \xrightarrow{ii} MO_{x}[R]$$

$$MO_{x}[] + H_{2}O \xrightarrow{iii} MO_{x}[OH] + H^{+} + e^{-}$$

$$MO_{x}[OH] + MO_{x}[R] \xrightarrow{iV} MO_{x}[ROH] + MO_{x}[] + H^{+} + e^{-}$$

$$MO_{x}[ROH] + MO_{x}[OH] \xrightarrow{V} MO_{x}[RO^{-}] + H_{2}O + MO_{x}[]$$

$$MO_{x}[RO^{-}] + MO_{x}[OH] \xrightarrow{Vi} + 2MO_{x}[]$$

$$HO \xrightarrow{O} OH + 2MO_{x}[] + H_{2}O + MO_{x}[]$$

$$HO \xrightarrow{O} OH + H_{2}O + MO_{x}[]$$

$$HO \xrightarrow{O} OH + H_{2}O + MO_{x}[]$$

R = phenol and  $MO_x$  = lead dioxide

- i The movement of the phenolic molecule (R) from the bulk of the solution to the electrode solution interface followed by the adsorption of the molecule onto the electrode.
- ii The movement of the adsorbed phenolic molecule onto an active site on the metal oxide electrode.

- iii The adsorption of water onto an active site on the metal oxide electrode, followed by the oxidation of the water molecule to a hydroxyl radical which remains bonded on the active site.
- iv The reaction between the bonded hydroxyl radical and the adsorbed phenol molecule on adjacent active sites leading to the formation of the hydroxylated product through oxidation.
- v The reaction between the hydroquinone and the electrode bonded hydroxyl radical leading to a organic radical.
- vi Reaction of the organic radical with the electrode bonded hydroxyl radical leading the 4,4-dihydroxycyclohexa-2,5-dien-1-one.
- vii Rearrangement of the 4,4-dihydroxycyclohexa-2,5-dien-1-one by the loss of water to the respective benzoquinone.
- viii A side reaction resulting in the electro-generated hydroxyl radical oxidation to molecular oxygen.

# 1.7 Objectives of study

When one considers the price of phenol on the international market and compares this with price levels for hydroxylated phenols, like hydroquinone, one sees a significant increase in value when introducing an extra OH group onto the aromatic ring. For example a good average value for phenol on the market is around 700 US \$ per metric ton, whilst the price for hydroquinone, based on a 2002 value, is 4000 US \$ per metric ton.<sup>90</sup>

As was discussed above, modern industrial chemical practice is turning increasingly towards electrochemical synthetic procedures, especially for the production of fine chemicals, such as pharmaceuticals, agricultural chemicals and important high value intermediates. This shift is mainly driven by environmental considerations and economic factors.

Substituted phenols, like 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol can readily be converted to the corresponding hydroquinones. Preliminary work showed that the electrochemical oxidation of phenol proceeded easier as the degree of substitution on the ring increased.<sup>91</sup> This could be accounted for by the increase in electron density on the aromatic ring upon substitution. Since the substituted hydroquinones formed in these cases, are also highly valued chemicals, it would be of interest to compare the electrochemical oxidation of phenol with these substituted phenols.

The overall objective of this investigation will therefore be to study the anodic oxidation of phenol, 2-*tert*-butyl phenol and 2,6-di-*tert*-butyl phenol with the aim of optimizing the electrochemical production of the corresponding hydroquinones. The specific objectives will then be to increase the amounts of the respective hydroquinones with regards to the respective catechols and resorcinols. In order to achieve this objective it is essential to gain fundamental information at laboratory scale, such as:

- Determine the possible mechanisms occurring during anodic oxidation of phenols, and optimize the relevant mechanisms.
- Confirm the choice of cell design and cell components.
- Determine the values of the various parameters for optimum reaction.
- To optimise fluid and mass transport.
- To obtain energy and mass balances.
- To evaluate various modes of process operation.
- To characterize by-products and evaluate product quality.
- To obtain a more detailed appreciation of reactor behaviour including cell voltage components, current and potential distribution, and local fluid flow and mass transport.
- To consider process improvements in the light of process experience, together with availability of new materials, ideas and information.

Factor not considered during the investigation are:

- To test long term integrity and stability of the reactor and its components.
- To achieve long term operation with consistent performance.
- To optimize the overall processes and rationalize the sensitivity of reactor performance to economics, technological, environmental and safety factors.
- To define other unit processes and their integration with the electrochemical reactor.

The remaining sections of this introductory chapter will deal with an overview of the starting materials, an overview of the possible products to be expected, and a summary of the present industrial methods for manufacturing the target products.

# **1.8 Overview on Starting Materials**

In this section the properties and uses of phenol, 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol will be presented.

# 1.8.1 Phenol

Phenol, (hydroxybenzene, carbolic acid,  $C_6H_5OH$  [108-95-2]) was first discovered in 1834 by F.Runge who isolated it in an impure form from coal tar and named it carbolic acid or coal oil acid.<sup>92,93</sup> Phenol was first purified and crystallised by Laurent in 1841 through the distillation of coal tar and chlorine.<sup>94,95</sup> It is the parent substance of a homologous series of compounds with the hydroxyl group bonded directly to the ring.<sup>96</sup>

Phenol occurs as either a free component or as an addition product in natural products and organisms. Phenol is formed as a metabolic product and can be found in human urine; it can also be liberated from lignin upon hydrolysis. Larger amounts can be formed in the coking or low-temperature carbonisation of wood, brown coal, hard coal and in oil cracking. The largest sources of phenol are in the carbonisation of coal and in oil cracking.<sup>96</sup>

Phenol has been an important chemical in history and was used in:

- Medicinal chemicals: The discovery of the disinfectant properties of phenol was made by Joseph Lister (1827-1912), who first used it as a disinfectant for wounds and surgical equipment in 1865.<sup>97</sup>
- Household chemicals: The discovery of the disinfectant properties of phenol lead to it's wide household use in a variety of formulations from disinfectant solutions to disinfectant soaps. Carbolic soap was widely used since the advantages of its use outweighed the disadvantages. The use of the soap was however discontinued when less dangerous alternatives became available.<sup>98</sup>

Phenol and phenol-containing compounds are important and indispensable compounds in everyday life. The major uses for phenol are given in Table 1.5 with estimated percentage values.<sup>99</sup>

Use	Percentage use
Production of bisphenol-A (4,4'-	35%
isopropylidenediphenol)	
Production of phenolic resins	34%
Production of caprolactams	15%
Production of aniline	5%
Production of alkylphenols	5%
Production of xylenols	5%
Other miscellaneous uses	1%; insecticides, explosives, wood
mainly including intermediates	preservatives, anti-oxidants, herbicides,
for the following	fungicides, insecticides, defoliants dyes

#### Table 1.5: Uses of phenol

#### **1.8.1.1 Properties**

Phenol is a clear solid at room temperature and melts at 40.9 °C, crystallizing into colourless prisms.<sup>101</sup> It is completely miscible with water at temperatures above 68.4 <sup>o</sup>C, whilst below this temperature its solubility decreases with temperature. Phenol is readily soluble in most organic solvents (aromatic hydrocarbons, alcohols, ketones, ethers, acids, halogenated hydrocarbons, etc.). Phenol is an acidic substance with a pKa value of 9.89. The reason for this acidity is the ability of the molecule to stabilize the negative charge formed upon proton loss through quinoid resonance structures. Because of this acidity phenols can form salts with aqueous alkali hydroxide solutions.<sup>96</sup>

Phenol has a relatively high boiling point (181.75 °C) due to hydrogen bond formation between molecules. Phenol can readily undergo electrophilic substitution; the reason for this is due to the contribution of the *o*- and *p*-quinoid resonance structures. Under oxidative conditions phenols can readily form free radicals, which can then undergo dimerization or further oxidation to dihydroxybenzenes and quinones. Since phenol radicals are relatively stable phenols can be used as radical scavengers and oxidation inhibitors.<sup>96</sup>

# **1.8.2 Tertiary butyl substituted phenols**

The substituted phenols investigated were 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol with particular emphasis being placed on 2-*tert*-butylphenol. The tertiary butylated phenols are produced from the alkylation of phenol in the presence of catalysts. The nature of the process and the type of catalyst governs the product distribution. An example of one such process is when sulphonated polystyrene-polydivinylbenzene ion exchange resin is used as the catalyst, forming mixtures of alkylated and di-alkylated phenols.<sup>101</sup>

2-Tert-butyl phenol and its isomers find uses in the following fields:<sup>102, 103</sup>

- Para-*tert*-butylphenol (PTBP) is mainly used in the manufacture of PTBP formaldehyde resins & ethylene-oxide condensates.
  - PTBP -formaldehyde resins are used in the manufacture of oil-soluble phenolic and modified phenolic resins for surface coating applications. These coatings when used along with suitable drying oils give films having good flexibility, better strength, improved heat and light resistance etc. They are used in varnishes, wire enamels, printing inks and in the formation of adhesives.
  - PTBP- formaldehyde resins find application as tackifiers for synthetic rubber and as adhesives in the tyre industry. They are also used in vulcanisation of natural and synthetic rubbers.
  - PTBP resins can be ethoxylated with ethylene oxide to form compounds which are used as de-emulsifiers in the petroleum industry.
- Hydrogenation of PTBP is useful in the manufacture of perfumes and odourants for the soap and cosmetic industries.
- PTBP is widely used as an intermediate in the manufacture of oil additives, polymerisation modifier for polycarbonate resins, ultraviolet light stabilizers, rubber chemicals, antiflex cracking agent, in brake and clutch linings, corrosion inhibitors and in insecticides.
- Tertiary butyl phenol when combined with neoprene and acrylic elastomers confer excellent tack properties to the polymer.

2,6-Di-*tert*-butylphenol finds application in similar fields to that of 2-*tert*-butylphenol.

## 1.8.2.1 Properties

As mentioned, the alkyl phenols used in the study were 2-*tert*-butylphenol and 2,6di-*tert*-butylphenol. These compounds are phenolic in nature but the presence of the bulky alkyl groups on the molecule has a pronounced effect on the properties of the substance. 2-*Tert*-butylphenol is not soluble in aqueous alkaline solutions of any concentration, so it is apparent that 2,6-di-*tert*-butylphenol will not be either, whilst phenol is.<sup>100</sup>

2-*Tert*-butylphenol is a clear liquid at room temperature, it melts at -7°C and boils at 221°C. It is insoluble in water but readily soluble in other organic solvents such as aromatic hydrocarbons, alcohols, ketones, ethers, acids, halogenated hydrocarbons, etc.<sup>106</sup>

2,6-Di-*tert*-butylphenol is a clear solid at room temperature, it melts at 39°C and boils at 133°C at 20 torr. It is insoluble in water but readily soluble in other organic solvents such as aromatic hydrocarbons, alcohols, ketones, ethers, acids, halogenated hydrocarbons, etc.<sup>103</sup> The difference between the boiling point of 2,6-di-*tert*-butylphenol, 2-*tert*-butyl phenol and that of phenol can be explained when considering the nature of the substituents on the ring. When comparing phenol to alkyl substituted phenols, the solubility of the phenol in water decreases with increasing size of the alkyl substituent to the point where it becomes insoluble as is the case with 2-*tert*-butyl phenol. The solubility in organic solvents follows this trend in reverse.<sup>100</sup> This is again ascribed to the bulky substituent; it decreases the polarity of the compound and inhibits solvation through the steric hindrance which the *tertiary* butyl group imparts.<sup>101</sup>

# 1.9 Overview of possible products formed during the electrochemical oxidation

# 1.9.1 Phenol as starting material

## 1.9.1.1 Introduction

Upon the oxidation of phenol, dihydroxybenzenes and p-benzoquinone are formed. All three isomers of the dihydroxybenzenes could be formed. These are

hydroquinone [123-31-9] (1,4-dihydroxybenzene, 1,4-benzenediol, *p*-dihydroxybenzene), catechol [120-80-9] (1,2-dihydroxybenzene, 1,2-benzenediol, *o*-dihydroxybenzene) and resorcinol [108-46-3] (1,3-dihydroxybenzene, 1,3-benzenediol, *m*-dihydroxybenzene). Scheme 1.11 gives the structures of these compounds.<sup>107,109,110</sup>



- Hydroquinone is a white crystalline substance, which was first discovered in 1820 from the dry distillation of quinic acid. Then, in 1844, it was described by Woehler when he obtained it from the reduction of 1,4benzoquinone.<sup>108,110</sup>
- Catechol is a slightly grey crystalline compound with a phenolic odour, and a sweet and bitter taste. It was first obtained in 1839 upon the dry distillation of catechin.<sup>110</sup>
- Resorcinol is a crystalline compound with a faint pink tinge and faint aromatic odour. It was first obtained in 1864 by the alkali fusion of galbanum and asafoetida resins.<sup>109,110</sup>

#### 1.9.1.2 Properties

As shown in Table 1.6, the dihydroxybenzene isomers do not have similar physical properties. The reason for this can be explained through hydrogen bonding, within and between molecules.

Properties	Catechol	Resorcinol	Hydroquinone
Melting point	105 °C	110 °C	172 °C
Boiling point	245 °C	277 °C	287 °C

Table1.6: Selected physical properties (dihydroxybenzenes)<sup>110</sup>

Looking at the melting and the boiling points, it can be seen that the increase in these properties is proportional to the separation between the hydroxy substituents in the molecule. This can be explained as follows: the closer the hydroxy groups are to each other, the greater the likelihood of hydrogen bonding within the molecule; hence there is a smaller amount of hydrogen bonding with surrounding molecules causing less attraction between molecules so there is less energy needed to separate these molecules from each other, resulting in the lower melting and boiling points.

There is a marked trend in the solubility of the dihydroxybenzene isomers, namely the solubility of hydroquinone in any solvent is always different from that of catechol and resorcinol, whose solubilities are always relatively close.<sup>110</sup>

The dihydroxybenzenes are weak acids with two dissociation constants, one for the loss of each proton. Catechol differs from the other dihydroxybenzenes in that it has the ability to complex most metal salts, due to the two adjacent hydroxy substituents.<sup>110</sup>

In general, the physical properties of hydroquinone vary to a great extent from those of catechol and resorcinol whose properties are close to each other.

The dihydroxybenzenes undergo all the typical reactions of phenol. When comparing the oxidation potential of the dihydroxybenzenes to that of the corresponding phenols, it is known that it is lower than that for phenol. This is because there is greater electron density on the ring of dihydroxybenzenes. With the exception of resorcinol, the dihydroxybenzenes are easily oxidised to the corresponding quinones.<sup>107,109,110</sup>

# **1.9.1.3** Uses and applications of products

Dihydroxybenzenes are primarily used as intermediates for the production of a variety of value-added products.

- \* Hydroquinone: The uses of hydroquinone are varied.<sup>111-121</sup>
  - Photography: The largest demand for hydroquinone is in this industry. It is used as a developing agent in black and white photography, lithography, photochemical machining, microfilm and X-ray film. A wide array of derivatives are used, including sulphate salts of *p*-N-methylaminophenol and potassium 2,5-dihydroxy-benzenesulfonate.
  - Rubber industry: This is the second largest consumer of hydroquinone and its derivatives:
    - Antioxidants and anti-ozonants: Examples of derivatives used in the industry are N,N'-diaryl-p-phenylenediamines, dialkylated hydroquinones, N-alkyl-p-aminophenols, dialkyl-p-phenylenediamines and aralkyl-p-phenylene-diamines.
    - Vulcanising agent: Hydroquinone has been used in fluoro rubbers.
  - Polymer industry:
    - The extensive use of hydroquinone as inhibitor: hydroquinone monomethyl ether and p-benzoquinone is used in the vinyl polymer industry to inhibit free radical polymerisation during processing and storage.
    - The use of hydroquinone, p-benzoquinone, 2-methylhydroquinone,
       2-tert-butylhydroquinone and 2,5-di-tert-butylhydroquinone as stabilisers in unsaturated polyester resins.

- The use as a chain extender of hydroquinone bis(2hydroxyethyl)ether in the production of thermosetting urethane polymers.
- Use as a intermediate in the production of antioxidants and antiozonants used in the polymer industry; examples of anti-oxidants are dialkylated hydroquinones, N-alkyl-p-amino phenol and mainly diaryl-p-phenylenediamines. Examples of hydroquinone intermediates used as anti-ozonants are, dialkyl and alkyl aryl substituted p-phenylenediamine.
- Food industry: Hydroquinones are used in the production of food antioxidants. Examples of these derivatives include, 2-tertbutylhydroquinone, and 2-tert-butyl-hydroxyanisol.
- Dyes and pigments: Hydroquinone dimethyl ether is used as a starting material for a family of dyes, based on 2-amino- and 2-amino-5-chloro derivatives such as quinizarin.
- Agricultural chemicals: A variety of fungicides and herbicides are produced using hydroquinone as intermediate. Examples of these are Chloroneb (fungicide), which is produced from hydroquinone dimethyl ether, ethofumesate (herbicide), which is produced from pbenzoquinone, and fluazifop-butyl, which is based on the o-alkylation of hydroquinone with 2-halopropionic acid derivatives.
- Pharmaceuticals: Hydroquinone and several derivatives are used as skin depigmentation and bleaching agents in topical formulations. Derivatives of hydroquinone find application in other pharmaceutical fields, for example gentisic acid is used in the medicinal preparation of analgesics and antirheumatics.

The field is still expanding with new applications for hydroquinone and its derivatives being discovered continuously. Examples of these applications are found in the fields of metal corrosion treatment and polymers (liquid crystals, new polymer and plastic formulations), since these new polymers exhibit good

strengths, weathering ability, solvent resistance, flame retardence, and temperature stability.

- Resorcinol: The uses of resorcinol are limited.<sup>109,110,122-125</sup>
  - Rubber industry: This is by far the largest consumer of resorcinol in the world. It is used in the production, reinforcement and vulcanization of rubber products. Here resorcinol can be used as an adhesion agent or an additive to the rubber in order to modify its properties. Resorcinol formaldehyde resins have also been used in non-crystalline rubbers as a vulcanization agent in eg. Neoprene and butyl rubbers.
  - Adhesives: This is the second largest consumer of resorcinol in the world. Here the largest application is in the field of wood adhesives, especially in the production of laminated wood beams. Resorcinol adhesives offer the advantage of room temperature curing, high bond durability and water resistance.
  - Dyes: Resorcinol finds wide application in this industry, it is used in the production of diazo dyes, flouricine and dye intermediates such as αresorcylic acid and β-resorcylic acid.
  - VV stabilizer: Resorcinol is a starting material for a important class of UV absorbers; these include benzophenones, β-resorcylic acid and resorcinol ethers.
  - Polymer: It is used in the production of resorcinol formaldehyde resins, which is used in the production of both rayon and nylon.
  - Pharmaceutical industry: Resorcinol is used in the formulations for the treatment of achne and other greasy skin conditions in conjunction with other treatments. It also finds application in anti-dandruff shampoos and sunscreen cosmetics and is used as a chemical intermediate in the synthesis of other pharmaceutical compounds, such as hexyl resorcinol which is used as an anthelmintic and topical antiseptic.

- Catechol: The uses of catechol are varied. The main use of catechol is as an intermediate in the production of other compounds used in the following industries:<sup>110</sup>
  - Pharmaceutical preparations: Guaiacol, and its benzoates, carbonates, salicylates, sulphonates and glyceryl ethers are used as expectorants. Veratrole and sassafras are used as antiseptics. It is also used as starting material in the production of synthetic catecholamines which have important physiological effects as neurotransmitters (such as epinephrine, adrenaline, norepinephrine, and dopamine).
  - Food industry: Veratrole is used as a meat additive, and as liquid smoking agents. *Tert*-butylcatechol is also used as an antioxidant for lard.
  - Perfume industry: Derivatives such as piperonal (cherry and vanilla) and eugenol (clove) are used as flavours.
  - Agricultural industry: Piperonal derivatives and arbofuran are also used as insecticides. Catechol phosphate is claimed to be a plant growth accelerator. Phosphoric and thiophosphoric esters of catechol are used as fungicides.
  - Rubber industry: Derivatives are also used in this industry: an example of this is the di-o-toluylguanidine salt of dicatechol-borate, which is used as a polymerization accelerator.
  - Polymer industry: Stannous derivatives of catechol are employed as catalysts for polyurethane foams. Salts of *tert*-butylcatechol are used to stabilize poly(vinyl chloride) polymers. *Tert*-butylcatechol is used as a stabilizer or polymerisation inhibitor for styrene, butadiene and other reactive monomers.
  - Paints and inks: Guaiacol is used as an anti-oxidant and anti-skinning additive to paints, varnishes, enamels and printing inks.
  - Photographic industry: It is used as a developing agent in the photographic industry.

# 1.9.1.4 Industrial processes for dihydroxybenzenes

Dihydroxybenzenes can be obtained from a variety of synthetic routes.<sup>108,109,110</sup> These routes are discussed below.

The manufacturing procedures used on an industrial scale for the manufacture of dihydroxybenzenes are shown in Table 1.7 and described below.

Dihydroxybenzene	Process	Location
Hydroquinone	Aniline oxidation	US, FRG, Japan, U.K.,
		People's Republic of China
	Phenol hydroxylation	France, Italy, Japan
	p-diisopropylbenzene	U.S., Japan
	oxidation	
Resorcinol	Benzene sulphonation	U.S., Italy, FRG, U.K.,
		Puerto Rico, Japan
	m-diisopropylbenzene	Japan
	oxidation	
Catechol	Phenol hydroxylation	France, Italy, Japan
	Coal-tar distillation	U.K.

Table1.7: Industrial production procedures for dihydroxybenzenes

- Oxidation of aniline: This is a three step process:
  - Oxidation of aniline with manganese dioxide (20% excess, pyrolusite ore can be used as a source) in sulphuric acid (5<sup>o</sup>C). This produces benzoquinone and manganese sulphate.

2 
$$H_2$$
 + 4 MnO<sub>4</sub>  
+ 5 H<sub>2</sub>SO<sub>4</sub> - 2  $H_2O$   
+ 4 MnSO<sub>4</sub> + 4 H<sub>2</sub>O  
+ 4 MnSO<sub>4</sub> (1.26)
- The benzoquinone is then separated from the reaction mixture by steam stripping.
- The separated benzoquinone is reduced to hydroquinone using an aqueous iron suspension (55 65 °C), which produces hydroquinone. This is separated from the iron and iron oxide through filtration. An alternative method to this is catalytic hydrogenation. The resulting hydroquinone is separated by centrifuging and the resulting product is vacuum dried yielding 85 % hydroquinone.

$$\begin{array}{c} O \\ O \\ O \\ O \end{array} + Fe + H_2O \longrightarrow OH \\ OH \end{array} + FeO$$
 (1.27)

- Hydroxylation of phenol: A mixture of catechol and hydroquinone is obtained by hydroxylation of phenol with hydrogen peroxide in the presence of a catalyst. The ratio of catechol to hydroquinone can range from (3:1) to (0.1:1). It is reported that with the aid of shape-selective zeolites a selectivity of 99 % can be obtained towards the hydroquinone. <sup>126</sup>
  - > A typical process involves the following steps:

 Dihydroxybenzenes are extracted with solvents and the oxidation mixture washed with water.

- The products are then separated from each other and the solvent through distillation.
- Oxidation of *p* and *m*-diisopropylbenzene: Benzene is alkylated with propene in the presence of a catalyst. The reaction products are isomerized to *p*- and *m*-diisopropylbenzene and oxidized to *p*- and *m*-diisopropylbenzene dihydroperoxide. An acid catalyst then cleaves these products in order to produce hydroquinone and resorcinol with an 80% yield. The reaction proceeds as follows:
  - p- and m-diisopropylbenzene are produced by the Friedel-Crafts alkylation of benzene with propene, and followed by isomerization to the desired isomers.



The purified diisopropylbenzene is converted to the dihydroperoxide by air oxidation under slightly alkaline conditions at 80 – 90 <sup>o</sup>C. This dihydroperoxide is purified and separated from the reaction mixture by either extraction or crystallization.



The dihydroperoxide is cleaved through the Hock rearrangement by treatment of the dihydroperoxide solution with a 0.2 - 1.0% sulphuric acid catalyst at 60 – 80 <sup>o</sup>C. The corresponding dihydroxybenzene and acetone is then separated and purified through crystallization.



- Sulphonation of benzene: In this process benzene is sulphonated with sulphur trioxide in sulphuric acid. This reaction mixture is neutralized, alkali fused with sodium hydroxide and acidified with sulphuric acid in order to produce resorcinol. This process produces a considerable amount of waste since mixtures of sulphur trioxide and sulphuric acid are used, which need to be neutralized with lime and then precipitated as gypsum and then landfilled. The process consists of three steps:
  - Sulphonation of benzene, by the use of sulphur trioxide in order to produce *m*-benzene disulphonic acid.



Neutralization of *m*-benzene disulphonic acid with a base like sodium sulphite, soda ash or sodium hydroxide to produce *m*-benzene disodium di-sulphonate.



Alkali fusion of the *m*-benzene di-sodium di-sulphonate with an excess of sodium hydroxide at 320 – 350 °C to produce di-sodium resorcinate and sodium sulphite.

The di-sodium resorcinate and sodium sulphite are treated with either a small quantity of water (which yields solid sodium sulphite containing some organic impurities) or a large quantity of water (which yields a saturated solution of the product). In both these processes the product is reacted with sulphur dioxide, sulphuric acid or hydrochloric acid. The dissolved product is then extracted with an organic solvent.



 <u>Miscellaneous</u>: Currently there are a number of methods, which show promise for the industrial synthesis of the dihydroxybenzenes.

- > Hydroquinone:
  - The carboxylate esters of aromatic diols can be prepared by the Bayer-Villiger oxidation of 4-hydroxy-substituted aromatic ketones with 97% conversion and selectivity.
  - Can be produced by the microbiological oxidation of both benzene and phenol with very high selectivities.
  - *p*-Benzoquinone is produced in selectivities greater than 90% by the air oxidation of phenol using a copper catalyst.
  - Can be produced from benzene in the presence of Cu(I) chloride or titanium.
  - *p*-Benzoquinone and hydroquinone can be obtained by reacting benzene with ozone in an aqueous medium.
  - Can be produced by the hydroxylation of *p*-isopropylphenylphenol using 30% hydrogen peroxide under acidic conditions.
  - Can be produced by a highly selective hydroxylation process using a proprietary shape-selective zeolite catalyst (HZSM-5) produced by Mobil.<sup>126</sup>
- Resorcinol:
  - Can be produced by the hydrogenation of 1,3-dinitrobenzene using a process developed by Koppers and Mitsui.
  - Can be produced using acetone and either methyl acrylate or acetonitrile, by the dehydrogenation of 1,3-cyclohexanedione formed, as developed by Hoechst.
- > Catechol:
  - Can be prepared from cyclohexane derivatives. The cyclohexanone is chlorinated and then hydrolyzed to 2hydroxycyclohexanone and 1,3-cyclohexanedione followed by dehydrogenation to catechol.

# 1.9.2 Tertiary butyl substituted phenols as starting material

### 1.9.2.1 Introduction

Upon the oxidation of 2,6-di-*tert*-butylphenol and 2-tert-butylphenol, the corresponding dihydroxybenzenes and p-benzoquinones are formed. In the case of 2,6-di-*tert*-butylphenol only the para isomer is formed and in the case of 2-*tert*-butylphenol only the ortho and para isomers of the tertiary butylated dihydroxybenzenes are formed. The possible products are therefore:

- ✤ 2,6-di-*tert*-butylhydroquinone and 2-di-*tert*-butylbenzoquinone.
- 2-tert-butylhydroquinone and 2-tert-butylbenzoquinone.<sup>127,128</sup>
- ✤ 2-*tert*-butylcatechol.

The reaction products are shown in Scheme 1.12 below.



2,6-di-tert-butylhydroquinone



2,6-di-tert-butylbenzoquinone



The 1,2-benzoquinone for the catechol is very unstable and was never picked up during analysis.

#### 1.9.2.2 Properties

The tertiary butylated dihydroxybenzenes show all the properties of normal dihydroxybenzenes; the presence of the tertiary butyl group does, however, affect the physical properties to a significant extent. This can be seen when comparing the solubilities, melting and boiling points of hydroquinone and tertiary butyl hydroquinones, shown in Table 1.8 below.

Table1.8: Comparison of some of the physical properties of hydroquinone and 2-*tert*-butyl hydroquinone<sup>108,127</sup>

Compound	Hydroquinone	2-tert-butyl hydroquinone
Solubility in water	70 g/L	Insoluble
Melting point in °C	172	127-129
Boiling point in °C	287	295

It is clear from the table that the presence of the tertiary butyl group does effect the physical properties of the compound.

The tertiary butyl-substituted dihydroxybenzenes undergo all the typical reactions of dihydroxybenzenes. When comparing the oxidation potential of the tertiary butyl dihydroxybenzenes to that of the corresponding dihydroxybenzenes, it is known that as the tertiary butyl substitution increases the oxidation potential decreases. This is because there is greater electron density on the ring of tertiary butyl dihydroxybenzenes, thus lowering the oxidation potential of the compound.

#### 1.9.2.3 Uses and applications of products

The tertiary-butylated dihydroxybenzenes are primarily used as intermediates for the production of a variety of value-added products.

- ✤ 2-*Tert*-butylhydroquinone (TBHQ):<sup>129-136</sup>
  - Polymers: TBHQ is used in the polymer industry as a polymerization inhibitor.
  - Anti-oxidant: TBHQ is used as a general purpose industrial anti-oxidant; it is a very versatile anti-oxidant and its anti-oxidant ability has been used in as wide a field as insecticide formulations.
  - Food industry: TBHQ is greatly utilized in the food industry since its FDA approval in 1972, where it is used to stabilize a variety of oils, fats and food products e.g. animal fats, vegetable oils and fried foods.
  - Adhesion promoting agents: TBHQ is used in the preparation of surfaces for adhesion of composite materials or resins; examples of these are dentin, enamel, or other natural or industrial substrates containing metallic ions or a capability to bind metallic ions.

The reason for the widespread use of 2-*tert*-butylhydroquinone as a antioxidant in the food industry can be summarized as follows:

- 2-Tert-butylhydroquinone is non-toxic at the required level of concentrations.
- > Addition of 2-*tert*-butylhydroquinone is easy.
- 2-Tert-butylhydroquinone does not give objectionable colour even in contact with metals like iron and copper.
- Reasonable cost Since 2-*tert*-butyl hydroquinone is added only in small quantities, the cost of addition is minimal.
- 2-Tert-butylhydroquinone is stable at high temperatures and wet environments; this makes 2-*tert*-butyl hydroquinone ideal for the preservation of foods during the frying process.
- ✤ 2-Tert-butylcatechol (TBC): <sup>110,137,139</sup>
  - Polymer industry: *Tert*-butylcatechol is used as a stabilizer and inhibitor in various monomers and polymers; examples of this are:
    - The heat stabilization of polyurethanes.

- The use as a inhibitor in order to prolong the shelf life eg. chloroprene monomers.
- The use as stabilizer and inhibitor for styrene butadiene.
- Pharmaceutical industry: *Tert*-butylcatechol is used as a topical skin depigmenting agent for both human and animal use.
- Anti-oxidant: *Tert*-butylcatechol is used as a anti oxidant for cottonseed, safflower, oil, lard, polypropylene glycol polyesters and olefin polymers.

#### **1.9.2.4** Industrial processes for tertiary butyl dihydroxybenzenes

The tertiary butyl dihydroxybenzenes are synthesized by C-alkylation processes, in the presence of Friedel-Craft catalysts using all the common alkylating agents that alkylate phenol. Examples of this process are shown in the equation 1.36 and 1.37 below.<sup>140,141</sup>



## **CHAPTER 2**

## **Experimental**

## 2.1 MATERIALS

## 2.1.1 Reagents for synthesis

All reagents used in the electrochemical synthesis procedures, together with their sources and respective grades, are listed in Table 2.1 and were used as received except for phenol which was dried in a vacuum desiccator.

Chemical name	Chemical formula	Source	Grade <sup>a</sup>
2-Propanol	(CH <sub>3</sub> ) <sub>2</sub> CHOH	Merck	AR
2-Tert-butylphenol	$C_4H_9C_6H_4OH$	Aldrich	AR
Acetic Acid	CH <sub>3</sub> COOH	Saarchem	AR
Acetone	(CH <sub>3</sub> ) <sub>2</sub> CO	Saarchem	AR
Acetonitrile	CH <sub>3</sub> CN	BDH	HPLC
Catechol	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	BDH	СР
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	Saarchem	AR
Ethyl Acetate	CH <sub>3</sub> CH <sub>2</sub> COOCH <sub>3</sub>	Saarchem	AR
Hexane	C <sub>6</sub> H <sub>12</sub>	Saarchem	AR
Hydroquinone	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	BDH	AR
Magnesium sulphate	MgSO <sub>4</sub>	Saarchem	СР
(anhydrous)			
Methanol	CH <sub>3</sub> OH	BCH	HPLC
N,N-dimethylformamide	HCON(CH <sub>3</sub> ) <sub>2</sub>	Merck	AR
n-Butanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	Saarchem	AR
n-Propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	Saarchem	AR
Phenol	C <sub>6</sub> H₅OH	Saarchem	AR
Propanoic Acid	CH <sub>3</sub> CH <sub>2</sub> COOH	Merck	AR

#### Table 2.1: Reagent for synthesis

a: Ar = Analytical Reagent, CP = Chemically Pure , HPLC = HPLC grade

Chemical name	Chemical formula	Source	Grade <sup>a</sup>
Resorcinol	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	Aldrich	AR
Sodium Chloride	NaCl	Saarchem	AR
Sodium hydroxide	NaOH	BDH	СР
Sulphuric Acid	$H_2SO_4$	Skychem	СР
t-Butanol	(CH <sub>3</sub> ) <sub>3</sub> COH	Saarchem	AR
Tetrahydrofuran	C <sub>4</sub> H <sub>8</sub> O	Merck	AR
Water	H <sub>2</sub> O	BHT DSA-30	12 µS.cm <sup>-1</sup>
		deionized	
		water system	

a: Ar = Analytical Reagent, CP = Chemically Pure , HPLC = HPLC grade

## 2.1.2 Reagents for analysis

Table 2.1: Continued

#### 2.1.2.1 Reagents for electro-analytical studies

Additional reagents used in the electro-analytical studies, together with their sources and respective grades, are listed in Table 2.2 and were used as received.

Table 2.2: Reagents for electro-analytical procedures

Chemical name	Chemical formula	Source	Grade <sup>a</sup>
2,6-Di- <i>tert</i> -	$(C_4H_9)_2C_6H_2O_2$	Synthesis	99 %
butylbenzoquinone			
2,6-Di- <i>tert</i> -	$(C_4H_9)_2C_6H_2(OH)_2$	Synthesis	98 %
butylhydroquinone			
2,6-Di- <i>tert</i> -butylphenol	$(C_4H_9)_2C_6H_3OH$	Aldrich	AR
2-Tert-butylbenzoquinone	$(C_4H_9)C_6H_3O_2$	Synthesis	99 %
2-Tert-butylhydroquinone	$(C_4H_9)C_6H_3(OH)_2$	Synthesis	98 %
Benzoquinone	(C <sub>6</sub> H <sub>4</sub> )O <sub>2</sub>	Aldrich	AR

a: Ar = Analytical Reagent, CP = Chemically Pure , HPLC = HPLC grade

### 2.1.2.2 Reagents for HPLC analysis

Additional reagents, not mentioned before, and used in the HPLC analysis, together with their sources and respective grades, are listed in Table 2.3 and were used as received.

#### Table 2.3: Reagents for HPLC analysis

Chemical name	chemical formula	source	Grade <sup>a</sup>
Phosphoric Acid	H <sub>3</sub> PO <sub>4</sub>	Skychem	СР
<i>p</i> -Nitrophenol	$(NO_2)C_6H_5$	Fluka	AR
Resorcinol	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	Aldrich	AR
<i>p</i> -Di-chloro benzene	$C_6H_4CI_2$	Merck	AR

a: Ar = Analytical Reagent, CP = Chemically Pure , HPLC = HPLC grade

## 2.1.3 Electrode materials

The electrode materials used in the electrochemical reactions were mostly obtained from the American company, Electrosynthesis, in Buffalo, USA and are listed in Tables 2.4 and 2.5 below. Those which were prepared in house are indicated by an "a", and those bought elsewhere with a "b"

Table 2.4: Electrode materials for batch cell electrolysis

Anodes	Cathodes
Lead dioxide on titanium mesh <sup>b</sup>	Platinum <sup>a</sup>
Platinum <sup>a</sup>	Nickel <sup>a</sup>
Graphite <sup>b</sup>	Stainless steel <sup>b</sup>
Lead <sup>a</sup>	Cadmium <sup>a</sup>
Lead dioxide on lead <sup>a</sup>	Graphite <sup>b</sup>
Titanium <sup>b</sup>	Titanium <sup>a</sup>
	Lead <sup>a</sup>

Total surface area of all electrodes =  $5 \text{ cm}^2$ 

Anodes	Cathodes
Graphite <sup>a</sup>	Nickel <sup>b</sup>
Platinum on Niobium <sup>b</sup>	Platinum on Niobium <sup>♭</sup>
Lead <sup>a</sup>	Graphite <sup>a</sup>
Lead dioxide on Titanium <sup>b</sup>	
Lead dioxide on lead <sup>a</sup>	

Table 2.5: Electrode materials for micro flow cell (batch recirculation electrolysis)

Designed to fit the Micro-01 flow cell (Electrosynthesis)

The lead dioxide on lead electrode was prepared by constant current electrolysis of a lead anode. The reaction medium consisted of 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid. Following electrolysis the samples were rinsed, dried and sent for XRD analysis using the method described in Section 2.3.10. The results indicated that the electrode surface contained lead, lead sulphate,  $\alpha$ -lead dioxide and  $\beta$ -lead dioxide. The prepared electrodes were cut to size from the respective plates.

A Micro-01 flow cell, obtained from Electrosynthesis (USA) was used for all undivided batch recirculation micro flow cell work at bench scale. The dimensions of the cell was: length = 9.5 cm, breadth = 4.5 cm and height > 30 cm.

#### 2.1.4 Synthesis of tert-butylated benzoquinones

The same method was used in order to produce both 2-*tert*-butylbenzoquinone and 2,6-di-*tert*-butylbenzoquinone. These benzoquinones were produced from the corresponding phenols through electrochemical oxidation in a divided cell. This divided cell was equipped with a nafion separator. The anode was a lead dioxide electrode and the cathode a platinum electrode.

The 2-*tert*-butylphenol (1.2 g; 8.8 mmol) or 2,6-di-*tert*-butylphenol (1.33 g; 8.8 mmol) was weighed into the anodic compartment of a divided cell reactor which contained acetonitrile (53 cm<sup>3</sup>; 1015 mmol). To this, an aqueous sulphuric acid solution ( $22 \text{ cm}^3$ ; 5 % v/v; 21 mmol) was added. After the addition of the same

amounts of the acetonitrile / sulphuric acid / water to the cathodic compartment, the solution was stirred at 1000 rpm at room temperature. The electrolysis was started at 800 mA and run to twice the theoretical amount of charge (8 F).

After electrolysis, the anolyte solution was poured into a separating funnel. This was extracted three times with 50 cm<sup>3</sup> portions of ethyl acetate. The organic portion was washed with 50 cm<sup>3</sup> of a saturated sodium bicarbonate solution followed by three portions of 50 cm<sup>3</sup> water. The resulting organic portion was dried over anhydrous magnesium sulphate, filtered and the ethyl acetate removed by evaporation. The resulting benzoquinone was stored in the dark in a vacuum desiccator. The identification and purity determinations of the standards were carried out using four techniques, GC-MS, IR, DSC and TLC. The results for 2-*tert*-butylbenzoquinone and 2,6-di-*tert*-butylbenzoquinone (Tables 2.6 and 2.7) indicated that the products were successfully synthesized, with acceptable purity.

Product	2-tert-butylbenzoquinone		
Melting point	76 °C (Ref: 75 °C) <sup>107</sup>		
MS trace	m/z 164 (M <sup>+</sup> ), m/z	149 ( $M^+$ - CH <sub>3</sub> ) bas	e peak, m/z 136 (M <sup>+</sup>
	- H <sub>2</sub> CCH <sub>2</sub> ), m/z 134	↓ (M <sup>+</sup> - 2CH <sub>3</sub> ), m/z <sup>-</sup>	107 (M <sup>+</sup> - C(CH <sub>3</sub> ) <sub>3</sub> )
Purity	99 %		
IR results: $Bo_{max}$	Functional group	Vibrational	Wavenumber cm <sup>-1</sup>
		mode	
	-CH <sub>3</sub>	C-H <sub>str</sub>	3000, 2950
		C-H <sub>def</sub>	1450,1400,
	-C(CH <sub>3</sub> ) <sub>3</sub>	C-H <sub>str</sub>	3000, 2950
	-	C-H <sub>def</sub>	1450,1400, 1350
	-CH=CH-trans	C-H <sub>str</sub>	3075
		C-H <sub>def out of plane</sub>	950
		C=C <sub>str</sub>	1600
	Quinone	C=O <sub>str</sub>	1650

Table	2.6:	2-tert-butylbenzoquinone
-------	------	--------------------------

Product	2,6-di-tert-butylbenzoquinone			
Melting point	64 - 67 °C (Ref: 64 – 68 °C) <sup>107</sup>			
MS trace	m/z 220 (M <sup>+</sup> ), m/z	163 (M <sup>+</sup> - C(CH <sub>3</sub> )	) <sub>3</sub> ), m/z 106 (M <sup>+</sup> - 2	
	C(CH <sub>3</sub> ) <sub>3</sub> )			
Purity	98 %			
<b>IR results:</b> Bບ <sub>max</sub>	Functional group Vibrational Wavenumber cm <sup>-1</sup>			
		mode		
	-CH <sub>3</sub>	C-H <sub>str</sub>	3000, 2950	
		C-H <sub>def</sub>	1450,1400,	
	-C(CH <sub>3</sub> ) <sub>3</sub>	C-H <sub>str</sub>	3000, 2950	
		C-H <sub>def</sub>	1450,1400, 1350	
	-CH=CH-trans	C-H <sub>str</sub>	3075	
		C-H <sub>def out of plane</sub>	950	
		C=C <sub>str</sub>	1600	
	Quinone	C=O <sub>str</sub>	1650	

Table 2.7: 2,6-di-tert-butylbenzoquinone

The melting points shown in Tables 2.6 and 2.7 were determined using DSC whilst the purity results were calculated as the GC-MS peak area percentage.

### 2.1.5 Synthesis of tert-butylated hydroquinone

2-*Tert*-butylhydroquinone and 2,6-di-*tert*-butylhydroquinone were synthesized from the corresponding benzoquinones, synthesized as described in Section 2.1.4, through electrochemical reduction in a divided cell. The divided cell was equipped with a nafion separator. The anode was a carbon electrode and the cathode a nickel electrode.

2-*Tert*-butylbenzoquinone (1.3 g; 8.8 mmol) or 2,6-di-*tert*-butylphenol (1.9 g; 8.8 mmol) was weighed into the cathodic compartment of a divided cell reactor which containing acetonitrile (53 cm<sup>3</sup>; 1015 mmol). To this was added an aqueous sulphuric acid solution ( $22 \text{ cm}^3$ ; 5 % v/v; 21 mmol). After the addition of the same amounts of the acetonitrile / sulphuric acid / water to the anodic, the solution was

stirred at 1000 rpm at room temperature. The electrolysis was started at 800 mA and run to twice the theoretical amount of charge (4 F).

After electrolysis, the cathodic reaction mixture was poured into a separating funnel. This was extracted three times with 50 cm<sup>3</sup> portions of ethyl acetate. The organic portion was washed with 50 cm<sup>3</sup> of a saturated sodium bicarbonate solution followed by three portions of 50 cm<sup>3</sup> water. The resulting organic portion was dried over anhydrous magnesium sulphate, filtered and the ethyl acetate removed by evaporation. The resulting hydroquinone was stored in the dark in a vacuum desiccator. The identification and purity of the hydroquinones were determined as before and the results obtained summarized (Tables 2.8 and 2.9) for 2-*tert*-butylhydroquinone and 2,6-di-*tert*-butylhydroquinone respectively.

The melting points shown in Tables 2.8 and 2.9 were determined using DSC whilst the purity results were calculated as the GC-MS peak area percentage.

Product	2- <i>tert</i> -butylhyd	roquinone		
Melting point	127 - 128 °C (Ref: 127 – 129 °C) <sup>107</sup>			
MS trace	m/z 166 (M <sup>+</sup> ), m	n/z 151 (M⁺ - CH₃) bas	se peak, m/z 136 (M <sup>+</sup>	
	-2CH <sub>3</sub> ), m/z 123	3 (M <sup>+</sup> - 2CH <sub>3</sub> -CH), m/z	2 107 (M <sup>+</sup> - C(CH <sub>3</sub> ) <sub>3</sub> )	
Purity	99 %			
IR results: Bບ <sub>max</sub>	Functional	Vibrational mode	Wavenumber cm <sup>-1</sup>	
	group			
	-CH <sub>3</sub>	C-H <sub>str</sub>	2950, 2900	
		C-H <sub>def</sub>	1450-1350,	
	-C(CH <sub>3</sub> ) <sub>3</sub>	C-H <sub>str</sub>	3000, 2950	
		C-H <sub>def</sub>	1450,1400, 1350	
	Aromatic	-C=C-arom str	1650-1525	
	-	-C-H <sub>str</sub>	3000, 3025	
		-C-H <sub>def</sub>	800, 750	
		-O-H <sub>str</sub>	3100 - 3500 broad,	
			3600	
		-C-O <sub>str</sub> or –O-H <sub>def</sub>	1200, 1300	

Table 2.8: 2-tert-butylhydroquinone

Product	2,6-di- <i>tert</i> -butylhydroquinone		
Melting point	128 °C (Ref: 127 – 129 °C) <sup>107</sup>		
MS trace	m/z 220 (M <sup>+</sup> ), m/z	163 (M <sup>+</sup> - C(CH <sub>3</sub>	) <sub>3</sub> ), m/z 106 (M <sup>+</sup> - 2
	C(CH <sub>3</sub> ) <sub>3</sub> )		
Purity	98 %		
IR results: Bບ <sub>max</sub>	Functional group	Vibrational	Wavenumber cm <sup>-1</sup>
		mode	
	-CH <sub>3</sub>	C-H <sub>str</sub>	2950, 2900
		C-H <sub>def</sub>	1450-1350,
	-C(CH <sub>3</sub> ) <sub>3</sub>	C-H <sub>str</sub>	3000, 2950
		C-H <sub>def</sub>	1450,1400, 1350
	Aromatic	-C=C-arom str	1650-1525
		-C-H <sub>str</sub>	3000, 3025
		-C-H <sub>def</sub>	800, 750
		-O-H <sub>str</sub>	3100 - 3500 broad,
			3600
		-C-O <sub>str</sub> or -O-	1200, 1300
		H <sub>def</sub>	

Table 2.9: 2,6-di-tert-butylhydroquinone

## 2.2 Experimental procedures

## 2.2.1 Divided cell batch electrolysis

The electrochemical cell, shown in Figure 2.1, consists of two compartments each 150 ml in volume, equipped with heating jackets, which were connected to a Labcon circulator in order to affect either heating or cooling. The two reactor compartments are separated from each other through the insertion of a membrane. Each reactor lid is equipped with quickfit and screw adapters for the insertion of a variety of accessories, such as a thermometer, a condenser and an electrode. The reactor was left open to the atmosphere through the condenser in order to prevent pressure build up resulting from gas formation due to electrolysis of the reaction medium.

The reactor was assembled by clamping a piece of hydrated nafion between the two compartments. The starting materials were weighed by difference into the reaction compartments and the reaction medium added, the lids attached and constant current electrolysis started by using an Amel Instruments 2051 General Purpose galvanostat / potentiostat.



Figure 2.1: Divided cell electrolysis setup

# 2.2.2 Undivided batch recirculation micro flow cell electrolysis

The electrochemical cell shown in Figure 2.2 consists of a double-walled reactor flask, 150 cm<sup>3</sup> in volume, equipped with a heating jacket, which was connected to a Labcon circulator in order to affect either heating or cooling. The reactor lid was designed with quickfit and screw top adapters for the insertion of flow inlet outlet tubes, thermometer and condenser. One of the quickfit adapters in the reactor lid

was always left open to the atmosphere, through a condenser, in order to prevent a pressure build-up in the reactor due to gas formation in the flow cell. The flow outlet from the reactor was connected to an Iwaki model WD-15FY-220N impeller pump which forced the liquid through a flow indicator into the Electrosynthesis Micro-01 flow cell whose electrodes were connected to an Amel Instruments 2051 General Purpose galvanostat / potentiostat. Both the inter-electrode gap and electrode area could be adjusted. The flow cell outlet fed back into the double walled glass reactor in order to complete the loop.



Figure 2.2: Batch recirculation micro flow cell electrolysis setup

The substrate was weighed by difference into the reactor and the appropriate solvent and supporting electrolyte mixture were directly added to the reactor. The reactor lid, into which the appropriate fittings were added, was then sealed onto the reactor. The Labcon circulator was used to maintain the desired temperature. A vacuum line was used to prime the feed line and impeller chamber of the pump. The pump was switched on and the flow adjusted at the flow indicator to the

appropriate flow rate. The electrolysis was conducted under constant current conditions, controlled by an Amel Instruments 2051 General Purpose galvanostat / potentiostat, in order to achieve the required current density.

## 2.2.3 Undivided batch cell electrolysis

The electrochemical cell shown in Figure 2.3 consists of a double-walled reactor flask, 150 cm<sup>3</sup> in volume, equipped with a heating jacket, which was connected to a Labcon circulator in order to affect either heating or cooling. The top of the reaction flask was designed with screw top and quickfit adapters for the insertion of electrodes, a thermometer, and a condenser. The condenser was always left open to the atmosphere in order to prevent a pressure build-up in the reactor due to gas formation in the reactor. The electrolysis was conducted under constant current conditions, controlled by an Amel Instruments 2051 General Purpose galvanostat / potentiostat, in order to achieve the required current density.

#### Figure 2.3: Batch electrolysis setup



The starting material was weighed by difference into the reactor and the reaction medium added, the lid attached and the electrolysis started through the application of current supplied by the Amel galvanostat. When the potential of the anode was monitored, a Ag / AgCl (3 mol dm<sup>-3</sup>) was inserted into the cell, as close as possible to the anode, and the potential measured using Amel Voltassist ver. 1.3 software.

## 2.2.4 Undivided batch recirculation flow cell electrolysis for scale-up

An ICI Electrochemical Processing Laboratory Package unit, shown in Figure 2.4, was used for the scale-up of the electrochemical oxidations. At the core of the process unit lies the FM-01 flow cell, which is based on the filter press or plateand-frame arrangement. The electrochemical setup consists of a four necked round bottom flask (500 cm<sup>3</sup> in volume), an electromantle heating mantle, an lwaki MD-30F impeller pump, a precision glass flow indicator (2 L.min<sup>-1</sup> max flow rate), the FM 01-LC flow cell, and a Lorin SCT 20-30 galvanostat. The flask was fitted with a condenser in order to prevent a pressure build-up in the system due to gas formation in the flow cell, an inlet tube from the electrolysis cell and a outlet tube to the impeller pump. The pump forced the liquid through the flow indicator into the flow cell, which was connected to the galvanostat. The flow cell outlet fed back into the round bottom flask in order to complete the loop. There was also a recycle loop which bypassed the flow meter and electrolysis cell and fed back into the reactor in order to allow the reaction medium to attain the desired temperature without exposing the electrically unprotected electrodes to the corrosive medium.



Figure 2.4: Batch recirculation flow cell for scale-up

The substrate was weighed by difference into the round bottom flask and the appropriate solvent and supporting electrolyte mixture was added. The system was closed and the heating mantle switched on in order to obtain the desired temperature of the reaction mixture. Once the desired temperature was attained, the outlet from the flow cell was connected to a vacuum line to prime the pump and the rest of the system. The pump was then switched on and the flow adjusted at the flow indicator to the appropriate flow rate. The electrolysis was conducted under constant current conditions of 12 A in order to achieve the required current density.

## 2.3 Analytical techniques

Several analytical procedures were employed for the analysis of substrates, intermediates, products and supporting electrolytes. Each analytical technique will be described separately.

## 2.3.1 High Pressure Liquid Chromatography (HPLC)

HPLC analyses were carried out on a Hewlett Packard 1100 series HPLC chromatograph with a dual pump system (G 1312A), equipped with a variable UV – Visible detector (G 1314A) and an auto sampler unit (G 1313A). Data was acquired with a personal computer loaded with HP Chemstation for LC software (ver A.06.03). All solvents were HPLC grade and were degassed prior to analysis with a Millipore vacuum-degassing unit. A 3.9 x 300 mm Waters µBondapak C18 (serial no. WAT027324) column fitted with a Supelco Discovery C<sub>18</sub> guard column was used for the analysis of the reaction samples.

As different substrates were used in the reactions, analysis of the mixtures required different LC conditions. These settings are summarized in Tables 2.10 - 2.11. An internal standard method was used for the analysis of individual components of the phenol, 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol reaction mixtures. Response factors for the compounds of interest were determined by means of a five-level calibration using standard solutions containing known amounts of the analytes and internal standards.

The sampling procedure for HPLC analysis from the electrochemical reactor, consisted of taking 0.50 cm<sup>3</sup> aliquot samples, followed by dilution, and addition of known amounts of an internal standard.

The internal standard used varied for the substrates under investigation and are given below:

- Phenol: Following the addition of 7.0 ml of methanol containing 6.3047 mmol/L of p-nitrophenol, the sample was injected into the liquid chromatograph.
- 2-*tert*-butylphenol: Following the addition of 7.0 ml of acetonitrile containing
   6.5478 mmol/L of p-dichlorobenzene, the sample was injected into the liquid chromatograph.
- 2,6-di-*tert*-butylphenol: The same procedure as for 2-*tert*-butylphenol was followed.

The usual work-up procedure (extraction of the reaction mixture with an organic solvent) was avoided for the following reasons:

- The substrates, reaction intermediates and products were only partly extracted from the reaction medium into the organic solvents, which resulted in large errors in analysis.
- The extraction procedure was very wasteful, leading to the consumption of large amounts of additional reagents.
- The extraction procedure was very time consuming.

Injector Volume	10 µl
Column	µBondpak C <sub>18</sub> 3.9 x 300 mm (Waters)
Wavelength	280 nm
Flow Rates	$1 \text{ cm}^3 \text{ min}^{-1}$
Mobile Phases	30% MeOH : 70% $H_2O$ buffered to pH = 3
	with H <sub>3</sub> PO <sub>4</sub>
Internal Standard	4-nitrophenol

#### Table 2.10: HPLC conditions (phenol reaction mixtures)

## Table 2.11: HPLC conditions (2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol reaction mixtures)

Injector Volume	10 µl
Column	µBondpak C <sub>18</sub> 3.9 x 300 mm (Waters)
Wavelength	220 nm
Flow Rates	$1 \text{ cm}^3 \text{ min}^{-1}$
Mobile Phases	55% MeCN : 45% $H_2O$ buffered to pH = 3
	with H <sub>3</sub> PO <sub>4</sub>
Internal Standard	p-di-chlorobenzene

# 2.3.2 Gas Liquid Chromatography - Mass spectrometry (GC-MS)

GC-MS analysis carried out on a Thermo-Finnigan Trace GC coupled to a Quadropole Trace MS plus detector. Separation was achieved with the aid of a

Restek-RTX 5 MS column (15 m x 0.25 mm i.d.). Helium was used as the carrier gas, with a flow rate of 40 cm<sup>3</sup> min<sup>-1</sup>. Data acquisition, manipulation and instrumental control were carried out with Excalibur ver. 1.3 software using a DELL personal computer. Use was made of a split / splitless injection mode using a GC syringe (supplied by Hamilton). Other important chromatographic conditions used are summarised in Table 3.12.

-	
Initial column temperature	70 °C
Initial column hold time	5 min
Heating rate	10 ºC min⁻¹
Final column temperature	270 °C
Final column hold time	5 min
Injector temperature	250 °C
Detector temperature	300 °C
Detector solvent delay	2 min

Table 3.12: GC-MS analysis conditions

#### 2.3.3 Cyclic Voltammetry (CV)

CV studies were performed on a BAS CV50 cyclic voltammetry system. A Gateway 2000 personal computer, running CV50 software, was used for both instrumental control and data acquisition. The electrochemical cell was equipped with platinum, glassy carbon and lead dioxide working electrodes, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. The potential of the working electrode was scanned over potential ranges permitted by the working electrode. The scan rates used ranged from 10 to 1000 mV s<sup>-1</sup> and sensitivities were varied as needed according to the sample concentrations and scan rate. Cyclic voltammograms were recorded for the substrates, intermediates and final products, so as to determine their oxidation potentials and the mechanistic pathway. The same solvent / supporting electrolyte systems used for the reactions was used as the analysis medium.

## 2.3.4 Differential Scanning Calorimetry (DSC)

A Mettler Toledo DSC 820 was used to determine the purity and melting point of the synthesised standards as well as their decomposition temperatures. The sample was placed in an aluminium sample pan (working range up to 400 °C) and sealed in a press. Data was analysed on a Mercer premium-X personal computer with the aid of Mettler STARe ver. 6.01 software.

## 2.3.5 UV/Visible Spectrophotometry

The optimum UV absorbance wavelength of HPLC standards was determined with the aid of a Beckman DU<sup>®</sup> 7500 double beam UV / Visible spectrophotometer with Beckman DU series 7000 software. Data transfer and further manipulation of data was achieved with the aid of a personal computer, data transfer cable and PC Plus software. A quartz sample cell (cuvette) was used with methanol or acetonitrile as solvent.

## 2.3.6 pH Determination

Use was made of an Inolab level 1 digital pH meter with a WTW Sentix single glass pH electrode (serial no C000304091) to adjust the pH of the aqueous phase (pH=3) for use in HPLC analysis.

## 2.3.7 Karl Fischer water coulometry

The water concentration change throughout electrolysis was determined by coulometric analysis, performed on a Metrohm 684 KF Coulometer, using 10 µl sample volumes.

## 2.3.8 Thin layer chromatography (TLC)

Thin layer chromatography was used in order to identify and separate the analytes from each other. This was done using a 70 : 30 hexane : ethyl acetate eluent mixture.

# 2.3.9 Fourier Transform Infra red spectrophotometry (FTIR)

FTIR analysis was performed using a Brüker Tensor 27 Fourier Transform spectrophotometer, using a DELL personal computer with OPUS ver. 4.2 software for data acquisition and instrument control. Analysis was performed using an internal reflectance cell utilizing CCl<sub>4</sub> as solvent to apply the sample, and allowing the CCl<sub>4</sub> to evaporate. The following FTIR conditions were used to obtain the results:

Background scans	x 15
Sample scans	x 15
Wavelength	4000 cm <sup>-1</sup> – 750 cm <sup>-1</sup>
Resolution	4 cm <sup>-1</sup>
Result spectrum	Transmittance

## 2.3.10 X-Ray diffraction spectrometry (XRD)

A Brüker D8 Advance X-ray powder diffractometer with copper radiation was used for all XRD analysis. The diffractogram was scanned from 20 to 50  $^{\circ}$  two  $\theta$  at every 0.02 increments, at 1 second per increment. The matching and identification of samples was done using PDF2 software.

# 2.3.11 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

The samples were digested in nitric and perchloric acid, and diluted with water to within the ICP's operating range and sent for analysis. The calibration standards for lead and the reagent blanks were made of the same solvent supporting electrolyte system and diluted in a similar manner. The standards and the samples were run on the Spectro Modular 8877/97 ICP at wavelength 220.353 nm connected to a personal computer running Smart Analyzer software for ICP Spectrometer ver. 2.25 software for instrumental control and data analysis. This technique was used in the determination of the lead content of the reaction mixtures.

## **CHAPTER 3**

## Mechanistic Aspects of the Electrochemical Oxidation of Phenols

## 3.1 General

An understanding of the reaction mechanism is of vital importance in order to develop the best possible process for the synthesis of a desired product. With a proper understanding of the mechanism, the effect of various factors such as solvent identity, supporting electrolyte and cell design on the reaction can be predicted. Also, with an understanding of the reaction mechanism, unwanted side reactions and by-products can be identified and steps can be taken to either eliminate or minimise them.

In this chapter possible electrode reactions will be discussed and the mechanism of the electrochemical oxidation of phenols will be investigated using a variety of different procedures. The results obtained will then be used to confirm the mechanistic pathways of the electrochemical oxidation of phenol.

The discussion in this chapter mainly relates to the oxidation of 2-*tert*-butylphenol; the reason for the selection of this compound is that the tertiary butyl group will not change the mechanism of oxidation but will impart some stability to the intermediates, thus allowing them to be better studied.<sup>142,143</sup> It is well known that phenol shows appreciable polymer formation during oxidation;<sup>143</sup> the presence of the *tertiary* butyl group on the molecule will minimize these reactions by the stability it imparts to the intermediates.<sup>142,143</sup>

## 3.2 Results

#### 3.2.1 Some definitions

Before the description and discussion of the results can commence, some important terms used in the work need to be clarified. These are shown in Equations 3.1 and 3.2 below.

Mass Balance(%) = 
$$\frac{\text{(moles of quantified products and substrate after reaction)}}{(moles of substrate charged)} \times \frac{100}{1}$$
 (3.1)

 $Current \ Efficiency = \frac{(\text{moles of desired product} \times \text{no. of electrons per molecule of product})}{(\text{moles of electrons charged})} \times \frac{100}{1}$ 

(3.2)

Desired products include either / or the respective hydroquinone, benzoquinone and catechol.

## 3.2.2 Cyclic Voltammetry

#### 3.2.2.1 Oxidation potentials

The first step in an electrochemical investigation is the determination of the oxidation potential of the compounds being investigated. This was done using cyclic voltammetry, where the potential of a working electrode, immersed in a solution containing the analyte, is varied first in one direction then in the other. Analytes are not the only electro-active species in solution; others include the solvent and the supporting electrolyte. It is important to know how the other constituents of the medium will react under applied potential.

In this work it was found that the oxidation potential of the medium  $(H_2O/H_2SO_4/MeCN)$  was above 2000 mV vs a Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode, higher than that of all the substrates and intermediates, except benzoquinone. The anodic limit of the medium is set by the oxidation of the water present in the electrolyte. From an electrochemical point of view it can therefore be

concluded that the oxidation of the substrate will take place before the oxidation of the reaction medium.

Oxidation potentials are usually measured as  $E_{pa}$ , indicating an anodic peak in cyclic voltammetry. Table 3.1 shows the results obtained during the investigation of the oxidation potential of phenol, 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol and their respective hydroquinones and benzoquinones. The analysis was performed on solutions containing 50 mmol dm<sup>-3</sup> analyte in the reaction medium consisting of 70% v/v acetonitrile, 27% v/v water and 3 % v/v sulphuric acid.

Substrate	Working electrode	Oxidation Potential mV <sup>a</sup>
Phenol	Pt	1348
Phenol	С	1348
Phenol	PbO <sub>2</sub>	Not observed
Hydroquinone	Pt	964
Hydroquinone	С	962
Hydroquinone	PbO <sub>2</sub>	Not observed
p-Benzoquinone	Pt	Not observed
p-Benzoquinone	С	Not observed
p-Benzoquinone	PbO <sub>2</sub>	Not observed
2-tert-butylphenol	Pt	1305
2-tert-butylphenol	С	1351
2-tert-butylphenol	PbO <sub>2</sub>	Not observed
2-tert-butylhydroquinone	Pt	754
2-tert-butylhydroquinone	С	816
2-tert-butylhydroquinone	PbO <sub>2</sub>	Not observed
2-tert-butylbenzoquinone	Pt	Not observed
2-tert-butylbenzoquinone	С	Not observed
2-tert-butylbenzoquinone	PbO <sub>2</sub>	Not observed
2,6-di-tert-butylphenol	Pt	1182
2,6-di-tert-butylphenol	С	1357
2,6-di-tert-butylphenol	PbO <sub>2</sub>	Not observed

Table 3.1: Cyclic voltammetry oxidation potentials

Substrate	Working electrode	Oxidation Potential mV <sup>a</sup>
2,6-di-tert-butylhydroquinone	Pt	728.5
2,6-di-tert-butylhydroquinone	С	816
2,6-di-tert-butylhydroquinone	PbO <sub>2</sub>	Not observed
2,6-di-tert-butylbenzoquinone	Pt	Not observed
2,6-di-tert-butylbenzoquinone	С	Not observed
2,6-di-tert-butylbenzoquinone	PbO <sub>2</sub>	Not observed

 Table 3.1 cont: Cyclic voltammetry oxidation potentials

a = Oxidation potentials measured using a Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode.

These results for platinum show the general trend, where the higher the activation of the aromatic ring, the lower the oxidation potential of the aromatic compound. The following observations regarding the results shown in Table 3.1 should be noted:

- Electrode material: Generally the use of platinum leads to a lower oxidation potential than carbon, with the difference between the values for platinum and carbon becoming greater as the degree of substitution of the phenol increases. It is also important to note that the oxidation peaks for the analytes are not observed for the lead dioxide electrode; this indicates that a different mechanism is at work on the lead dioxide electrode compared to the platinum and graphite electrodes. This will be further discussed in the section dealing with cyclic voltammetry.
- Organic substrates: From an electrochemical point of view, the compound with the lower oxidation potential will be oxidised preferentially to others with higher oxidation potentials. It can be seen from Table 3.1 that the desired hydroquinone has a lower oxidation potential than the parent phenol, whilst the benzoquinone is stable towards further oxidation. This suggests that during oxidation at the anode, the phenol will first be oxidized to the respective hydroquinone, which will immediately undergo further oxidation to the corresponding benzoquinone, and which should accumulate at the anode in the cell.
- Reversible electrochemical equilibrium:<sup>82</sup> In an undivided cell the resultant benzoquinone will be in a reversible electrochemical equilibrium with its respective hydroquinone, as shown in Equation 3.3.



 $R_1$  and  $R_2 = H$  or  $C(CH_3)_3$ 

This benzoquinone is reduced to reform the hydroquinone at the cathode. This reduction reaction will occur in addition to the normal cathodic reduction reaction in acidic media, namely the reduction of protons to hydrogen gas (Equation 3.4):

$$2 H^+ + 2 e^- \longrightarrow H_2(g)$$
 (3.4)

Although the reduction of the benzoquinone (Equation 3.3) requires protons, reaction 3.4 is the only reaction that physically consumes protons as the oxidation of the hydroquinone to the benzoquinone will supply the protons required during reduction.

#### 3.2.2.2 Cyclic voltammetry investigation

Possible anodic mechanisms for the electrochemical oxidation of phenolic compounds were discussed in Section 1.5. An important factor governing which mechanism dominates is the nature of the electrode material. In this section, cyclic voltammerty was used to elucidate the electro-organic mechanism at the various anodes. This investigation was performed using 50 mmol dm<sup>-3</sup> analyte solutions in the reaction medium consisting of 70% v/v acetonitrile and 27 % v/v water and 3 % v/v sulphuric acid. The analytes were phenol, 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol and their respective, hydroquinones and benzoquinones, but only the results for the 2-*tert*-butylphenol investigation are shown and discussed. The reasons for this are two-fold:

- The conclusions drawn from the phenol and 2-*tert*-butylphenol results are the same.
- The tertiary butyl group imparts stability to the molecule resulting in longer lived intermediates, allowing for easier investigation.<sup>142,143</sup>

In these experiments the scan rate was varied from 10 to 1000 mV/s. By varying the scan rate, different species in the mechanism can be investigated, even short-lived ones. Reverse sweep and multiple sweeps also allow further investigation of the species formed at the electrode during the electrochemical reaction.

As an illustration the voltammograms for phenol and 2-*tert*-butylphenol are shown in Figures 3.1 and 3.2.



Figure 3.1: Cyclic voltammogram of a 50 mmol dm<sup>-3</sup> phenol solution

(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; 100 mV s<sup>-1</sup> scan rate; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)



Figure 3.2: Cyclic voltammogram of a 50 mmol dm<sup>-3</sup> 2-*tert*-butylphenol

(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; 100 mV s<sup>-1</sup> scan rate; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

Both the voltammograms show the oxidation peak for the respective phenol in the anodic sweep. The difference between the voltammograms are indicated and discussed below:

- Peak potential: The peak potential for 2-*tert*-butylphenol is slightly lower than for phenol, since the more activated (higher electron density on the ring) phenol (2-*tert*-butylphenol) will be oxidised easier.
- Peak shape: The shape of the oxidation peak for 2-*tert*-butylphenol is distorted compared to that of phenol. This is due to the stability which the *tertiary* butyl group imparts on 2-*tert*-butylphenol and its oxidation intermediates through the stabilization of both the radicals and the cations.<sup>142,143</sup> Since the increased stability of the intermediates increases their residence time in the reaction medium, they can be observed in the voltammogram.

#### 3.2.2.2.1 Platinum and Glassy carbon

The results discussed in this section were obtained using a platinum working electrode, and using scan rates ranging from 10 to 1000 mV s<sup>-1</sup>. The results obtained at higher scan rates show the same trends, while the results obtained for the glassy carbon working electrode are quite similar except for the actual oxidation potentials.

Figure 3.3 shows the cyclic voltammograms for the supporting electrolyte carried out at four different scan rates.



Figure 3.3: Cyclic voltammograms: Supporting electrolyte solution

(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

The optimum range for the specific supporting electrolyte solvent system ranges from -200 to 2200 mV vs. Ag/AgCl (3 mol dm<sup>-3</sup>). Two electrochemical processes are observed: these are the anodic oxidation of water and the cathodic reduction of protons.

Figure 3.4 shows the cyclic voltammograms for 2-*tert*-butylbenzoquinone carried out at four different scan rates.



Figure 3.4: Cyclic voltammograms: 2-tert-butylbenzoquinone

(50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

Figure 3.4 shows no peaks in the first anodic sweep indicating that there are no oxidisable species present initially. On the cathodic sweep there is a cathodic peak at approximately -26 mV due to the reduction of 2-tert-butylbenzoguinone to 2-tertbutylhydroquinone. On the second anodic sweep there is now an anodic peak at approximately 730 mV due to the oxidation of 2-tert-butylhydroquinone to 2-tertbutylbenzoquinone, showing that 2-tert-butylhydroquinone is produced by the reduction of 2-tert-butylbenzoquinone in the previous sweep. As the cycles continue the peaks reoccur and the peak size decreases; this decrease is due to the depletion of the analytes surrounding the working electrode. Increasing the scan rates indicate that there are no short lived species present in either the 2-tert-butylbenzoguinone, or the oxidation of reduction of the 2-tertbutylhydroquinone. It is also noted that as the scan rate increases, the ratio of 2*tert*-butylbenzoquinone to 2-*tert*-butylhydroquinone decreases. This can be
ascribed to the reduction being performed on the 2-*tert*-butylbenzoquinone which is present in the solution, but the oxidation peak being performed on the 2-*tert*butylhydroquinone which is only formed on the surface of the electrode: the longer it takes for the reverse sweep to occur, the more of the 2-*tert*-butylhydroquinone diffuses from the electrode surface into the bulk of the solution, thus giving smaller peaks. As the scan rate increases, 2-*tert*-butylhydroquinone diffuses to a lesser extent from the electrode into the bulk of the solution, hence peak size increases.

Figure 3.5 shows the cyclic voltammograms for 2-*tert*-butylhydroquinone carried out at four different scan rates.



Figure 3.5: Cyclic voltammograms: 2-tert-butylhydroquinone

(50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

The same trends are visible as in Figure 3.4, except that there is no peak present which corresponds to the reduction of 2-*tert*-butylbenzoquinone in the first cathodic sweep. After the first anodic sweep and the oxidation of 2-*tert*-butylbydroquinone, a peak resulting from the reduction of 2-*tert*-butylbenzoquinone appears on the next cathodic sweep, indicating that the 2-*tert*-butylbenzoquinone is produced by

the oxidation of 2-*tert*-butylhydroquinone. The 2-*tert*-butylhydroquinone shows the same peak ratio phenomena observed in the 2-*tert*-butylbenzoquinone study and this can be explained in a similar manner.



Figure 3.6: Cyclic voltammograms: 2-tert-butylphenol (Pt working electrode, Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

Figure 3.6 represents the cyclic voltammetry studies performed on a 50 mmol dm<sup>-3</sup> 2-*tert*-butylphenol solution at the four different scan rates. The first anodic sweep shows a group of peaks at approximately 1075 mV relating to the oxidation of 2-*tert*-butylphenol. The first cathodic sweep shows a peak at approximately 55 mV relating to 2-*tert*-butylbenzoquinone reduction. The second anodic sweep shows a peak at approximately 670 mV relating to 2-*tert*-butylhydroquinone oxidation, followed by the peaks observed in the first anodic sweep.

The grouping of peaks relating to 2-*tert*-butylphenol oxidation is as a result of the oxidation of the phenol to intermediates which are stable enough for the duration of the analysis to produce the respective peaks. The reason for their stability is the

<sup>(50</sup> mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

*tertiary* butyl group, which imparts some stability to the primary oxidation intermediates of 2-*tert*-butylphenol.<sup>142,143</sup>

When the scan rate is increased, additional anodic peaks appear after those of 2*tert*-butylphenol. The intensity of these peaks increases relative to the other peaks with an increase in scan rate. This is an indication that these peaks could be associated with short lived species in the reaction mixture.

### 3.2.2.2.2 Lead dioxide anode

The results discussed in this section were obtained with a lead dioxide working electrode and scan rates ranging from 10 to 1000 mV s<sup>-1</sup>. Higher scan rates show the same trends. Figure 3.7 shows the cyclic voltammograms for the supporting electrolyte solution at four different scan rates.





(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid;  $PbO_2$  working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

The lead dioxide electrode was made by the anodic electrolysis of a lead surface in aqueous sulphuric acid. This oxidised the lead surface to lead sulphate and the lead sulphate to lead dioxide, it is thus clear that the electrode surface will contain some lead sulphate and this is demonstrated in the cyclic voltammograms. From Figure 3.7 it can be seen that in the first anodic sweep there is a peak at approximately 1965 mV corresponding to the oxidation of lead sulphate to lead dioxide, followed by a rise resulting from the oxidation of water. On the first cathodic sweep a peak at approximately 1300 mV, corresponding to the reduction of lead dioxide to lead sulphate is observed.





(50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; PbO<sub>2</sub> working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)





(50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; PbO<sub>2</sub> working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

Figure 3.8 shows the cyclic voltammograms for 2-*tert*-butylbenzoquinone and 2-*tert*-butylhydroquinone carried out at two different scan rates using a lead dioxide working electrode. No extra peaks are observed for the oxidation or reduction of the substrates. Figure 3.9 shows the cyclic voltammograms for 2-*tert*-butylphenol carried out at two different scan rates and using a lead dioxide working electrode. As before, no peaks that can be ascribed to substrate oxidation can be observed.

The results for the oxidation of phenolic substrates at a lead dioxide electrode surface suggest that the oxidation proceeds according to a different mechanism, as that at platinum or carbon electrodes.

### 3.2.3 Reaction potential scans

The anodic potential at a platinum and lead dioxide electrode was monitored as a function of time in an undivided, constant current batch cell during electrolysis using the reaction conditions shown in Table 3.2 in Section 3.2.5 except that a

Ag/AgCl (3 mol dm<sup>-3</sup>) reference electrode was added to the reaction set-up. The results (Figure 3.10) show that at a lead dioxide working electrode, the potential remains relatively constant throughout the reaction. At the platinum working electrode, however, there are noticeable variations in the potential throughout the electrolysis. This strongly suggests that at a lead dioxide electrode, one single reaction dominates during the electrolysis of 2-*tert*-butylphenol. With platinum as working electrode, however, it would appear as if several processes having different oxidation potentials, lead to variations in the anodic potential. This suggests that there are different oxidation mechanisms at play at each anode.

Figure 3. 10: Potential scan of phenol (PbO<sub>2</sub> or Pt working electrode, Ag / AgCl (3 mol  $dm^{-3}$ ) reference electrode)



### 3.2.4 Typical product distribution profiles

From the studies discussed in Chapters 4 and 5, Figures 3.11 and 3.12 are taken as example for the purpose of this discussion.

Figures 3.11 and 3.12 show the product distribution diagrams obtained for the electrolysis of 2-*tert*-butylphenol using a flow cell and the reaction conditions shown in Table 4.4, at a platinum and lead dioxide electrode.



Figure 3.11: Product Distribution Diagram: Lead dioxide on Lead Anode

Figure 3.12: Product Distribution Diagram: Platinum on Niobium Anode



Figures 3.11 and 3.12 clearly show distinctly different behaviours for a platinum anode and a lead dioxide anode. The main features of these product distribution diagrams are as follows:

- In both cases, the substrate 2-*tert*-butylphenol (2-tbPhOH) is smoothly oxidised to reaction products over the range 0 12 Faraday's of charge per mole of substrate.
- In the case of a lead dioxide anode, the reaction products are essentially 2tert-butylhydroquinone (2tbHQ) and 2-tert-butylbenzoquinone (2tbBQ) as is indicated by the smooth and continuous increase in the sum of these two products, as well as the relative constant mass balance.
- For the platinum anode, however, the formation of reaction products (up to ~ 8 F of charge per mole of substrate) cannot be explained in terms of the formation of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone. As the substrate is consumed the sum of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone increases only very slowly, and the overall mass balance shows a steady decrease. After ~ 8 Faradays of charge per mole substrate, however, there is a rapid increase in 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone formation, which is accompanied by a sudden increase in the overall mass balance of the reaction. Interestingly, this rapid formation of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone formation, yet noticeable decrease in the rate of substrate oxidation.
- Additional observations regarding the above behaviour, and which are not shown by the product distribution diagrams shown in Figures 4.11 and 4.12, but which will be shown in later chapters, are:
  - The observed mass balance drop for the platinum anode may also be observed for lead dioxide electrodes where lead dioxide is formed on a supporting metal plate (eg. titanium) and where some part of the supporting metal is also exposed to the reaction medium.
  - The observed mass balance drop is much more pronounced in a flow cell than in a batch cell.
  - The observed mass balance drop is more pronounced at lower temperatures.

The observed mass balance drop is more pronounced for 2-tertbutylphenol and 2,6-di-tert-butylphenol than for phenol itself.

## 3.2.5 Divided cell electrolysis

Divided cell electrolysis was performed on 2-*tert*-butylphenol using lead dioxide as the anode and nickel as the cathode material. The reactions were performed using the experimental setup discussed in Section 2.2.1 and the reaction conditions shown in Table 3.2.

Variable	Value
Acid conc. (% v/v)	4.9
Organic solvent (% v/v)	70
Current density (A m <sup>-2</sup> )	2000
Organic solvent	Acetonitrile
2- <i>tert</i> -butylphenol loading (% m/v)	4.0
Temperature (°C)	50
Anode	Lead dioxide on titanium mesh
Separator	Nafion
Cathode	Nickel

Table 3.2: Standard conditions for the divided batch cell electrolysis

Figure 3.13 shows the product distribution diagram for the anodic compartment (oxidation of 2-*tert*-butylphenol) and Figure 3.14 shows the product distribution for the cathodic compartment (reduction of 2-*tert*-butylbenzoquinone). These figures show the percentages of the 2-*tert*-butylphenol, 2-*tert*-butylhydroquinone, 2-*tert*-butylbenzoquinone, mass balance (sum of 2-*tert*-butylhydroquinone, 2-*tert*-butylbenzoquinone and 2-*tert*-butylphenol) and current efficiency as the reaction proceeds.



Figure 3.13: Product distribution diagram for the anodic electrolysis of 2-*tert*-butylphenol in a divided cell

Figure 3.14: Product distribution diagram for the cathodic electrolysis of 2-*tert*-butylbenzoquinone in a divided cell



The most important observations from these results are as follows:

- During the anodic oxidation of 2-*tert*-butylphenol in a divided cell, the substrate is oxidised rapidly, and with high selectivity to produce mainly 2-*tert*-butylbenzoquinone. While small amounts of 2-*tert*-butylhydroquinone may be detected in the anodic compartment, it is not clear whether such 2-*tert*-butylhydroquinone is the result of the oxidation of 2-*tert*-butylphenol at the anode, or whether it is as a result of the slow diffusion of the 2-*tert*-butylbenzoquinone or 2-*tert*-butylhydroquinone between the anodic and cathodic compartments. It is, however, more likely to be the result of the former, the oxidation of the 2-*tert*-butylphenol.
- The current efficiency is remarkably high up to ~ 4 Faradays of charge per mole of substrate. This is in sharp contrast to the oxidation in an un-divided cell where the current efficiency is normally significantly lower (Figure 4.13 for example).
- The cathodic reduction of 2-*tert*-butylbenzoquinone at a nickel cathode produces 2-*tert*-butylhydroquinone exclusively. This process is very rapid, and is probably the source of most of the 2-*tert*-butylhydroquinone normally detected during oxidation reactions in undivided cells.

## 3.2.6 Discussion

### 3.2.6.1 General

The results described in the preceding section strongly suggest the existence of different mechanisms for the oxidation of phenol and *tertiary* butyl-substituted phenols at a lead dioxide anode on the one hand, and platinum and carbon on the other. Any proposed mechanism for the anodic process must be able to explain several important observations. These are:

- Cyclic voltammetry shows no peaks that can be ascribed to the oxidation of substrate and oxidation intermediates when using a lead dioxide electrode, but clear distinct peaks when using a platinum or carbon electrode.
- The observed variation in the potential of a platinum anode during an oxidation reaction as compared to the very constant potential of a lead dioxide anode.

- The observed differences in the behaviour of the reaction mass balance when using a lead dioxide anode and when using a platinum anode. In the case of lead dioxide the reaction mass balance typically remains quite high (but see remark in section 3.2.4) while for platinum a distinct drop in the reaction mass balance occurs that is rapidly restored towards the end of the oxidation.
- The remarkable selectivity of the electrochemical oxidation of phenol and substituted phenols to the respective hydroquinone and benzoquinone.

The difference in the cyclic voltammetry results can possibly be explained by proposing two distinct reaction mechanisms for the oxidation of phenol / substituted phenols at a lead dioxide anode on the one hand, and for platinum and carbon (and other metals) on the other. It is therefore proposed that for lead dioxide there is no direct electron transfer between the anode and the substrate, and oxidation must therefore involve the oxidation of the substrate by some form of activated species on the surface of the electrode which is subsequently regenerated electrochemically.

In order to obtain some idea as to the possible nature of the activated species it is of interest to note that:

- (a) No oxidation of the substrate occurs when exposing the substrate to the electrode (lead dioxide) material for prolonged periods of time in the absence of current.
- (b) The reaction is highly dependent on the nature of the supporting electrolyte; replacing sulphuric acid with any other acid completely destroys electrode activity completely; and
- (c) The electrode potential of the lead dioxide anode remains remarkably constant during oxidation.

From (a) above it should be clear that the active species cannot be lead dioxide (a known oxidant for certain organic substrates) itself, but some or other species derived from lead dioxide. Point (b) above suggests that lead sulphate is a key intermediate in the oxidation process since removing the source of sulphate

destroys activity. The last point suggests that the electrochemical process occurring at the lead dioxide is a relatively simple one *i.e.* it involves the oxidation of one particular species.

In the case of platinum (and other materials), there is clearly a direct transfer of electrons between the substrate and the anode and the mechanism is probably a typical ECE type mechanism. This would also explain the observation of peaks in the cyclic voltammogram that results from the oxidation of oxidizable intermediates, such as hydroquinone.





R1 and R2 in this investigation was H or C(CH<sub>3</sub>)<sub>3</sub>

The observed mass balance behaviour can only be explained in terms of the formation of an intermediate complex that cannot be detected by simple GC-MS, or HPLC (UV) analysis as used during this investigation. It was initially suspected that the observed mass balance deviation was as a result of the formation of quinhydrone-type complexes (Figure 3.15) between the benzoquinone and hydroquinone present simultaneously in the reaction mixture, but this was discarded due to the following considerations:

- i Quinhydrone-type complexes will not readily form with the *tertiary* butylsubstituted hydroquinone and benzoquinone due to the interference of the large *tertiary*-butyl group with hydrogen bonding.
- ii The fact that the decreasing mass balance phenomena is especially noticeable with the substituted phenols.

iii The fact that the intermediate at some stage during the oxidation process decomposes to produce both hydroquinone and benzoquinone. A quinhydrone-type complex will always be present (as long as both the benzoquinone and the hydroquinone is present in the same solution) and will thus not give the observed rapid increase in mass balance towards the end of the oxidation reaction.

Careful analysis of reaction mixtures during oxidation reactions of 2-*tert*butylphenol by means of GC-MS revealed the presence of small amounts of the dimer 1,1'-biphenyl-4,4'-diol (Figure 3.16). Dimer and higher oligomer formation is a well documented phenomena during electrochemical (also catalytic and stoichiometric) oxidation of phenols.<sup>80,142,144</sup> It is not unfeasible for such dimeric species to undergo further oxidation to the respective biphenoquinones (see Scheme 3.2). Such biphenoquinones are not easily analyzed by means of GC-MS and UV / HPLC analysis, and could explain the "loss" in the reaction mass balance in the middle part of the oxidation reactions.



R in this investigation was H or  $C(CH_3)_3$ 

Before presenting the proposed reaction mechanisms the exceptional selectivity to hydroquinone and benzoquinone needs some comment. The catalytic hydroxylation of phenol with hydrogen peroxide (using acid catalysis) produces both hydroquinone and catechol in a roughly 1:2 statistical ratio. In contrast, the electrochemical oxidation of phenol produces only trace amounts of catechol. This observation clearly indicates a different reaction mechanism to that at work during catalytic hydroxylation. One way of introducing such high regioselectivity during

the electrochemical oxidation of phenols is through the intermediate cyclohexa-2,5-dienone cation and cyclohexa-2,5-dienone radical (Figure 3.17).



R in this investigation was H or C(CH<sub>3</sub>)<sub>3</sub>

While it is possible to form the cyclohexa-2,4-dienone cation and radical, it is known to be considerably less stable than cyclohexa-2,5-dienone cation and radical and hence, more difficult to generate. The instability of the cyclohexa-2,4-dienone cation and radical, relative to the cyclohexa-2,5-dienone cation and radical accounts for the preferential formation of the respective hydroquinones instead of the catechols.

### 3.2.6.2 Reaction mechanisms

Taking the preceding considerations into account, two reaction mechanisms are proposed for the selective electrochemical oxidation of phenols to their respective hydroquinones and benzoquinones. For convenience we will refer to these two mechanisms as the "Direct Electrochemical Oxidation Mechanism" and the "Indirect Electrochemical Oxidation Mechanism".

## 3.2.6.2.1 Indirect electrochemical oxidation mechanism<sup>83,84,85,86,88</sup>

As discussed above, the electrochemical oxidation of phenols at a lead dioxide electrode probably does not involve the direct transfer of electrons between the substrate and the electrode. It is, instead, believed that the oxidation is achieved by the interaction of an electrochemically formed activated species on the lead dioxide electrode surface and substrate molecules. One possible way by which



Scheme 3.1: Indirect oxidation of phenols at a lead dioxide electrode

R = phenol and  $MO_x$  = lead dioxide

- i The movement of the phenolic molecule (R) from the bulk of solution to the electrode solution interface followed by the adsorption of the molecule onto the electrode.
- ii The movement of the adsorbed phenolic molecule onto an active site on the metal oxide electrode.

- iii The adsorption of water onto an active site on the metal oxide electrode, followed by the oxidation of the water molecule to a hydroxyl radical which remains bonded on the active site.
- iv The reaction between the bonded hydroxyl radical and the adsorbed phenol molecule on adjacent active sites leading to the formation of the hydroxylated product through oxidation.
- v The reaction between the hydroquinone and the electrode bonded hydroxyl radical leading to an organic radical.
- vi Reaction of the organic radical with the electrode bonded hydroxyl radical leading the respective 4,4-dihydroxycyclohexa-2,5-dien-1-one.
- vii Rearrangement of the respective 4,4-dihydroxycyclohexa-2,5-dien-1-one by the loss of water to the respective benzoquinone.
- viii A side reaction resulting in the electro-generated hydroxyl radical oxidation to molecular oxygen.

## 3.2.6.2.2 Direct electrochemical oxidation mechanism<sup>80,81</sup>

As discussed above, the electrochemical oxidation of phenols at a platinum (and other materials) electrode involves the direct transfer of electrons between the substrate and the electrode. This involves the "Direct Electrochemical Oxidation Mechanism", where direct electron transfer takes place between the electrode surface and the phenolic substrate, resulting in a radical cation which then undergoes further reaction to form the hydroxylated products. Scheme 3.2 shows this proposed mechanism.



Scheme 3. 2: Direct electrochemical oxidation of phenol

The mechanism can be broken down into the following steps:

i E: Anodic oxidation of the aromatic substrate at the electrode surface in order to produce the radical cation, followed by resonance stabilization of this radical. The extent to which this occurs depends on the oxidation potential of the phenolic compound. The lower the oxidation potential the greater the extent of the reaction.

- ii C: The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical. The location from which this proton is lost depends on the acidity of the phenolic group and the reaction medium. This is a rapid reaction due to the acidity of the phenolic radical cation, since the pKa value is in the range of 9.98 for unsubstituted phenol.<sup>79</sup>
- iii E: The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- iv C: Nucleophilic attack of water on the cation, resulting in a highly unstable structure, which is then rapidly rearranged, with the loss of a proton.
- v C: Rearrangement of the compound to hydroquinone.
- vi E: Anodic oxidation of the hydroquinone at the electrode surface in order to produce the radical cation.
- vii C: The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical.
- viii E: The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- ix C: Nucleophilic attack of water on the cation, resulting in an unstable structure, which is then rapidly rearranged, with the loss of a proton in order to produce the cyclohexadienyl compound.
- x This cyclohexadienyl compound then loses water in order to produce the benzoquinone.

The above mechanism (Scheme 3.2) is a widely accepted direct electron transfer mechanism. The problem is that this mechanism does not explain the pronounced mass balance change observed during the product distribution diagrams. It is well known that phenol undergoes dimerization and polymerization at a platinum anode,<sup>80,144,145</sup> and one of the dimers (the respective 1,1'-biphenyl-4,4'-diol) was detected in trace amounts. Scheme 3.3 shows a mechanism which proposes to explain the mass balance change.

Scheme 3.3: Proposed direct electrochemical mechanism (dimer route)



R1 and R2 in this investigation was H or  $C(CH_3)_3$  (from step iv to step xi the R groups are not displayed due to space limitation)

The mechanism can be broken down into the following steps:

- i Anodic oxidation of the aromatic substrate at the electrode surface in order to produce the radical cation.
- ii The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical. The location from which this proton is lost depends on the acidity of the phenolic group and the reaction medium. This is a rapid reaction due to the acidity of the phenolic radical cation, since the pKa value is in the range of 9.98 for unsubstituted phenol.<sup>79</sup>
- iii Coupling of the radicals in order to produce the dimeric isomers of the respective 1,1'-biphenyl-4,4'-diols.
- iv The loss of an electron from the 1,1'-biphenyl-4,4'-diols in order to produce the radical cation, followed by resonance stabilization of this cation.
- The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical.
- vi The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- vii The loss of a proton from the organic cation in order to produce the respective biphenoquinone.
- viii The loss of an electron from the biphenoquinone in order to produce the radical cation, followed by resonance stabilization of this radical cation.
- ix Nucleophilic attack of water on the radical cation, resulting in a hydroxylated radical.
- x Loss of an electron forming the hydroxylated radical leading to a organic cation.
- xi Nucleophilic attack of water on the organic cation, resulting in the respective 1,1'-dihydroxy-1,1'-bi(cyclohexa-2,5-dien-1-yl)-4,4'-diones.
- xii The addition of a proton to the respective 1,1'-dihydroxy-1,1'-bi(cyclohexa-2,5-dien-1-yl)-4,4'-dione, leading to its break up into the respective hydroquinone and organic cation.
- xiii A typical two electron oxidation of the respective hydroquinone to the respective benzoquinone.
- xiv The loss of a proton from the organic cation yielding the respective benzoquinone.

The electrochemical oxidation of phenolic compounds at platinum and graphite anodes probably occurs according to both the known mechanism shown in Scheme 3.2 and the proposed mechanism shown in Scheme 3.3. An explanation for the mass balance change could not be found in the literature, so the investigation was used to propose the mechanism shown in Scheme 3.3.

### 3.2.6.2.3 Cathodic reduction

The benzoquinones produced during the anodic reactions can be readily reduced at the cathode in a well known electrochemical reduction, shown in Scheme 3.4.<sup>82</sup> It can be seen that this is an ECEC mechanism, and it is discussed below.



Scheme 3. 4: Electrochemical reduction of benzoquinone to hydroquinone

 $R_1$  and  $R_2$  in this investigation was H or  $C(CH_3)_3$ 

The mechanism takes place in the following steps:

i E: A one electron reduction of the benzoquinone at the cathode in order to produce the radical anion. This radical can then be resonance stabilized. The ease with which this occurs depends on the reduction potential of the molecule.

- ii C: The addition of a proton to the radical anion followed by electron rearrangement within the molecule in order to produce the aromatic radical.
- iii E: The gain of an additional electron to the molecule so as to form an anion, which is resonance stabilized. In a protic media, this species will be short lived, due to the high proton affinity of the anion.
- iv C: The anion will then rapidly accept a proton from almost any source in order to produce the hydroquinone.

# **3.3 Conclusion**

The divided cell electrolysis study showed that a particular phenol is oxidised at the anode to the respective hydroquinone; this hydroquinone, having a lower oxidation potential than the phenol, is then immediately oxidised to the respective benzoquinone. The resulting benzoquinone can then be cathodically reduced to the corresponding hydroquinone.

- Platinum and graphite anodes: The results showed that electrochemical oxidation of phenols at platinum and graphite anodes proceeds through two different direct electrochemical oxidation mechanisms: one of which is the well known ECE mechanism shown in Scheme 3.2; the other being the proposed direct radical cation mechanism shown in Scheme 3.3.
- Lead dioxide anode: The results showed that electrochemical oxidation of phenols at the lead dioxide anode proceeds through two different mechanisms. The indirect electrochemical oxidation mechanism utilizing the electrode bonded electro-generated hydroxyl radical shown in Scheme 3.1 and to a lesser extent the proposed direct electrochemical oxidation mechanism shown in Scheme 3.3. It was also shown that the direct mechanism is not due to the lead dioxide electrode, but is due to the electron transfer reactions of the phenols with the base onto which the lead dioxide is plated.

The investigation also yielded a possible explanation for the increased ratio of hydroquinone to catechol observed during the electrochemical oxidation. The

explanation for this is that both the mechanisms produce the products through either the cyclohexa-2,5-dienone cation or cyclohexa-2,5-dienone radical.

# **CHAPTER 4**

# **Electrochemical Oxidation of Substituted Phenols**

# **4.1 Introduction**

In this chapter the constant current electrolysis of 2-*tert*-butylphenol is investigated so as to determine the experimental parameters which favour maximum yield to 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone (Scheme 4.1).

Scheme 4.1: Oxidation of 2-*tert*-butylphenol to 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone



The electrochemical oxidation of an un-substituted phenol results in a number of different isomeric compounds (Scheme 4.2).



#### Scheme 4.2: Electrochemical oxidation of phenol

Phenol is first oxidized to hydroquinone, resorcinol and catechol, followed by further oxidation to benzo-1,2-quinone and benzo-1,4-quinone. The benzo-1,3-quinone is not formed due to its instability.<sup>89</sup> Not shown in the scheme is the formation of oligomeric and polymeric products during electrolysis due to O-C and C-C coupling reactions between primary oxidation products and substrate and / or oxidation products. Such coupling reactions are particularly problematic during electrolytic oxidation reactions if primary oxidation intermediates are allowed to accumulate at the electrode surface. Polymer formation on the anode surface can often be observed during these oxidation reactions. When one or more positions adjacent to the phenolic hydroxyl group is substituted, especially with a bulky substituent such as a *tertiary* butyl group, the tendency to form C-O coupled oligomers is reduced. For this reason the sum of all phenolic starting materials and oxidation products has been determined throughout the investigation so as obtain some measure of the extent of oligomer formation.

The remainder of this chapter describes the results obtained for the electrochemical oxidation of 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol, while the results for the oxidation of phenol itself is described in the following chapter.

Two different electrolysis procedures, have been used for the oxidation of 2-*tert*butylphenol, namely simple undivided batch cell electrolysis and flow cell batch recirculation electrolysis, also in the undivided mode. These procedures were fully described in Chapter 2.

## 4.2 Effect of reaction variables

The actual settings of reaction variables will have a distinct effect on the electrolysis, since they affects both the electrode reactions, as well as the follow up chemical reactions.

The following experimental variables were investigated:

Temperature<sup>145</sup>: Temperature not only affect the kinetics of all steps of the reaction, electrochemical and chemical, but also the physical properties of

the reaction medium. Examples of the latter include solubility of compounds, conductivity of the electrolytic solution, mass transport conditions in the cell, etc.

- Substrate loading: The optimum substrate loading is a function of both the nature (mechanism) of the product formation reactions and the nature of byproduct formation reactions. It is desirable to have as high a substrate loading as possible to maximise equipment utilization and the optimum substrate loading is often a compromise between these different demands.
- Acid concentration: Variations in the sulphuric acid concentration can influence both the electrochemical and chemical steps of the oxidation reaction as well as the physical properties of the reaction medium such as conductivity.
  - From Schemes 1.8 and 1.10 it can be seen that proton exchange plays an important role in the oxidation mechanism: too low a concentration of acid may promote dimerization.
  - Since protons can be reduced at the cathode to hydrogen gas, this reaction could compete with the reduction of benzoquinone to hydroquinone. It is also known that gas formation at an electrode drastically increases mass transport at the electrode.
- Nature of organic solvent: Variation of the organic solvent can affect the reaction in the following ways:
  - The nature of the solvent determines the solubility of the substrate in the reaction medium, and may also interact chemically with the intermediates.
  - The solvent can affect the electrochemical reaction since certain solvents can act as nucleophiles whereas others have their own distinctive electrochemical behaviour, such as being able to produce radicals.
- Solvent composition: For an aqueous / organic mixture the ratio of water to solvent not only governs the solubility of the organic substrate in the reaction medium, but may also determine the extent to which water may participate in the reaction:
  - From Schemes 1.8 and 1.10 it can be seen that water can act as both a nucleophile and source of hydroxyl radicals in the reaction medium.

- Water can be oxidised at the anode to oxygen gas, and this reaction could compete with the oxidation of phenol to benzoquinone. The formation of oxygen gas may also affect the mass transport to and from the electrode surface.
- Current density: A higher current density means that more current is passed through the system in a given amount of time, which will influence the extent of oxidation as compared to a lower current density. Current density can also play a role in determining the dominant reaction at the electrode surface.
- Nature of electrode: As discussed previously in Section 1.6 the nature of an electrode can drastically affect the reactions occurring at an electrode.

Additional variables for flow cell electrolysis are:

- Electrode separation: The electrode separation has a distinct effect on the reaction, since higher electrode separations will increase the IR drop between the electrodes, hence the cell potential during constant current electrolysis.
- Flow rate: The flow rate through the flow cell will have an effect on the mass transport within the cell.

# 4.3 Results and discussion for 2-tert-butylphenol

In this section the following abbreviations will be used in order to simplify the presentation of the graphical data:

- ✤ 2-*tert*-butylphenol = 2tbPhOH
- 2-tert-butylhydroquinone = 2tbHq
- 2-*tert*-butylbenzoquinone = 2tbBq

## 4.3.1 Undivided batch cell electrolysis

Table 4.1 gives the settings of experimental variables that were used as standard conditions for the electrochemical oxidation of 2-*tert*-butylphenol. Table 4.2 gives the range of settings investigated for each variable so as to determine the optimum value for each variable. The variation of each variable was compared with the standard control settings. The charge passed through the cell in each

case was 4 F, the theoretical amount required to fully convert the phenolic substrate to the benzoquinone in a divided cell.

Variable	Value
Anode	Lead dioxide on titanium
	mesh
Cathode	Nickel
Organic solvent	Acetonitrile
Organic solvent (% v/v)	67.5
$H_2SO_4$ conc. (% v/v)	4.9
Substrate loading (% m/v)	4.0
Current density (A m <sup>-2</sup> )	2000
Temperature (°C)	40
Charge (F)	4
Total solvent volume (organic + water + H <sub>2</sub> SO <sub>4</sub> )	40 ml

 Table 4.1: Standard conditions: 2-tert-butylphenol undivided batch cell electrolysis

Table 4.2: Reaction variables: 2-tert-butylpheno	ol undivided batch cell electrolysis
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Variable	Value
Anode	Lead dioxide on titanium mesh, Graphite
Cathode	Nickel, Stainless steel, Graphite, Titanium
Organic solvent	Methanol, Ethanol, n-Propanol, n-Butanol, Acetic
	acid, Propanoic acid, 2-propanol, <i>t</i> -butanol,
	Acetonitrile, Tetrahydrofuran, N,N'-
	Dimethylformamide
Organic solvent (% v/v)	55, 68, 80, 90, 94
Acid conc. (% v/v)	0.325, 1.625, 3.250, 4.875, 8.125, 11.375
Substrate loading (% m/v)	2.0, 4.0, 8.0, 16.0
Current density (A m <sup>-2</sup> )	300, 500, 1000, 1500, 2000, 2500, 3000, 3500
Temperature (°C)	40, 50, 60, 70, 80

### 4.3.1.1 Anode material investigation

Electrolysis was carried out according to the standard conditions in Table 4.1, with the only variable being the particular electrode under investigation. The total charge passed through the cell in each case was 4 F and solutions were analyzed for the various components present: 2-*tert*-butylphenol, 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone using the analytical procedure given in Section 2.23.

It should be kept in mind that the surface areas of the cathodes used were not exactly the same in each case, so that results can only be used for a qualitative comparison.

Figure 4.1 shows the results obtained when using lead dioxide on titanium and carbon as anode. In these experiments nickel was the cathode.

Both 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone can be regarded as a successful outcome of the oxidation of the substrate 2-*tert*-butylphenol, hence the sum of the two can be taken as an indication of the overall oxidation selectivity. The results for lead dioxide are slightly better than those for carbon.

Figure 4.1: Anode Material Investigation



### 4.3.1.2 Cathode material

Figure 4.2 depicts the results obtained for the electrolysis of 2-*tert*-butylphenol when using different cathode materials and using lead dioxide on titanium as anode.

The cathodic function of the electrode is the reduction of 2-*tert*-butylbenzoquinone to 2-*tert*-butylhydroquinone. The best cathode materials will be those which produce the highest ratio of 2-*tert*-butylhydroquinone to 2-*tert*-butylbenzoquinone. The three electrodes which perform the best are nickel, carbon and cadmium. Of these, nickel and cadmium have very high hydrogen overpotentials, which allow the electrodes to cathodically reduce 2-*tert*-butylbenzoquinone in preference to hydrogen ion reduction. Of these, nickel gave the best results and was therefore selected as the cathode material in further work.

Figure 4.2: Cathode Material Investigation



### 4.3.1.3 Type of organic solvent

Various organic solvents were evaluated, one at a time, as the organic medium for the electrolysis. The standard conditions listed in Table 4.1, with the exception of the type of organic solvent, were used for these conditions.

Figure 4.3 summarizes the results obtained and the summary for the solvent identities are as follows: methanol (MeOH), ethanol (EtOH), n-propanol (n-PrOH), 2-propanol (2-PrOH), n-butanol (n-BuOH), *tert*-butanol (t-BuOH), acetic acid (AcOH), propanoic acid (PrOH), acetonitrile (MeCN), tertrahydrofuran (THF) and N,N-dimethylformamide (DMF).

Figure 4.3 Effect of Organic solvent



The following observations are noteworthy:

Alcohols: Primary alcohols resulted in the formation of small amounts of ring substituted products such as 2-*tert*-butyl-4-methoxyphenol, 2-*tert*-butyl-4ethoxyphenol and 2-*tert*-butyl-4-propoxyphenol. Secondary alcohols yielded similar results but to a lesser extent (2-*tert*-butyl-4-isopropoxyphenol, 2-*tert*butyl-4-butoxyphenol), but tertiary butanol did not produce substitution compounds. The decrease in the extent of ring substitution when moving from primary to tertiary alcohols can probably be ascribed to the decrease in nucleophilic strength of the alcohols as we move from primary to tertiary alcohol. The possible mechanism for these reactions is shown in Scheme 4.3.





ROH = Alcohol

- Carboxylic acids: Carboxylic acids also produced small amounts of ring substituted products such as 3-*tert*-butyl-4-hydroxyphenyl acetate and 3-*tert*butyl-4-hydroxyphenyl propionate. Acetic acid gave relatively good results for the mass balance, current efficiency and amount of 2-*tert*-butylhydroquinone, but as the carboxylic acid chain length increases, the results deteriorate. This is probably due to a lowering of the oxidation potential of the carboxylic acid as the chain length increases. This lowering in the oxidation potential will increase the extent to which the Kolbe reaction (Section 1.6.2.1) occurs.<sup>79</sup>
- Acetonitrile: Acetonitrile gave the best results of all the organic solvents investigated. Only trace amounts of side products were observed and the likely reactions resulting in these side products are shown below:



> Various isomers of 3,3'-di-*tert*-butyl-1,1'-biphenyl-4,4'-diol (Reaction 4.1)

The solvents tetrahydrofuran (THF) and dimethylformamide perform very poorly with large amounts of unreacted 2-*tert*-butylphenol and only small amounts of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone.

Using the sum of the 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone, and the current efficiency as key responses, the best three solvents were acetic acid (HOAc), *tertiary*-butanol (t-BuOH) and acetonitrile (MeCN).

In order to evaluate each of the three most promising solvents in more detail, full product distribution diagrams were constructed for each as a function of charge per mol / F passed through the cell. The electrolysis was carried out using the standard conditions listed in Table 4.1, with the exception that the organic solvent was varied and that the electrolysis was extended beyond 4F. Samples were drawn at regular intervals and analyzed for the various constituents. The resultant product distribution diagrams, are shown in Figures 4.4 - 4.6.



Figure 4.4: Product Distribution Diagram using tertiary-butanol as solvent

Figure 4.5: Product Distribution Diagram using acetonitrile as solvent




Figure 4.6: Product Distribution Diagram using acetic acid as solvent

All three solvents show similar trends, but with different efficiencies. The rate of oxidation of 2-tert-butylphenol, and consequently the rate of formation of 2-tertbutylhydroquinone and benzoquinone, is the highest in acetonitrile, followed by tert-butanol and acetic acid. This observation is probably the result of the higher electrochemical stability of acetonitrile. The oxidation of 2-tert-butylphenol will compete with all oxidation reactions that can occur. In the case of acetic acid this is the Kolbe reaction (Section 1.6.2.1). The oxidation of tert-butanol occurs to a lesser extent than acetic acid, hence, the oxidation of 2-tert-butylphenol occurs to a greater extent in *tert*-butanol than in acetic acid. The trend in the current efficiency values (MeCN > t-BuOH > HOAc) can possibly also be explained using the decreasing occurrence of competing oxidation reactions as discussed above. The mass balance for the reaction which is the sum of the 2-tert-butylphenol, 2tert-butylhydroquinone and 2-tert-butylbenzoquinone, is the highest in acetonitrile followed by tert-butanol and acetic acid. The mass balance shows an interesting characteristic in all three solvents: an initial loss of the material, followed by a tendency towards 100 % recovery. This was suggested in Chapter 3 to be due to

the formation of a "intermediate" which breaks down to form the 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone.

From these results it would appear as if acetonitrile and water is the best solvent combination for the electrochemical oxidation of 2-*tert*-butylphenol when using a lead dioxide anode.

#### 4.3.1.4 Amount organic solvent

The effect of varying the acetonitrile : water ratio on the oxidation of 2-*tert*butylphenol was investigated by using the standard conditions listed in Table 4.1, but varying the amounts of acetonitrile : water. Figure 4.7 shows the data of this investigation

There is an increase in the sum of 2-*tert*-butylphenol, 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone as the percentage acetonitrile increases, with a maximum at about 90 %, at which point very little 2-*tert*-butylphenol is oxidised.



Figure 4.7: Effect of Organic Solvent Percentage

The amounts of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone formed remains virtually constant up to a acetonitrile percentage of 80 %, after which there is a drastic decrease. These observations mirror the decrease in the rate of 2-*tert*-butylphenol oxidation in the same range of solvent compositions and, consequently, the variation in current efficiency.

It is clear from the results obtained that the optimum acetonitrile : water ratio lies in the range 55 : 45 to 75 : 25. Below 55 % acetonitrile the oxidation is probably limited by the solubility of the substrate in the increasing aqueous mixture, while above 75 % acetonitrile, several factors may start to impact upon the oxidation, e.g. conductivity, proton exchange, etc.

#### 4.3.1.5 Acid concentration

Figure 4.8 shows the effect of an increase in the sulphuric acid concentration on the oxidation of 2-*tert*-butylphenol carried out under the standard conditions listed in Table 4.1. All variables, except the acid concentration, were kept constant, and the total charge passed through the cell was 4 F in each case.

Figure 4.8: Effect of Acid Concentration



The results for the rate and extent of 2-*tert*-butylphenol oxidation, amounts of 2*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone and current efficiency remains remarkable constant as the sulphuric acid concentration is increased from 0.325 to 11 %. This is particularly so in the range from about 1.5 to 5 % sulphuric acid. Below a sulphuric acid loading of 1.5 % there is a slight drop in performance, probably as a result of a combination of factors such as electrical conductivity and proton availability. Above a 5 % sulphuric acid loading, it is not unreasonable to propose that side reactions which are catalyzed by sulphuric acid such as oligomer formation, are inhibiting the oxidation process. The relatively low mass balance (~80 %) is most likely due to the formation of an intermediate that cannot be detected using the present analytical method. This is particularly true at 4 F of charge. It will be demonstrated later that at higher levels of charge (~8F), the mass balance improves significantly.

#### 4.3.1.6 Substrate loading

The effect of substrate loading on the oxidation of 2-*tert*-butylphenol was investigated using the standard conditions given in Table 4.1, with the percentage substrate loading being the only variable that was changed. The charge passed through the cell was 4 F, after which the reaction mixtures were analyzed. Figure 4.9 illustrates the results obtained for this investigation.





The results for rate and extent of 2-*tert*-butylphenol oxidation, 2-*tert*butylbenzoquinone, current efficiency and mass balance decrease noticeably as the substrate loading is increased from 2 to 8 %, whereas, the extent of 2-*tert*butylhydroquinone formation increases within the same range. As the substrate loading is increased further from 8 to 16 % all the responses, except for 2-*tert*butylhydroquinone which decreases, follow their original trends to a lesser extent. The decrease in the current efficiency and mass balance (sum 2-*tert*-butylphenol, 2-*tert*-butylbenzoquinone and 2-*tert*-butylhydroquinone) as the substrate loading increases indicates that the extent of the proposed "intermediate" formation increases with substrate loading. The decrease in the rate of 2-*tert*-butylphenol oxidation with increasing substrate loading can be related to an increase in the extent of competing anodic reactions with increasing substrate loading, such as further oxidation of the "intermediate". As the substrate loading increases, the oxidation of 2-*tert*-butylhydroquinone is suppressed while the reduction of 2-*tert*-butylbenzoquinone is relatively unaffected, resulting in a build up of the 2-*tert*-butylhydroquinone in the reaction medium. The results at 4 F indicate that the reaction proceeds best at low substrate loadings of about 4 %; this may however change as the charge sent through the system is increased.

#### 4.3.1.7 Current density

The effect of increased current density on the oxidation of 2-*tert*-butylphenol was investigated using the standard conditions listed in Table 4.1, with the exception that the anodic and cathodic current density was varied. Figure 4.10 illustrates the results obtained.





The results for rate and extent of 2-tert-butylphenol oxidation, 2-tertbutylhydroquinone and current efficiency decrease as the current efficiency is increased from 300 to 3500 A m<sup>-2</sup>, whereas, the extent of 2-*tert*-butylbenzoquinone and mass balance increase within the same range. The mass balance results could possibly indicate that it is just a case that a certain minimum current density is required for efficient oxidation. The 2-tert-butylhydroquinone and 2-tertbutylbenzoquinone results indicate that as the current density increases the oxidation rate of 2-tert-butylhydroquinone to 2-tert-butylbenzoquinone becomes faster than the rate of 2-*tert*-butylhydroquinone transport away from the electrode surface resulting in less accumulation of 2-*tert*-butylhydroguinone. The decrease in current efficiency with an increase in current density probably results from the loss of current due to the reversible oxidation of 2-tert-butylhydroguinone to 2-tertbutylbenzoquinone. The decrease in the extent of 2-*tert*-butylphenol oxidation with increasing current density is probably a mass transport phenomenon. The results for the batch cell at 4 F indicate that the reaction proceeds best at low current densities ranging from 500 to 1000 A m<sup>-2</sup>; this may however change as the charge sent through the system is increased.

#### 4.3.1.8 Reaction temperature

The effect of the reaction temperature on the oxidation of 2-*tert*-butylphenol was investigated using the standard conditions listed in Table 4.1, except that the reaction temperature was varied. Electrolysis was carried out until 4 F of charge had passed through the cell, after which the electrolysis solution was analyzed. Figure 4.11 depicts the results obtained.





The results for rate and extent of 2-tert-butylphenol oxidation, 2-tertbutylhydroquinone and current efficiency increase as the reaction temperature is increased from 25 to 80 °C, whereas, the extent of 2-tert-butylbenzoquinone and mass balance remains relatively constant within the same range. It should be noted that at 50 °C and above, the increase in the responses seems to level out, except for the mass balance which drops slightly from 40 °C followed by an increase from 60 °C with temperature, and the 2-tert-butylhydroquinone and 2-tertbutylbenzoquinone which increase and decrease respectively at temperatures above 70 °C. The drop in the mass balance at 50 °C can be ascribed to increased amounts of un-analyzed intermediate formation; the increase beyond 60 °C could be due to the instability of the "intermediate" at higher temperature, resulting in an increase in 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone. The results for the batch cell at 4 F indicate that the reaction proceeds best at temperatures above 50 °C; this could however change as the charge sent through the system is increased.

#### 4.3.1.9 Optimum conditions for batch cell electrolysis

Table 4.3 summarizes the optimum conditions for the oxidation of 2-*tert*butylphenol using an undivided batch electrolytic cell, as determined in the preceding sections.

Variable	Optimum Condition
Acid Concentration (% m/v)	1.5 - 5
Organic Solvent Percentage (% v/v)	67.5 - 80
Current Density (A m <sup>-2</sup> )	500
Organic solvent	Acetonitrile
Substrate Loading (% m/v)	2 - 4
Reaction Temperature (°C)	50 and above
Anode	Lead Dioxide
Cathode	Nickel

 Table 4.3: Optimum Conditions Undivided Batch Cell Electrolysis

The above investigation was performed as a preliminary study in order to eliminate the obvious ineffectual variables from further investigation, resulting in the results shown in Table 4.3 only being applicable to the specific system investigated. What was clear from this and subsequent investigations was that the charge sent through the system has a significant effect on the optimum conditions, this being due to the break up of the un-analyzed intermediate at higher charges; this is especially clear when considering substrate loading.

#### 4.3.2 Micro-flow cell electrolysis

The electrochemical oxidation of 2-*tert*-butylphenol using a flow cell was investigated using the same approach as for batch cell oxidation. The experimental setup of the flow cell was described in Section 2.2.2.

Table 4.4 lists the standard conditions used for the flow cell oxidations, and Table 4.5 gives the variables investigated and their respective ranges studied. Each

variable was investigated one at a time, whilst keeping all other conditions constant.

Variable	Value
Anode material	Lead dioxide on lead
Cathode material	Nickel
Electrode separation (mm)	6
Flow rate (cm <sup>3</sup> min <sup>-1</sup> )	168
Substrate loading (% m/v)	4.0
Current density (A m <sup>-2</sup> )	2000
Acid conc. (% v/v)	3
Organic solvent (% v/v)	70
Organic solvent	Acetonitrile
Temperature (°C)	50

Table 4.4: Standard conditions: 2-tert-butylphenol micro-flow cell electrolysis

Variable	Value
Anode Material	Graphite, Platinum on Niobium, Lead, Lead
	dioxide on Titanium, Lead dioxide on lead
Cathode Material	Graphite, Nickel, Platinum on Niobium
Electrode Separation (mm)	4, 6, 10
Flow Rate ( $cm^3 min^{-1}$ )	118, 168, 220
Substrate loading (% m/v)	4, 20
Anodic current density (A m <sup>-2</sup> )	667 – 6000
Cathodic current density (A m <sup>-2</sup> )	667 – 6000

Some variables examined in the batch investigation (acid concentration, organic solvent percentage, temperature) were not investigated during the flow cell electrolysis as it was expected that their effect will be the same for the flow cell. A number of new variables were investigated for the flow cell (flow rate and electrode separation). Preliminary work showed that the presence of a turbulence frit had no effect on the reaction outcome, hence was not included in the investigation.

For this investigation product distribution diagrams were generated as a function of charge per mol / F, passed through the flow cell. This provided a more detailed insight into the performance of the flow cell as compared to a "one sample point" analysis.

#### 4.3.2.1 Anode material

Three different materials were evaluated as anodes in the flow cell for the oxidation of 2-*tert*-butylphenol. The different electrodes were: lead dioxide on lead, lead dioxide on titanium, and platinum on niobium. The standard conditions as listed in Table 4.4 were used using nickel as cathode in each case. Samples were withdrawn at regular intervals and analyzed for the usual components. Figures 4.12 - 4.14 show the product distribution diagrams for each anode tested.



Figure 4.12: Product Distribution Diagram: Lead dioxide on Lead Anode



Figure 4.13: Product Distribution Diagram: Lead Dioxide on Titanium Anode

Figure 4.14: Product Distribution Diagram: Platinum on Niobium Anode



The results for rate and extent of 2-tert-butylphenol oxidation, amounts of 2-tertbutyl hydroquinone and 2-tert-butylbenzoquinone, mass balance and current efficiency show that the lead dioxide anodes outperform the platinum on niobium anode. The mass balance results for the anodes indicate an increase in performance going from platinum on niobium to lead dioxide on titanium to lead dioxide on lead. The mass balance change was at a maximum at the platinum on niobium anode, decreasing to the lead dioxide electrodes with the lead dioxide on lead showing almost no mass balance loss. This mass balance drop is due to the formation of an un-analyzed "intermediate", this indicates that there are at least two mechanisms at work: one that forms no intermediate and one that does. The platinum anode requires ~ 8 electrons per molecule to form and decompose the intermediate into 2-tert-butylhydroquinone and 2-tert-butylbenzoquinone, indicating that the "intermediate" mechanism dominates. For lead dioxide, irrespective of the base metal, the "non-intermediate" mechanism seems to dominate, but again it would seem that  $\sim 8$  electrons per molecule are required to complete the oxidation.

The results show that the lead dioxide on titanium favours the 2-tertbutylhydroquinone and the lead dioxide on lead the 2-tert-butylbenzoquinone production; this could be explained through current density. The two dimensional electrode area was controlled but since the electrodes were manufactured using different methods, the three dimensional surface area varies with lead dioxide on titanium having a higher current density, so the rate of 2-tert-butylbenzoquinone production is higher while the rate of 2-*tert*-butylbenzoguinone reduction remaining constant; this is also shown by the rate of 2-tert-butylphenol oxidation. The current efficiency results indicate that the lead dioxide on titanium is the best anode followed by lead dioxide on lead and the platinum electrode yielding the worst results. Platinum has a much lower oxygen overpotential than lead dioxide so the electrolysis of water is greater on the platinum electrode surface, and a larger portion of the current will be lost on water electrolysis.<sup>83</sup> The current efficiency difference for the lead dioxide electrodes can be explained by the permeability of the lead dioxide, allowing contact of the electrolysis solution with the base metal; titanium will not undergo any reaction but lead can convert to lead dioxide so

consuming current. The rate of 2-*tert*-butylphenol oxidation can be explained using a similar discussion as that for the current efficiency above.

The better performance was shown by the two lead dioxide electrodes. Table 4.6 summarizes some important data when comparing the two lead dioxide electrodes, and it can be seen that, in overall performance, the two electrodes are very similar. Better 2-*tert*-butylphenol and 2-*tert*-butylhydroquinone oxidation are shown on the lead dioxide on titanium electrodes.

Electrodes	Responses at 8 F				
	%	% Current	% 2tbHq	% 2tbBq	% Mass
	2tbPhOH	Efficiency			Balance
PbO <sub>2</sub> on Ti	2	43	38	50	90
PbO <sub>2</sub> on Pb	7	44	64	25	96
Electrodes	Responses at 10 F				
	%	% Current	% 2tbHq	% 2tbBq	% Mass
	2tbPhOH	Efficiency			Balance
PbO <sub>2</sub> on Ti	1	39	40	59	100
$PbO_2$ on $Pb$	4	41	65	29	98

Table 4.6: Responses at 8 F and 10 F for the lead dioxide electrodes

#### 4.3.2.2 Cathode material

Three different materials were evaluated as cathodes in the flow cell for the oxidation of 2-*tert*-butylphenol, namely nickel, platinum on niobium and graphite. The standard conditions in Table 4.4 were used with lead dioxide on titanium as anode to construct the respective product distribution diagrams shown in Figures 4.15 - 4.17.



Figure 4.15: Product Distribution Diagram: Nickel Cathode

Figure 4.16: Product Distribution Diagram: Platinum on Niobium Cathode





Figure 4.17: Product Distribution Diagram: Graphite Cathode

The results for rate and extent of 2-*tert*-butylhydroquinone, mass balance and current efficiency show that the cathodes follow the decreasing trend: nickel, platinum and graphite. The rate and extent of production of 2-*tert*-butylphenol oxidation and 2-*tert*-butylbenzoquinone formation show that the cathodes follow the decreasing trend graphite, platinum and nickel. The mass balance results indicate a much smaller change when compared to the anode investigation due to a smaller extent of "intermediate" production, indicating that the formation of the "intermediate" is an anode dependent phenomena. The number of electrons per molecule needed for the formation and oxidation of the "intermediate" to 2-*tert*-butylbenzoquinone, cannot be clearly identified due to a premature stop in the graphite electrolysis; it does however appear to be 10 electrons per molecule. The cathode efficiency for 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone varies, suggesting that the ratio is a cathodic phenomenon possibly related to the hydrogen overpotential of the

cathodes.<sup>83</sup> Taking all the parameters into consideration, the nickel electrode seems to be the best cathode.

#### 4.3.2.3 Electrode separation

Three different electrode separations were evaluated for the flow cell oxidation of 2-*tert*-butlyphenol namely 4, 6 and 10 mm. The standard conditions in Table 4.4 were used to construct the respective product distribution diagrams shown in Figures 4.18 - 4.20.

It should be noted that electrode separation can be related to flow rate: at lower electrode separation the effective flow rate through the electrolysis cell is higher than at larger electrode separations, thus electrode separation also affects mass transport. It should also be noted that an increase in electrode separation increases the IR drop between the electrodes. So at low electrode separations the IR drop will be smaller so the effective electrolysis potential will be lower than at higher electrode separations.



Figure 4.18: Product Distribution Diagram: 4mm Electrode Separation



Figure 4.19: Product Distribution Diagram: 6mm Electrode Separation

Figure 4.20: Product Distribution Diagram: 10mm Electrode Separation



The results for rate and extent of 2-tert-butylhydroquinone and mass balance show that the electrode separation follows the decreasing trend 6, 4 and 10 mm, and that for 2-tert-butylbenzoquinone the reverse of the trend. The rate and extent of 2tert-butylphenol and current efficiency show that the electrode separation follows the decreasing trend 4, 10 and 6 mm. The drop in mass balance is most pronounced at electrode separations above and below 6 mm, but all the mass balance curves return to close to 100 % after 8 electrons per molecule has been passed, indicating that the formation of the "intermediate" is favoured at high and low electrode separations. The 2-*tert*-butylhydroquinone and 2-tertbutylbenzoquinone results indicate that the ratio of these compounds change with electrode separation. The above observations can probably be explained as a result of the optimum mass transport conditions The current efficiency and 2-tertbutylphenol results can be explained through the IR drop since when the IR drop increases more current is wasted in heating the reaction medium. The results indicate that an electrode separation of 6 mm or lower should be used.

#### 4.3.2.4 Flow rate

Three different flow rates were evaluated in the flow cell for the oxidation of 2-*tert*butylphenol, namely 118 to 220 (cm<sup>3</sup> min<sup>-1</sup>). The standard conditions in Table 4.4 were used to construct the respective product distribution diagrams shown in Figures 4.21 - 4.23.





Figure 4.22: Flow Rate Investigation: 168 cm<sup>3</sup> min<sup>-1</sup>



Figure 4.23: Flow Rate Investigation: 220 cm<sup>3</sup> min<sup>-1</sup>



The results for rate and extent of 2-*tert*-butylhydroquinone and mass balance show that the flow rate is at an optimum at 168 cm<sup>3</sup> min<sup>-1</sup> whereas that for 2-*tert*-butylbenzoquinone is at an optimum at 118 - 168 cm<sup>3</sup> min<sup>-1</sup>, and the current efficiency remains constant throughout the investigation. The extent of 2-*tert*-butylphenol oxidation is at a slight minimum at a flow rate of 168 cm<sup>3</sup> min<sup>-1</sup>. The mass balance drop is observed to be the smallest at a flow rate of 168 cm<sup>3</sup> min<sup>-1</sup>, but present none the less; it is however clear that the mass balance return requires 8 F to form and oxidise the "intermediate" to 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone. The variation in the ratio of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone, could be related to the mass transfer conditions at the cathode, since the current efficiency remains constant. From the above results it can be seen that the flow rate has no real effect on any of the responses investigated except for the ratio of 2-*tert*-butylhydroquinone to 2-*tert*-butylbenzoquinone.

#### 4.3.2.5 Substrate loading

Two different substrate loadings were evaluated in the flow cell with batch recirculation for the oxidation of 2-*tert*-butylphenol, namely 4 % and 20 %. The standard conditions in Table 4.4 were used to construct the respective product distribution diagrams shown in Figures 4.24 - 4.25.



Figure 4.24: Product Distribution Diagram: 4 % Substrate Loading



Figure 4.25: Product Distribution Diagram: 20 % Substrate Loading

The results for rate and extent of 2-*tert*-butylphenol oxidation, amounts of 2-*tert*butylhydroquinone and 2-*tert*-butylbenzoquinone and current efficiency indicate that a lower substrate loading yields the best results for all the responses investigated except for the 2-*tert*-butylbenzoquinone. This could indicate that the formation of the bi-phase medium at 20 % substrate loading changes the polarity of the reaction medium, possibly affecting the adsorption of the 2-*tert*butylbenzoquinone on the cathode thus resulting in the low yields of 2-*tert*butylhydroquinone. The slow 2-*tert*-butylphenol consumption and the mass balance drop for the 20 % substrate loading could be ascribed to the fact that at these high substrate loadings the rate of "intermediate" production is so fast that the "intermediate" can deactivate the anode, resulting in a decreased oxidation rate. Performing the reactions at lower substrate loadings is thus suggested.

#### 4.3.2.6 Anodic current density

The effect of anodic current density on the oxidation of 2-*tert*-butylphenol was investigated using the standard conditions listed in Table 4.4, with the exception that the anodic current density was varied from 667 A m<sup>-2</sup> to 6000 A m<sup>-2</sup>. Figures 4.26 to 4.29 illustrate the results obtained.



Figure 4.26: Product Distribution Diagram: Anodic Current Density 667 A m<sup>-2</sup>



Figure 4.27: Product Distribution Diagram: Anodic Current Density 2000 A  $\mathrm{m}^{\text{-2}}$ 

Figure 4.28: Product Distribution Diagram: Anodic Current Density 3000 A m<sup>-2</sup>





Figure 4.29: Product Distribution Diagram: Anodic Current Density 6000 A m<sup>-2</sup>

The results for the rate and extent of 2-*tert*-butylhydroquinone formation shows an optimum at 667 A m<sup>-2</sup> decreasing to 2000 A m<sup>-2</sup> and increasing to 6000 A m<sup>-2</sup>; the results for 2-*tert*-butylbenzoquinone are reversed. The results for the mass balance show that as the anodic current density increases the faraday count at which the mass balance returns to close to 100 % increases, indicating that the mass balance change is an anodic reaction due to an "intermediate" that is produced and oxidised to 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone. The current efficiency is at an optimum at 2000 to 3000 A m<sup>-2</sup>. The rate and extent of 2-*tert*-butylphenol oxidation remains constant but deteriorates at 6000 A m<sup>-2</sup>.

#### 4.3.2.7 Cathodic current density

The effect of cathodic current density on the oxidation of 2-*tert*-butylphenol was investigated using the standard conditions listed in Table 4.4, with the exception that the cathodic current density was varied from 667 A m<sup>-2</sup> to 6000 A m<sup>-2</sup>. Figures 4.30 to 4.33 illustrate the results obtained.



Figure 4.30: Product Distribution Diagram: Cathodic Current Density 667 A m<sup>-2</sup>



Figure 4. 31: Product Distribution Diagram: Cathodic Current Density 2000 A m<sup>-2</sup>



Figure 4.32: Product Distribution Diagram: Cathodic Current Density 3000 A m<sup>-2</sup>

Figure 4.33: Product Distribution Diagram: Cathodic Current Density 6000 A m<sup>-2</sup>



The results for rate and extent of 2-*tert*-butylhydroquinone formation and current efficiency decrease as the cathodic current density is increased from 667 to 6000 A m<sup>-2</sup>, whereas, the 2-*tert*-butylbenzoquinone formation shows an increasing trend with increasing cathodic current density. The results for rate and extent of 2-*tert*-butylphenol oxidation show no change with increasing cathodic current density. The mass balance change throughout the variable range are all quite similar, with the largest drop occurring at the highest cathodic current density. The faraday values at which the "intermediate" oxidises completely to 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone does however increase with increasing cathodic current density for these reactions appears to be 667 A m<sup>-2</sup>.

#### 4.3.2.8 Optimum conditions for micro flow cell electrolysis

Table 4.7 shows the optimum conditions for the electrolysis of 2-*tert*-butylphenol using the batch recirculation micro flow cell electrolysis.

Variable	Optimum Conditions
Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	Negligible within range investigated
Electrode separation (mm)	Below 6
Substrate Loading (% m/v)	Low substrate loadings
Turbulence frit	No real difference
Anode material	Lead dioxide
Cathode material	Nickel
Anodic Current Density (A m <sup>-2</sup> )	3000
Cathodic Current Density (A m <sup>-2</sup> )	667

 Table 4.7: Optimum Conditions Undivided Batch recirculation Micro Flow Cell

 Electrolysis

# 4.3.3 Comparison of undivided batch and undivided micro flow cell batch recirculation electrolysis

From the results the following observations can be made:

- Mass Balance: The mass balance indicated that the flow cell electrolysis yielded the best results. This is because the mass transport conditions in the flow cell are better than in a batch cell, resulting in the products formed at the anode desorbing into the solution to a greater extent so limiting over oxidation. This increased mass transport also limits the extent to which the "unidentified" product formation occurs, since the "unidentified" product in solution is transported to the electrode surface to a greater extent, resulting in a greater break up of the "unidentified" product in solution leading to a lower loss in mass balance.
- 2-tert-butylhydroquinone: The 2-tert-butylhydroquinone results show that more 2-tert-butylhydroquinone is produced during the batch cell electrolysis. The reason being that in the batch cell electrolysis the ratio of cathodic to anodic current density was lower than in the flow cell. This results in less hydrogen at the cathode being formed in the batch electrolysis than in the flow cell, since the formation of hydrogen competes with the reduction of 2tert-butylbenzoquinone at the cathode.
- 2-tert-butylbenzoquinone: The results indicate a greater extent of 2-tertbutylbenzoquinone formation in the flow cell than the batch cell; the reason for this is as explained above for 2-tert-butylhydroquinone.
- Current Efficiency: The current efficiency results indicate that the batch cell electrolysis yields better current efficiency results. The reason for this is that the mass transport conditions in the flow cell are better than that in the batch cell; this results in an increased transport rate of the 2-*tert*-butylbenzoquinone produced at the anode moving to the cathode and the 2-*tert*-butylhydroquinone produced at the cathode moving to the anode. This translates into a drop in current efficiency due to the continual oxidation and reduction of the 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone respectively.
- 2-tert-butylphenol: The results indicate that the apparent rate of 2-tertbutylphenol oxidation is greater in the batch cell electrolysis than in the flow cell electrolysis. The reason for this is the same as that explained for current

efficiency: this is the repeated oxidation of the 2-*tert*-butylhydroquinone to the 2-*tert*-butylbenzoquinone and the reduction of the 2-*tert*-butylbenzoquinone to the 2-*tert*-butylhydroquinone. Since the oxidation of the 2-*tert*-butylhydroquinone will compete with the oxidation of the 2-*tert*-butylphenol the apparent rate of 2-*tert*-butylphenol oxidation in the flow cell is decreased.

## 4.4 Results and discussion for 2,6-di-*tert*butylphenol

In this section the optimum parameters determined for the electrolysis of 2-*tert*butylphenol will be applied to the electrolysis of 2,6-di-*tert*-butylphenol. One example will be described for a batch cell process and another example will be described for a micro-flow cell process.

In this section the following abbreviations will be used in order to simplify the presentation of the graphical data:

- ✤ 2,6-di-*tert*-butylphenol = 26dtbPhOH
- ✤ 2,6-di-*tert*-butylhydroquinone = 26dtbHq
- 2,6-di-*tert*-butylbenzoquinone = 26dtbBq

#### 4.4.1.1 Undivided batch cell electrolysis

The standard reaction conditions used during the investigation are shown in Table 4.8 below.

Variable	Value
Acid conc. (% v/v)	3
Organic solvent (% V/V)	70
Current density (A m <sup>-2</sup> )	2000
Organic solvent	Acetonitrile
Substrate loading (% m/v)	5.5
Temperature (°C)	50
Anode	Lead dioxide on titanium mesh
Cathode	Nickel

 Table
 4.8:
 Standard
 conditions:
 2,6-di-*tert*-butylphenol
 Undivided
 Batch
 Cell
 Electrolysis

Figure 4.34 shows the product distribution diagram for this experiment.





Figure 4.34 shows the same trends observed throughout this chapter, that is the gradual decrease in the amount of 2,6-di-*tert*-butylphenol, the gradual increase in the 2,6-di-*tert*-butylhydroquinone and 2,6-di-*tert*-butylbenzoquinone, the gradual decrease of current efficiency and the change in the mass balance of the reaction due to the formation of an "intermediate" and its oxidation to 2,6-di-*tert*-butylhydroquinone and 2,6-di-*tert*-butylbenzoquinone.

The observations made for each response will now be discussed below:

- Mass balance: The mass balance in the reaction medium shows a decrease to 55 % at 9 F followed by an increase to close to 100 % at 11 F. The large dip in the curve indicates that the extent to which the "intermediate" is formed is large.
- 2,6-di-tert-butylhydroquinone: The results for 2,6-di-tert-butylhydroquinone show an increase as the reaction proceeds. It should be noted that from 8 faradays onwards there is a drastic rise in the amount of 2,6-di-tertbutylhydroquinone in the reaction medium, due to the break up of the "intermediate".
- 2,6-di-*tert*-butylbenzoquinone: The yield of 2,6-di-*tert*-butylbenzoquinone is generally very low, which indicates that very efficient reduction takes place to the 2,6-di-*tert*-butylhydroquinone.
- Current efficiency: The current efficiency in the reaction mixture shows a decrease as the reaction proceeds, levelling of in the range 8 10 F, where the "intermediate" compound breaks down forming the 2,6-di-*tert*-butylhydroquinone and 2,6-di-*tert*-butylbenzoquinone.
- 2,6-di-tert-butylphenol: The amount of 2,6-di-tert-butylphenol in the reaction medium shows a gradual decrease as the reaction proceeds.

#### 4.4.1.2 Undivided micro flow cell batch recirculation electrolysis

This section will describe the micro-flow cell oxidation of 2,6-di-*tert*-butylphenol under the standard conditions evaluated for 2-*tert*-butylphenol. The standard reaction conditions used during the investigation are shown in Table 4.9 below.

Variable	Value
Acid conc. (% v/v)	3
Organic solvent (% v/v)	70
Current density (A m <sup>-2</sup> )	2000
Organic solvent	Acetonitrile
Substrate loading (% m/v)	5.5
Temperature (°C)	50
Anode	Lead dioxide on lead
Cathode	Nickel
Flow rate (cm <sup>3</sup> min <sup>-1</sup> )	168
Electrode separation (mm)	6

Table 4. 9: Standard conditions: 2,6-di-tert-butylphenol micro-flow cell electrolysis

Figure 4.35 Show the product distribution diagram for the reaction.





- Mass balance: The mass balance in the reaction medium shows a decrease to 75 % at 7 F followed by an increase to close to 100 % at 8.5 F. This dip is again associated with the formation and oxidation of the "intermediate".
- 2,6-di-*tert*-butylhydroquinone: The results for 2,6-di-*tert*-butylhydroquinone show an increase as the reaction proceeds. It should be noted that from 8 F onwards there is a drastic rise in the amount of 2,6-di-*tert*-butylhydroquinone in the reaction medium.
- 2,6-di-tert-butylbenzoquinone: The yield of 2,6-di-tert-butylbenzoquinone is generally very low, indicating very efficient reduction to 2,6-di-tertbutylhydroquinone.
- Current efficiency: The current efficiency in the reaction mixture shows a gradual decrease as the reaction proceeds.
- 2,6-di-tert-butylphenol: The amount of 2,6-di-tert-butylphenol in the reaction medium shows a gradual decrease as the reaction proceeds. However after 10 F still 30 % of the 2,6-di-tert-butylphenol is present, indicating inefficient oxidation, presumably due to the solubility problem associated with the 2,6di-tert-butylphenol in the reaction medium. This solubility problem results in bad contact of the particular phenol with the electrodes so resulting in inefficient electrochemical oxidation.

### 4.5 Conclusion

The investigation into the electrochemical oxidation of substituted phenols has produced the following important points:

- Electrolysis of 2-*tert*-butylphenol produces the 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone, and an unstable "intermediate" compound, with generally only trace amounts of other side products being formed.
- The 2-*tert*-butylhydroquinone yield always exceeds the 2-*tert*butylbenzoquinone yield, except under high current density conditions.
- The "intermediate" compound, formed to varying extent during the electrolysis, depending on the conditions, always breaks down at a particular charge per mole value (generally approximately 8 F). This point always corresponds to a decrease in the rate of 2-*tert*-butylphenol oxidation and
results in the formation of more 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone, yielding a mass balance of close to 100 % soon afterwards.

- The charge per mole required to oxidise the 2-*tert*-butylphenol completely is generally about 8 F, twice the theoretical value, using either of the two electrochemical processes.
- The anode material investigation showed that there are at least two possible anodic mechanisms in the reaction and that they are anode material dependent. The "non-intermediate" mechanism dominates for a lead dioxide anode, irrespective of base metal, and the "intermediate" mechanism dominates for platinum.
- Both the batch cell and the flow cell produced good results, with the batch cell giving better overall performance. Optimum operating conditions for both methods are listed in Tables 4.3 and 4.9.
- Current efficiency values are generally low due to the reversible redox reactions between 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone at the electrodes, coupled with competing reactions producing hydrogen and oxygen.
- The main problem with the oxidation of the 2,6-di-*tert*-butylphenol was its solubility in the medium. The "intermediate" compound complex in this case breaks down to form only the 2,6-di-*tert*-butylhydroquinone and not the 2,6di-*tert*-butylbenzoquinone.

# **CHAPTER 5**

# **Electrochemical Oxidation of Phenol**

# **5.1 Introduction**

In this chapter the electrochemical oxidation of phenol is investigated, using the two electrochemical procedures used in the previous chapter, namely constant current batch electrolysis and the micro-flow cell batch recirculation electrolysis. Experimental parameters will be varied using the same approach as was applied for the oxidation of 2-tert-butylphenol and some of the variables which were evaluated in the previous chapter will be assumed to have the same effect during the oxidation of phenol itself.

The anode and cathode used in each procedure was lead dioxide on titanium and nickel respectively; the organic solvent used was acetonitrile.

Since the oxidation of phenol may give rise to more isomers than is the case with 2-tert-butylphenol, the analysis of the electrolysis solution will be extended to include catechol and resorcinol.

Product distribution diagrams will be generated for each variable investigated in order to determine the effect of each variable on the electrolysis.

# 5.2 Results and discussion

It will be seen that no resorcinol was detected during the electrolysis of phenol. This is due to the para-directing effect of the phenolic group and the instability of the meta-benzoquinone, which makes the formation of the resorcinol isomer very difficult. In this section the following abbreviations will be used in order to simplify the presentation of some of the tables:

- Phenol = PhOH
- Hydroquinone = Hq
- Catechol = Cat
- Benzoquinone = Bq
- Mass balance = MB
- Current efficiency = CE

# 5.2.1 Undivided batch cell electrolysis

Table 5.1 gives the experimental variables that were accepted as standard conditions for the electrochemical batch cell hydroxylation of phenol. Table 5.2 gives the range of values, experimentally set for each variable so as to determine the optimum values of that variable, one at a time. The variation of each variable was then compared with the standard control settings.

The investigation involves generating a product distribution diagram of all the parameters measured as a function of charge per mole / F, passed through the batch cell. Each of the variables will then be discussed in turn.

Variable	Value
Acetonitrile (% v/v)	70
Acid conc. (% v/v)	3
Substrate loading (% m/v)	2.5
Current density (A/m <sup>2</sup> )	2000
Temperature (°C)	50
Anode	Lead dioxide on titanium mesh
Cathode	Nickel

Table 5.1: Standard conditions: phenol undivided batch cell electrolysis

Variable	Value
Acetonitrile (% v/v)	30, 50, 70
Acid conc. (% v/v)	1.5, 3.0, 4.5
Substrate loading (% m/v)	1.25, 2.5 ,5.0
Current density (A/m <sup>2</sup> )	1000, 2000, 3000
Temperature (°C)	30, 50, 70

Table 5.2: Reaction variables: phenol undivided batch cell electrolysis

The actual settings of reaction variables will have a distinct effect on the electrolysis, since they affect both the electrode reactions, as well as the follow up chemical reactions. The general experimental variables selected for the electrolysis are shown in Section 4.2. When comparing the reaction variables given in Table 5.2 with those investigated for the electrochemical oxidation of 2-*tert*-butylphenol shown in Chapter 4 it can be seen that some variables have been left out. These are the organic solvent, and anode and cathode identities. These variables should have the same effect on the oxidation of phenol as what they had on the oxidation of 2-*tert*-butylphenol.

#### 5.2.1.1 Amount of organic solvent

The effect of varying the acetonitrile : water ratio on the oxidation of phenol was investigated by using the standard conditions listed in Table 5.1, but varying the amounts of acetonitrile : water. Figures 5.1 to 5.4 show the data of this investigation



Figure 5.1: Product Distribution Diagram: Organic Solvent Percentage 30%

Figure 5.2: Product Distribution Diagram: Organic Solvent Percentage 50%





Figure 5.3: Product Distribution Diagram: Organic Solvent Percentage 70%

Figure 5.4: Product Distribution Diagram: Organic Solvent Percentage 90%



The results for rate and extent of formation of hydroquinone, catechol and current efficiency indicate an increase with increasing organic solvent percentage up to 70 %, followed by a decrease to a minimum at 90 %. The benzoquinone values are similar, but the decrease to 90 % organic solvent percentage is not observed. The results for rate and extent of phenol oxidation remain constant up to 70 % organic solvent percentage followed by a decrease to 90 % organic solvent percentage. The mass balance results show a decrease in the extent of the "unidentified" product formation with increasing organic solvent percentage up to 70 % organic solvent percentage, after which it remains relatively constant. The results indicate  $\sim$  8 F is required to completely oxidise the "intermediate" to hydroquinone and benzoguinone. The results indicate that the electrochemical oxidation of phenol at a lead dioxide anode to hydroquinone and benzoquinone is dependent on the amount of water in the reaction medium. Table 5.3 summarizes some of the important data at some of the organic solvent percentage values examined. The results suggest that the best organic solvent percentage for the oxidation of phenol is 70 %.

Organic solvent	Responses at 8 F					
percentage (%	% PhOH	% CE	% Hq	% Cat	% Bq	% MB
v/v)						
30	16	28	65	4	7.5	92.5
50	18	29	56	6	6	86
70	11	35	70	7	8	96
90	27	26	49	6	10	92

Table 5.3: Responses at 8 F for the organic solvent percentage investigation

#### 5.2.1.2 Acid concentration

The effect of a change in acid concentration on the oxidation of phenol was investigated by using the standard conditions listed in Table 5.1, but varying the acid concentration. Figures 5.5 to 5.7 show the data of this investigation



Figure 5.5: Product Distribution Diagram: 1.5 % Sulphuric Acid

Figure 5.6: Product Distribution Diagram: 3 % Sulphuric Acid





Figure 5.7: Product Distribution Diagram: 4.5 % Sulphuric Acid

The results for rate and extent of phenol oxidation, formation of hydroquinone and benzoquinone and current efficiency indicate an increase with increasing acid concentration, whilst the rate and extent of catechol formation follow the reverse trend. The ratio of hydroquinone to benzoquinone shows no change. The rate and extent of "intermediate" formation also shows an increase with acid concentration, but in all cases the point where the "intermediate" is completely oxidised to hydroquinone and benzoquinone is  $\sim$  7 to 8 F. These results could indicate that the increase in reaction medium conductivity resulting from the increased acid concentration results in better conditions for the oxidation of phenol to hydroquinone and benzoquinone. Table 5.4 shows some of the data obtained at the three different acid concentrations. The results suggest that the best acid concentration for the oxidation of phenol lies between 3 and 4.5 %.

Acid	Responses at 8 F					
concentration	% PhOH	% CE	% Hq	% Cat	% Bq	% MB
(% v/v)						
1.5	14	29	65	8	8	95
3.0	9	34	70	6	9	94
4.5	13	33	68	6.5	8.5	96

Table 5.4: Responses at 8 F for the acid concentration investigation

## 5.2.1.3 Substrate Loading

The effect of substrate loading was evaluated in the batch cell for the oxidation of phenol, by varying the percentage from 1.25 % to 5 %. The standard conditions in Table 5.1 were used to construct the respective product distribution diagrams shown in Figures 5.8 to 5.10.

Figure 5.8: Product Distribution Diagram: 1.25 % Substrate Loading





Figure 5.9: Product Distribution Diagram: 2.5 % Substrate Loading

Figure 5.10: Product Distribution Diagram: 5 % Substrate Loading



The results for rate and extent of phenol oxidation and formation of hydroquinone indicate an increase with increasing substrate loading, whereas the rate and extent of formation of benzoquinone and catechol and the current efficiency follow the reverse trend. The ratio of hydroquinone to benzoquinone shows that as the substrate loading increases, the production of hydroquinone is favoured over that of benzoquinone. The mass balance loss due to "intermediate" formation increases with increasing substrate loading, but the "intermediate" oxidation to hydroquinone and benzoquinone remains constant at ~ 7,5 F; this could suggest that the "intermediate" is oligomeric in nature. Discrepancy at 2.5 % substrate loading is ascribed to experimental error. Table 5.5 shows some of the important data at the different substrate loadings. The results suggest that the working range should be 2.5 - 5 % substrate loading, in order to have a higher hydroquinone yield.

	•			•	-	
Substrate	Response	Responses at 8 F				
loading (% m/v)	% PhOH	% CE	% Hq	% Cat	% Bq	% MB
1.25	16	32	59	7	14	96
2.5	17	34	63	7	7	94
5	15	30	64	5	9	93

Table 5.5: Responses at 8 F for the substrate loading investigation

### 5.2.1.4 Current Density

The effect of increased current density on the oxidation of phenol was investigated using the standard conditions listed in Table 5.1, with the exception that the anodic and cathodic current density was varied. Figures 5.11 to 5.13 illustrate the results obtained.



Figure 5.11: Product Distribution Diagram: Current Density 1000 A m<sup>-2</sup>

Figure 5.12: Product Distribution Diagram: Current Density 2000A m<sup>-2</sup>





Figure 5.13: Product Distribution Diagram: Current Density 3000A m<sup>-2</sup>

The results for rate and extent of phenol oxidation, formation of hydroquinone and catechol and the current efficiency indicate a decrease with increasing current density, whereas the rate and extent of benzoquinone formation follow the reverse trend. The ratio of hydroquinone to benzoquinone shows that as the current density increases, the production of benzoquinone is favoured over that of hydroquinone. The mass balance loss due to "intermediate" formation is similar with increased substrate loading, but the "intermediate" oxidation to hydroquinone and benzoquinone remains constant at ~ 6.5 F only increasing to 9.5 F at a current density of 3000 A m<sup>-2</sup>. These results suggest that as the current density is increased the oxidation of water and protons to oxygen and hydrogen respectively, becomes more dominant. The hydroquinone to benzoquinone ratio could indicate that the extent of gas formation is more prominent at the cathode than the anode. Table 5.6 shows some of the data at the different current densities. The results suggest that the reaction proceeds best at a current density of 1000 A m<sup>-2</sup>.

Current density	Responses at 8 F						
(A/m <sup>2</sup> )	% PhOH	% CE	% Hq	% Cat	% Bq	% MB	
1000	10	35	72	8	5	95	
2000	17	34	63	7	7	94	
3000	19	34	60	7	9	95	

Table 5.6: Responses at 8 F for the current density investigation

## 5.2.1.5 Reaction temperature

The effect of the reaction temperature on the oxidation of phenol was investigated using the standard conditions listed in Table 5.1, except that the reaction temperature was varied. Figures 5.14 to 5.16 show the product distribution diagrams obtained.

Figure 5.14: Product Distribution Diagram: Reaction Temperature 30°C





Figure 5.15: Product Distribution Diagram: Reaction Temperature 50°C

Figure 5.16: Product Distribution Diagram: Reaction Temperature 70°C



The results for rate and extent of phenol oxidation, catechol formation and current efficiency indicate no change with increasing reaction temperature. The results for rate and extent of hydroquinone formation show a slight increase with increasing reaction temperature, whereas benzoquinone shows a slight decrease. The ratio of hydroquinone to benzoquinone shows that as the reaction temperature increases, the production of hydroquinone is favoured over that of benzoquinone. The mass balance loss due to "intermediate" formation shows both a decrease in the extent of "intermediate" formation and the faraday value at which the mass balance returns to 100 % due to the "intermediates" oxidation to hydroquinone and benzoquinone. This could indicate that the "intermediate" is unstable at higher temperatures in the reaction medium. Table 5.7 shows some of the data obtained at the three different temperatures investigated. The results suggest that temperature has no significant effect on the oxidation of phenol, with slightly better results obtained at 30 °C.

	-				- J	
Reaction	Response	Responses at 8 F				
temperature	% PhOH	% CE	% Hq	% Cat	% Bq	% MB
(°C)						
30	14	34	68	7	8	97
50	17	34	63	7	7	94
70	15	33	66	6.5	6.5	94

Table 5.7: Responses at 8 F for the reaction temperature investigation

#### 5.2.1.6 Optimum conditions for batch electrolysis for phenol

Table 5.8 shows the optimum conditions for the electrolysis of phenol using the undivided batch cell electrolysis, as determined in the preceding sections.

Variable	Optimum Condition
Organic Solvent Percentage (% v/v)	70 %
Acid Concentration (% v/v)	3 – 4.5 %
Substrate Loading (% m/v)	2.5 – 5 %
Current Density (A/m <sup>2</sup> )	1000
Reaction Temperature (°C)	30

Table 5.8: Optimum Conditions Batch Cell Electrolysis

# 5.2.2 Micro flow cell electrolysis

The electrochemical oxidation of phenol using a flow cell was investigated using the same approach as for batch cell oxidation. The experimental setup of the flow cell was described in Section 2.2.

Table 5.9 list the standard conditions used for the flow cell oxidations, and Table 5.10 gives the variables investigated and their respective ranges studied. Each variable was investigated one at a time, whilst keeping all other conditions constant.

Variable	Value
Electrode separation (mm)	6
Flow rate (cm <sup>3</sup> /min)	168
Current density (A/m <sup>2</sup> )	2000
Organic solvent (% v/v)	70
Acid conc. (% v/v)	3
Substrate loading (% m/v)	2.5
Temperature (°C)	50
Organic solvent identity	Acetonitrile
Anode	Lead dioxide on lead
Cathode	Nickel

 Table 5.9: Standard conditions: phenol micro flow cell electrolysis

Variable	Value
Electrode Separation (mm)	4, 6, 10
Flow Rate (cm <sup>3</sup> /min)	118, 168, 220
Current density (A/m <sup>2</sup> )	667 – 6000

Table 5.10: Reaction variables: phenol undivided batch cell electrolysis

A number of variables, fully investigated during the flow cell work on 2-*tert*butylphenol, and the batch cell work on phenol, will be kept constant at their optimum value. These are: organic solvent percentage, acid concentration, substrate loading, temperature, anode material and cathode material. It was felt that these variables would not cause a change in going from a batch cell to a flow cell. For this investigation product distribution diagrams were generated as a function of charge per mol / F, passed through the flow cell.

#### 5.2.2.1 Electrode separation

Three different electrode separations were evaluated for the flow cell oxidation of phenol namely 4, 6 and 10 mm. The standard conditions in Table 5.9 were used to construct the respective product distribution diagrams shown in Figures 5.17 - 5.19, with the only variable being the electrode separation.



Figure 5.17: Product Distribution Diagram: Electrode Separation 4 mm

Figure 5.18: Product Distribution Diagram: Electrode Separation 6 mm





Figure 5.19: Product Distribution Diagram: Electrode Separation 10 mm

The results for rate and extent of phenol oxidation, current efficiency, and amounts of hydroquinone, benzoquinone and catechol formed show that the electrode separation has no significant effect on the oxidation of phenol. The decrease in mass balance due to the formation of the "intermediate" shows a maximum at 6 mm electrode separation and the faraday value at which the mass balance return occurs is shifted to a higher faraday value of ~ 8 F compared to ~6.8 F for 4 and 10 mm electrode separation. This indicates that the "intermediate" is stabilized at an electrode separation of 6 mm. The above observations could be related to the optimum mass transfer conditions for the oxidation of phenol to hydroquinone and benzoquinone at electrode separations. The results show that electrode separation has no real effect on the electrolysis within the electrode separation range investigated.

Electrode	Responses at 8 F					
separation (mm)	% PhOH	% CE	% Hq	% Cat	% Bq	% MB
4	15	34	46	6	30	97
6	15	33	48	4	29	96
8	15	35	44	5	30	94

Table 5.11: Responses at 8 F for the electrode separation investigation

## 5.2.2.2 Flow rate

Three different flow rates were evaluated in the flow cell for the oxidation of phenol, namely 118 to 220 cm<sup>3</sup>. The standard conditions in Table 5.9 were used to construct the respective product distribution diagrams shown in Figures 4.20 - 4.22.

Figure 5.20: Product Distribution Diagram: 118 cm<sup>3</sup>/min





Figure 5.21: Product Distribution Diagram: 168 cm<sup>3</sup>/min

Figure 5.22: Product Distribution Diagram: 220 cm<sup>3</sup>/min



The results for rate and extent of phenol oxidation and amounts of hydroquinone and benzoquinone formed show an increase with increasing flow rate. The results for the rate and extent of the catechol formation showed no change with increasing flow rate. The lack of change in the hydroquinone to benzoquinone ratio indicates that the change in flow rate affects each similarly. The decrease in mass balance due to the formation of the "intermediate" is similar, whilst the faraday value at which the "intermediate" is oxidised to hydroquinone and benzoquinone is however shifted to a higher faraday value of ~ 9 F compared to ~ 8 F as a flow rate 220 cm<sup>3</sup>/min. The above results could be explained by considering the increased mass transport associated with increased flow rate. Table 5.12 shows some of the data obtained for this investigation. The results show that the best flow rate for the oxidation of phenol to hydroquinone and benzoquinone

	-			-		
Flow rate Responses at 8 F						
(cm <sup>3/</sup> min)	% PhOH	% CE	% Hq	% Cat	% Bq	% MB
118	19	32	45	5	25	94
168	15	34	48	5	29	96
220	18	33	45	5	21	89

Table 5.12: Responses at 8 F for the flow rate investigation

# 5.2.2.3 Anodic current density

The effect of anodic current density on the oxidation of phenol was investigated using the standard conditions listed in Table 5.9, with the exception that the anodic current density was varied from 667 A m<sup>-2</sup> to 6000 A m<sup>-2</sup>. Figures 5.23 to 5.26 illustrate the results obtained.



Figure 5.23: Product Distribution Diagram: Anodic Current Density 667 A.m<sup>-2</sup>

Figure 5.24: Product Distribution Diagram: Anodic Current Density 2000 A.m<sup>-2</sup>





Figure 5.25: Product Distribution Diagram: Anodic Current Density 3000 A.m<sup>-2</sup>



Figure 5.26: Product Distribution Diagram: Anodic Current Density 6000 A.m<sup>-2</sup>

The results for the rate and extent of phenol oxidation show a slight decrease with increasing anodic current density. The results for the rate and extent of hydroquinone formation show a decrease with increasing anodic current density up to 3000 A m<sup>-2</sup> after which it increases for the value of 6000 A m<sup>-2</sup>. The results for benzoguinone formation and current efficiency are the reverse of this. The results for the rate and extent of catechol formation show no significant change with increasing current density. The mass balance results show that the extent of "intermediate" formation is constant as the anodic current density increases, whilst the faraday count at which the "intermediate" is oxidised to hydroquinone and benzoquinone increases with anodic current density up to 3000 A m<sup>-2</sup>; after this point it decreases, confirming that the mass balance change is an anodic reaction. The above trends could be explained by the increased oxygen formation at the anode with increasing anodic current density, first resulting in a loss of current due to oxygen evolution and secondly, at 6000 A m<sup>-2</sup>, resulting in the increased mass transport to the electrode associated with gas evolution. Table 5.13 shows some of the data obtained for this investigation. The results show that slightly better results are obtained at a current density of 667 A m<sup>-2</sup>.

Anodic current	Responses at 8 F						
density (A/m²)	% PhOH	% CE	% Hq	% Cat	% Bq	% MB	
667	14	33	57	5	19	95	
2000	12	35	47	6	33	98	
3000	29	28	40	6	16	91	
6000	18	34	48	6	31	93	

Table 5.13: Responses at 8 F for the anodic current density investigation

## 5.2.2.4 Cathodic current density

The effect of cathodic current density on the oxidation of phenol was investigated using the standard conditions listed in Table 5.9, with the exception that the cathodic current density was varied from 667 A m<sup>-2</sup> to 6000 A m<sup>-2</sup>. Figures 5.27 – 5.30 illustrate the results obtained.

Figure 5.27: Product Distribution Diagram: Cathodic Current Density 667 A.m<sup>-2</sup>





Figure 5.28: Product Distribution Diagram: Cathodic Current Density 2000 A.m<sup>-2</sup>

Figure 5.29: Product Distribution Diagram: Cathodic Current Density 3000 A.m<sup>-2</sup>





Figure 5.30: Product Distribution Diagram: Cathodic Current Density 6000 A.m<sup>-2</sup>

The results for rate and extent of phenol oxidation and current efficiency show no significant change with increasing cathodic current density, except for a slight decrease at 3000 A m<sup>-2</sup>. The results for the rate and extent of catechol formation show no change with increasing cathodic current density. The results for the rate and extent of hydroquinone formation show a decrease with increasing cathodic current density. The results for the rate and extent of benzoguinone formation show a slight minimum at 667 A m<sup>-2</sup> followed by a increase to a slight plateau ranging from 2000 A m<sup>-2</sup> to 6000 A m<sup>-2</sup>, with increasing cathodic current density. The ratio of hydroquinone to benzoquinone shows that the hydroquinone is produced at the cathode. The mass balance results show that the extent of "intermediate" formation increases with increasing cathodic current density; the faraday count at which the "intermediate" is oxidised to hydroguinone and benzoquinone increases with cathodic current density to 3000 A m<sup>-2</sup> after which it decreases, confirming that the mass balance change is an anodic reaction. The above results can be explained by the increased hydrogen formation at the cathode with increasing cathodic current density, resulting in increased competition of the hydrogen formation reaction with the reduction of benzoquinone. Table 5.14 shows some of the data obtained for the investigation. The results show that the optimum current density is 2000 A  $m^{-2}$ .

Cathodic current	Responses at 8 F							
density (A/m²)	% PhOH	% CE	% Hq	% Cat	% Bq	% MB		
667	14	34	48	6	28	96		
2000	12	35	47	6	33	98		
3000	28	30	40	6	19	93		
6000	12	36	38	6	36	92		

 Table 5.14: Responses at 8 F for the cathodic current density investigation

## 5.2.2.5 Optimum conditions for micro flow cell electrolysis

Table 5.15 shows the optimum conditions for the electrolysis of phenol using the micro flow cell.

Variable	Optimum Conditions
Electrode separation (mm)	No real effect, but low electrode separations
	are suggested
Flow Rate (cm <sup>3</sup> /min)	Slight effect showing a flow rate of 168 as
	optimum
Anodic Current Density (A/m <sup>2</sup> )	667
Cathodic Current Density (A/m <sup>2</sup> )	2000

Table 5.15: Optimum Conditions Micro Flow Cell Electrolysis

# 5.3 Comparison of phenol and 2-*tert*-butylphenol electrolysis

Tables 5.16 and 5.17 compare the optimum conditions for the batch and flow cell respectively for 2-*tert*-butylphenol and phenol. It can be seen in both cases that the conditions for both substrates are very similar, as would be expected, since both compounds have roughly the same chemical properties. One can therefore

predict that the optimum conditions for the electrolysis of 2,6-di-*tert*-butylphenol will be very similar to those of 2-*tert*-butylphenol, assuming one overcomes the solubility problem associated with the 2,6-di-*tert*-butylphenol.

Variable	Optimum Condition					
	2-tert-butylphenol	Phenol				
Acid Concentration (% m/v)	1.5-5	3 – 4.5				
Organic Solvent Percentage (% v/v)	67.5-80	70				
Current Density (A/m <sup>2</sup> )	500 -1000	1000				
Organic solvent	Acetonitrile	Used acetonitrile				
Substrate Loading (% m/v)	2 - 4	2.5 - 5				
Reaction Temperature (°C)	50 and above	30 °C				
Anode	Lead Dioxide	Used lead dioxide				
Cathode	Nickel	Used nickel				

Table 5.16 Optimum Conditions Undivided Batch Cell Electrolysis

Variable	Optimum Conditions					
	2-tert-butylphenol	Phenol				
Flow Rate (cm <sup>3</sup> /min)	Negligible within	Slight effect showing a flow				
	range investigated	rate of 168 as optimum.				
Electrode separation	Below 6	No real effect, but low				
(mm)		electrode separations are				
		suggested.				
Substrate Loading (%	Low substrate	Used low substrate loadings.				
m/v)	loadings					
Anode material	Lead dioxide	Used lead dioxide				
Cathode material	Nickel	Used nickel				
Anodic Current Density	3000	667				
(A/m <sup>2</sup> )						
Cathodic Current	667	2000				
Density (A/m <sup>2</sup> )						

Table 5.17: Optimum Conditions Micro Flow Cell Electrolysis

Tables 5.18 and 5.19 summarizes the performance for each cell by reporting the relevant responses calculated, both at 8 and 11 F, for three different investigations carried out with the flow and batch cell on the electrochemical oxidation of phenol.

Batch	70 %	organic	3 % acid		2.5 %	substrate
Cell	solvent				loading	
	8 F	11 F	8 F	11 F	8 F	11 F
% PhOH	11	4	9	3	17	11
% CE	35	26	34	26	34	27
% Hq	70	70	70	71	63	65
% Cat	7	6	6	5	7	7
% Bq	8	13	9	13	7	10
% MB	96	93	94	92	94	93

Table 5.18: Summary of batch cell results for phenol

Flow	6 mm	electrode	Flow rate	2	Anodic	current
Cell	separation	ı			density 2000 A m <sup>-2</sup>	
	8 F	11 F	8 F	11 F	8 F	11 F
% PhOH	15	9	15	9	12	8
% CE	33	26	34	25	35	26
% Hq	48	45	48	45	47	39
% Cat	4	3	5	3	6	4
% Bq	29	36	29	36	33	41
% MB	96	94	96	93	98	92

 Table 5.19: Summary of flow cell results for phenol

When comparing the performance of the flow cell with that of the batch cell for the electrolysis of phenol, it is observed that the batch cell in each case, gives larger yields of hydroquinone than the flow cell, whilst the flow cell gives higher yields in benzoquinone than the batch cell. Also the charge required to oxidise the phenol completely seem to be slightly better for the batch cell.

The difference in performance between the two cells must be largely due to the size of the electrodes and the mass transport between the electrodes in each case.

Tables 5.20 and 5.21 compare 2-*tert*-butylphenol with phenol using the flow cell electrolysis for two different investigations.

Phenol	Flow rate 2			4 mm electrode separation		
	6 F	8 F	10 F	6 F	8 F	10 F
% PhOH	27	15	10	25	15	12
% CE	40	33	27	41	34	28
% Hq	39	48	46	42	56	40
% Cat	5	5	4	6	6	5
% Bq	19	29	34	20	30	35
% MB	90	97	94	93	97	92

Table 5.20: Summary for 2-tert-butylphenol flow cell electrolysis

2-tert-	Flow rate 2			4 mm electrode separation			
butylphenol	6 F	8 F	10 F	6 F	8 F	10 F	
% PhOH	21	7	2	5	2	2	
% CE	53	45	37	54	45	40	
% Hq	59	64	65	35	46	50	
% Bq	20	25	33	45	48	46	
% MB	100	96	100	85	96	98	

Table 5.21: Summary for 2-tert-butylphenol flow cell electrolysis

When comparing the electrolysis of the different phenols it is seen that as the degree of substitution on the phenol increases all the responses under investigation (hydroquinone, benzoquinone, phenol, mass balance, current efficiency) generally increase. This is explained as follows:

- In comparison to phenol, the substituted phenols are more readily oxidized.
   This has been shown to be due to their lower oxidation potential, which decreases with the degree of substitution.
- The *tertiary*-butyl group has the ability to stabilize charges and radicals, so as the degree of *tertiary*-butyl substitution increases the stability of the radicals and cations increases.

# **5.4 Conclusion**

- The electrochemical oxidation of phenol produces large amounts of hydroquinone and smaller amounts of benzoquinone, with a very low yield of catechol and a varying amount of an "intermediate" substance. No resorcinol was formed.
- The oxidation of phenol requires up to 12 F for the substrate to reach concentrations of less than 5 %. This is three times the theoretical amount.
- Both the batch cell and the flow cell showed good performance with the batch cell yielding more hydroquinone than the flow cell, whilst the flow cell gave more benzoquinone than the batch cell.
- Optimum conditions for each cell are displayed in Tables 5.8 and 5.15.

- The temperature effect was found not to be as critical as for the 2-*tert*butylphenol investigation, presumably for solubility reasons.
- The concentration of the catechol isomer was found to be low in all cases, in the range of 4 – 7 %.
- The apparent loss in mass balance during electrolysis was found to be due to a "intermediate" substance, which decomposes later in the electrolysis into hydroquinone and benzoquinone. In some cases more hydroquinone seems to be produced than benzoquinone. This "intermediate" is suggested to be a dimer, as discussed in Chapter 3.
# **CHAPTER 6**

# Scale-up, Mass Balance and Energy Aspects

## **6.1 Introduction**

During the development of any chemical process it is necessary to investigate the scale-up of the process, in order to fully understand and summarize the work done by the chemical technologist and to be competitive in a market where quantity and quality of the products are essential. Reactions conducted at bench scale will be affected by a move to larger scale processes which utilize larger scale equipment such as bigger cells, pumps, tanks and pipes.

The scale-up of conventional chemical procedures sometimes utilizes small multiples of reactors. In electrochemical scale-up this is the norm and the multiples are often large. Electrochemical scale-up procedures are less complicated, since additional electrodes can simply be added to the reactor and data generated in bench scale can be used in the design of continuous electrolysis procedures. In many cases only the addition of a separation facility is necessary.

The aims of the initial scale-up performed on the hydroxylation of phenols were as follows:

- Confirm the choice of cell design.
- Test the stability and integrity of reactor components.
- Obtain mass balances.
- Evaluate the process under more realistic operating conditions, specifically higher substrate loadings.

In view of the considerations above it was decided to investigate the scale-up of the electrochemical hydroxylation of phenol and 2-*tert*-butylphenol in a batch recirculation fashion using a flow electrolysis cell.

Scale-up work was performed using an ICI processing package and the experimental procedure as discussed in Section 2.2.4. The optimum experimental conditions selected from the investigations in Chapters 4 and 5 were selected as the starting point for the investigation.

### 6.2 Results and discussion

### 6.2.1 Scale-up

As mentioned earlier scale-up was performed on an ICI processing unit; this unit utilizes a FM-01 flow cell and operates in a batch recirculation fashion. Since the micro flow cell procedure was fully investigated in Chapters 4 and 5, the optimum conditions found for the electrolysis were applied to the scale-up directly, increasing only the substrate loading. The reaction conditions for the scale-up experiments are shown in Table 6.1 below. It can be seen that there are some deviations from those found to be at an optimum, namely:

- Substrate loading: The substrate loading was increased above that used in the bench scale work, so as to test the electrolysis procedure for higher substrate loading. There was also a difference in the substrate loadings for phenol and 2-*tert*-butylphenol; the reason being that the amount of moles in the reaction medium was kept constant, so as to keep the electrolysis time constant.
- Anodic to cathodic current density ratio: Separators could not be cut, so the effective electrode area could not be changed.
- Electrode separation: Due to the design of the FM-01 electrolyzer, the electrode separation could not be taken below 6 mm.

Variable			Value		
Electrode separation (mm)			6		
Flow rate (cm <sup>3</sup> min <sup>-1</sup> )			168		
Current density (A m <sup>-2</sup> ) Ano Cath		Anodic	2000		
		Cathodic	2000		
Acetonitrile (% v/v)			70		
Acid conc. (% v/v)			3		
Substrate loading	Phenol		10 %		
(% m/v)	2-tert-butylphenol		16 %		
Temperature (°C)			60		
Organic solvent			Acetonitrile		
Anode			Lead dioxide on lead		
Cathode			Nickel		

Table 6.1: Standard conditions: Scale-up electrolysis

#### 6.2.1.1 Phenol

The reaction was performed using the variables shown in Table 6.1 with 10 % substrate loading; samples were removed for analysis at regular intervals and the product distribution diagram constructed.

Figure 6.1 shows the product distribution diagram for the scale-up experiment conducted for the phenol electrolysis. It should be noted that the product distribution diagram shows all the trends observed and discussed in Section 5.3 for the reaction performed on phenol using micro flow cell electrolysis. The following important observations can be made from Figure 6.1.

- The oxidation of phenol proceeds smoothly up to 9 F, whereupon the reaction slows down, giving about 6 % residual phenol after 10.5 F.
- The hydroquinone curve rises to a maximum of 68 % at 8 F, after which the hydroquinone yield decreases.
- The benzoquinone yield is much lower than that of the hydroquinone, steadily increasing as the electrolysis proceeds, reaching a value of 15 % at 10 F.

- The sum of hydroquinone and benzoquinone reaches a maximum of 80 % at 8 F.
- The catechol yield remains low throughout the electrolysis, giving a maximum value of 2 % at 5 F.
- The mass balance curve giving the sum of phenol, hydroquinone, benzoquinone and catechol, show only a slight dip as expected for the lead dioxide electrode. The mass balance curve reaches a maximum close to 100 % at 8 F.
- The current efficiency decreases as the electrolysis proceeds.
- No resorcinol was detected in the electrolysis solution, as was the case in the bench work.



Figure 6.1: Product Distribution Diagram: Phenol scale-up 10 % substrate loading

Table 6.2 shows a comparison of the results obtained during the micro flow cell investigation with those obtained for the scale-up procedure, at 8 F of charge.

	-		-	-		
Electrolysis	Responses at 8 F					
procedure	% PhOH	% CE	% Hq	% Cat	% Bq	% MB
Scale-up	14	35	68	2	13	97
Micro flow cell	15	34	48	5	29	96

Table 6.2: Phenol responses at 8 F: Comparison Scale-up vs. Micro flow cell

From Table 6.2 it is clear that the only responses that show a significant difference when moving to the scale-up of the phenol electrolysis is the yield of catechol, hydroquinone and benzoquinone, but that the sum of hydroquinone, benzoquinone and catechol remains approximately the same. The reason for the observed differences may possibly be related to the difference in the size of the electrodes used in the scale-up work relative to the bench work.

#### 6.2.1.2 2-tert-butylphenol

The reaction was performed using the variables shown in Table 6.1, with 16 % substrate loading; samples were removed for analysis at regular intervals and the product distribution diagram constructed.

Figure 6.2 shows the product distribution diagram for the scale-up experiment conducted for the 2-*tert*-butylphenol electrolysis. It should be noted that the product distribution diagram shows similar trends observed and discussed in Section 4.3.2 for the reaction performed on 2-*tert*-butylphenol using micro flow cell electrolysis:

- A total charge in excess of 10 F is necessary to completely oxidise 2-*tert*butylphenol, using both the FM-01 flow cell and the micro flow cell.
- The current efficiency steeply decreases as electrolysis progresses.
- The mass balance percentage generally shows the same trend with the cyclic return to 100 % at 8 F.
- The sum of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone increases as electrolysis continues, reaching nearly 100 % at 8.5 F of charge.
- None of the corresponding resorcinol or catechol is produced during the reaction.



Figure 6.2: Product Distribution Diagram: 2-*tert*-butyl-phenol scale-up, 16 % substrate loading

Table 6.3: 2-*tert*-butylphenol oxidation responses at 8 F: Comparison Scale-up vs. Micro flow cell

Electrolysis	Responses at 8 F				
procedure	% PhOH	% CE	% Hq	% Bq	% MB
Scale-up	7	35	76	11	94
Micro flow cell	7	45	64	25	96

Table 6.3 gives a comparison of the scale-up versus the micro flow cell results for 2-*tert*-butylphenol at 8 F of charge. It is clear that the only responses that show a significant difference when moving to the scale-up of the 2-*tert*-butylphenol electrolysis are:

The sum of hydroquinone and benzoquinone is approximately the same but the ratio of hydroquinone to benzoquinone in the FM-01 electrolyzer is greater than that in the micro flow cell. This is mainly due to the formation of a two-phase medium at the higher substrate loading used during scale-up: the two-phase medium will decrease the efficiency of the electrolysis, especially the reduction of the 2-*tert*-butylbenzoquinone, as seen from the results.

- The current efficiency is lower in the FM-01 electrolyser than in the micro flow cell. The reason for this is probably related to the formation of the two-phase medium. This will cause a larger portion of the current to be wasted on the electrolysis of water to oxygen, since the adsorption of the 2-*tert*-butylphenol onto the anode surface will be negatively affected.
- The mass balance drop is more significant in the FM-01 electrolyser when compared to the micro flow cell. The reason for this is not clear.

Taking into consideration the results obtained for scale-up for both phenol and 2*tert*-butylphenol it can be said that similar results are obtained when going from the micro flow cell electrolysis to the scale-up electrolysis. The only difference is an increase in the hydroquinone yields and a decrease in the benzoquinone yields and, and in the case of 2-*tert*-butylphenol, a decrease in current efficiency due to solubility problems with the substrate.

These results then clearly indicate that the electrolysis system is quite robust with regards to scale-up, showing the same pattern each time.

#### 6.2.2 Mass balance

In both laboratory scale and industrial scale reactions an accounting of all the reagents added to the reaction mixture is of real importance for the proper understanding of the reaction process; this is referred to as a mass or material balance.

Mass balance procedures were undertaken for both the phenol and 2-*tert*butylphenol using the batch cell electrolysis, described in Section 2.2.3.

The reactions were conducted using the standard reaction conditions shown in Table 6.3 below and the electrolysis stopped at 6.5 F, since this resulted in a convenient electrolysis time.

Variable	Value		
Substrate	Phenol	2-tert-butylphenol	
Organic solvent (% v/v)	70	70	
Acid conc. (% v/v)	3	3	
Substrate loading (% m/v)	10	16	
Current density (A m <sup>-2</sup> )	2000	2000	
Temperature (°C)	50	50	
Organic solvent	Acetonitrile	Acetonitrile	
Anode	Lead dioxide on titanium	Lead dioxide on	
	mesh	titanium mesh	
Cathode	Nickel	Nickel	

Table 6.4: Standard conditions: phenol and 2tert-butylphenol mass balance

The oxidation was started and continued until 6.5 F had passed through the cell. The organic solvent was removed by vacuum distillation (40 °C, 350 kPa); the product-containing aqueous medium was extracted with diethyl ether and the crude organic product isolated by vacuum distillation (40 °C, 800 kPa). The aqueous medium was vacuum distilled (90 °C, 90 kPa) and the sulphuric acid recovered was weighed. The mass balance summary for the phenol oxidation is shown in Figure 6.3 whilst that for 2-*tert*-butylphenol is shown in Figure 6.4.



Figure 6.3: Mass Balance phenol electrolysis



Figure 6.4: Mass balance 2-tert-butylphenol electrolysis

The above analysis shows that, for both phenol and 2-*tert*-butylphenol, 100 % of the acetonitrile and 98 % of the sulphuric acid is accounted for. The water showed a 31 % loss in each case: part of this is used in the hydroxylation reaction of the phenol for the conversion of phenol to the relevant hydroquinone;

$$C_6H_5OH + H_2O \longrightarrow C_6H_4(OH)_2 + 2 H^+ + 2 e^-$$
  
(6.1)

The further reaction when converting the particular hydroquinone to the benzoquinone, does not consume water:

$$C_6H_4(OH)_2 \longrightarrow C_6H_4O_2 + 2 H^+ + 2 e^-$$
  
(6.2)

In the case of phenol, 8 mmoles of hydroquinone were formed, requiring 8 mmoles of water. This only amounts to 1.07 % of the water present initially. Thus the large majority of the water (i.e. 30 %), is either due to water electrolysis, or due to physical loss during work up. A similar calculation for 2-*tert*-butylphenol shows the same observation.

The phenol mass balance shows that 87 % of the phenol is accounted for, indicating an apparent loss of 13 % in organic material. This amount agrees closely with the apparent loss in material as shown in the mass balance of Figure 6.1 at 6.5 F of charge.

The mass balance for 2-*tert*-butylphenol (Figure 6.4) also shows a loss of organic material, in this case amounting to 21.5 %. This again correlates remarkably well with the apparent mass balance loss as shown in Figure 6.2 at 6.5 F of charge.

In order to reduce the apparent loss of material, it is necessary to carry out the electrolysis of the material up to 8.5 F in the case of 2-*tert*-butylphenol and 8 F in the case of phenol.

### 6.2.3 Energy aspects

For both phenol and the 2-*tert*-butylphenol the energy input can be calculated from the current and potential inputs into the cell, which were monitored and found to be constant throughout the electrolysis. Since the temperature of the electrolysis was kept constant by the resistive heating in the flow cell, and no heating or cooling was used once the electrolysis started, an approximate energy balance can be performed on the reactions at the temperature of electrolysis.

- The total energy entering the system can be calculated, since the cell current and cell potential was constant throughout the electrolysis time.
- The heat of reaction can be calculated, this can be done from the thermodynamic bond enthalpies.

This calculation is shown below:

#### 6.2.3.1 Heat of reaction, ΔH

The reactions taking place in the cell are as shown in Scheme 6.1; it should be remembered that the hydroquinone is immediately oxidised further to the benzoquinone and Section 3.2.5 showed that most of the hydroquinone present in the reaction medium is as a result of the benzoquinone reduction. The oxidation to benzoquinone requires 4 F and the reduction of benzoquinone to hydroquinone 2 F; this resembles a paired electrolysis system and since the anodic reaction uses 4 F and the cathodic 2 F, more energy is needed for the anodic reaction and so the calculations are performed on the anodic reaction.



 $R = H \text{ or } CH_3$ 

From a thermodynamic point of view the energy required to either break or form bonds can be calculated. When considering Scheme 6.1 it can be seen that during reaction, six bonds are broken (3 O-H, C-H, C=C, C-O) and four bonds are formed (2 H-H, 2 C=O). The enthalpy values for these bonds are known, and the heat of reaction can be calculated from these values.<sup>146</sup>

#### **Bonds Broken**

3 O-H 3 x 460 = 1380 kJ C-H 414 = 414 kJ C=C 611 = 611 kJ C-O 339 = 339 kJ Total = + 2744 kJ

#### **Bonds Formed**

2 H-H 2 x 435 = 870 kJ 2 C=O 2 x 741 = 1482 kJ Total = - 2352 kJ

 $\Delta$ H for reaction = 2744 kJ - 2352 kJ = + 392 kJ mol<sup>-1</sup>

It is seen therefore that the reaction is endothermic and requires 392 kJ mol<sup>-1</sup> at 60  $^{\circ}$ C.

#### 6.2.3.2 Energy entering

In this section the input electrical energy is calculated for phenol and 2-*tert*-butylphenol, for the scale-up experiment.

Phenol: The current and potential applied was 13 A and 8.25 V respectively, for a duration of 7h 3 min 30 sec to reach a maximum sum of hydroquinone and benzoquinone giving a relative yield of 80.9 % using 0.4270 moles of substrate. Since the temperature of the electrolysis was constant at 60 °C, this can be considered as a temperature reference line.
 Electrical energy input at 60 °C = 13 A x 8.25 V = 107.25 W = 107.25 J s<sup>-1</sup> Total electrical energy = 107.25 J s<sup>-1</sup> x 25410 s = 2725.2 kJ

Energy required for reaction =  $392 \text{ kJ mol}^{-1} \times 0.4270 \text{ mol} \times 0.809 = 135.41 \text{ kJ}$ Percentage of electrical energy used in reaction = 5.0 %

2-*tert*-butylphenol: The current and potential applied was 13 A and 16.5 V respectively, for a duration of 7h 21 min to reach a maximum sum of hydroquinone and benzoquinone of relative yield 92.9 % using 0.4222 moles of substrate. Since the temperature of the electrolysis was constant at 60 °C, this can again be considered as a temperature reference line.
 Electrical energy input at 60 °C = 13 A x 16.5 V = 214.5 W = 214.5 J s<sup>-1</sup> Total electrical energy = 214.5 J s<sup>-1</sup> x 26460 s = 5675.7 kJ
 Energy required for reaction = 392 kJ mol<sup>-1</sup> x 0.4222 mol x 0.929 = 153.75 kJ
 Percentage of electrical energy used in reaction = 2.7 %

It is interesting to note that the percentage of current used in the phenolic reaction is higher than that used in the 2-*tert*-butylphenol reaction. The reason for this could be the formation of a two-phase system at the high 2-*tert*-butylphenol substrate loadings. This two-phase system will result in a less effective contact of the organics with specifically the anode resulting in a greater extent of water electrolysis. Also the lower conductivity of the reaction mixture requires a higher voltage for the current to pass through, thereby increasing the electrical energy input.

The results indicate that only a small amount of the current entering the cell is used in the production of the organic products. The reason for this could be the formation of by-products in the reaction medium and the electrolysis of the reaction medium itself. The by-product formation is unlikely since the mass balance of the reaction is very high. Since the reaction is carried out in an aqueous medium the electrolysis of the water in the medium is the likely cause of the drop in current efficiency and the percentage of electrical energy consumption.

The chemical decomposition of water by electrolysis in an electrolytic cell can be represented by Reaction 6.3.<sup>147</sup>

$$2 H_2 0(I) + 572 kJ \longrightarrow 2 H_2(g) + O_2(g)$$
 (6.3)

Since the moles of water lost by electrolysis can be taken as 0.2, from the mass balance, it follows that 57.2 kJ were required for water electrolysis, representing 2.1 % for phenol and 1.0 % for 2-*tert*-butylphenol of the total electrical input. The rest of the energy must have been lost in the evaporation of the reaction medium into the condenser and maintaining the reaction medium at 60  $^{\circ}$ C.

There are two ways in which the electrical input can be reduced: a lowering of the inter-electrode gap and an increase in the conductivity of the reaction medium; both these factors would lower the potential needed to supply the desired current so decreasing the electrical input and lowering the resistive heating. This would lead to a more energy efficient system.

#### 6.2.4 Electrode stability

The short term stability of both the nickel cathode and the lead dioxide anode was investigated through mass loss. These results indicated no mass loss over the short term electrolysis, but ICP analysis on the reaction medium indicated that up to 10 ppm lead is present in the electrolysis medium, decreasing in concentration as electrolysis proceeds. The small amount of lead detected in the electrolysis solution could be due to carry over of lead from the previous experiment where the lead dioxide surface was produced from a lead electrode in 10 M sulphuric acid at constant current. Despite several attempts at cleaning the electrode setup afterwards, a small amount of lead could still be present in the setup. The reason for the decrease in lead content with electrolysis is probably due to the plating of lead on the cathode.

### **6.3 Conclusion**

During the scale-up investigation it was found that the reaction is fairly robust when moving up in substrate loading and using a different flow electrolyser, yielding better hydroquinone yields than with the micro flow cell. This was found to be the case for both phenol and 2-*tert*-butylphenol.

The mass balance indicated a significant water loss during electrolysis, whilst the sulphuric acid and acetonitrile showed close to 100 % recovery. The organic products for both the phenol and the 2-*tert*-butylphenol mass balance investigation showed a significant deviation from 100 %; these organic results, however, indicated a good correlation with the product distribution diagram investigations in Chapter 4 and 5. This indicates that the "intermediate" compound, suggested in Chapter 3, does not break up during work-up and extraction procedures. It would therefore be best to completely electrolyze and break up the "intermediate" compound, in order to eliminate the complicated product isolation and extraction procedures. One should therefore carry on with the electrolysis up to 8 F for phenol and 8.5 F for 2-*tert*-butylphenol.

The electrical energy efficiency was showed to be very low, with the results for 2*tert*-butylphenol being lower than that for phenol.

The electrode stability investigation showed that over short term electrolysis the electrodes are fairly stable but that the lead dioxide anode could contaminate the reaction stream.

## **CHAPTER 7**

### **Summary and Concluding Remarks**

The industrial production of hydroquinone is performed using a variety of procedures of which only one utilizes phenol as starting material, namely the hydroxylation of phenol with hydrogen peroxide in the presence of a catalyst. Inherent to this process is the need for better isomeric control in terms of hydroquinone since a mixture of hydroquinone and catechol is produced. In addition, this system usually gives only moderate to good yields at low conversions, and the resulting product streams contain large amounts of phenol and acid. This normally necessitates complex recovery and recycle procedures. The *tert*-butylated hydroquinones are produced by the additional alkylation of hydroquinone.

When one considers the price of phenol on the international market and compares this with price levels for hydroxylated phenols, like hydroquinone, one sees a significant increase in value when introducing an extra hydroxyl group onto the aromatic ring. Recently the gradual increase in phenol supply, resulting in a lowering of price relative to the starting materials for the other production procedures, renewed the pursuit of an economically viable phenol-based technology for the production of hydroquinone. The increasing need for anti-oxidants has also increased the need for *tert*-butylhydroquinones and an improvement on the current process could prove financially viable.

The original objective of this investigation was to re-evaluate the anodic oxidation of phenol, 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol with the aim of optimizing the electrochemical production of the corresponding hydroquinones in an aqueous medium. This system was identified, from open and patent literatures, to offer the most potential for industrial implementation.

The experimental investigation has shown a number of interesting points:

- Electrolysis of phenols produces the respective hydroquinones and benzoquinones, and an unstable "intermediate" compound whose concentration increases with increasing *tert*-butyl substitution. Generally only trace amounts of other side products are formed.
- The "intermediate" upon further oxidation results in an increase in both the respective hydroquinones and benzoquinones.
- The mechanism of electrochemical oxidation of phenols was found to depend on the anode material used, with lead dioxide undergoing an indirect type mechanism involving hydroxyl radical formation from the water, whilst other materials (platinum and carbon) gave a more direct mechanism.
- Electrolysis of phenol results in small amounts of catechol, but no resorcinol, while electrolysis of 2-*tert*-butylphenol and 2,6-di-*tert*-butylphenol yields only the respective hydroquinones.
- Taking all the reaction responses into account the electrolysis efficiency of phenols increases with increasing *tert*-butyl substitution, assuming that the phenol remains soluble in the reaction medium.
- Both the batch and the flow cell produced good results, with the batch cell giving a slightly better performance.
- The charge per mole required to oxidise phenols completely decreases with increasing *tert*-butyl substitution.
- Current efficiency values are generally low due to the reversible redox reactions between the respective hydroquinones and benzoquinones at the electrodes, coupled with competing reactions producing hydrogen and oxygen. The current efficiency does however increase with increasing *tert*butyl substitution.
- The solubility of the respective phenol in the reaction medium is an important factor in phenolic oxidations.
- Scale-up of the phenolic electrochemical oxidation showed that the system is fairly robust when moving to different substrate loadings and electrolysis cells.
- The mass balance investigation for the starting materials, intermediates and products during scale-up showed similar results to those observed in the product distribution diagrams from small scale investigations, with minimal

loss of sulphuric acid and acetonitrile. A significant loss of water, not related to the phenolic organic reactions was observed, indicating water electrolysis. This was also shown in the electrical energy efficiency which proved to be very low.

The electrode stability investigation showed that over short term electrolysis the electrodes are fairly stable but that the lead dioxide anode could contaminate the reaction stream.

This investigation has led to a better understanding of phenolic oxidations at an anode. With this knowledge, reaction mechanisms for the oxidation of phenols at various anodes were proposed to explain the observed experimental results. The single most important element of the proposed mechanisms was the proposal that the primary oxidation intermediate, formed from the oxidation of phenols, is the cyclohexa-2,5-dien-1-one radical or cation. The formation of all the secondary oxidation products, at all anodes, could be explained in terms of further reactions of the cyclohexa-2,5-dien-1-one radical or cation. This cyclohexa-2,5-dien-1-one radical or cation intermediate could also explain the isomeric selectivity of the primary oxidation products. A novel mechanism was then proposed for the formation of the "intermediate" compound observed and its further oxidation to the respective hydroquinones and benzoquinones. It was suggested that this intermediate could be a dimer.

The results showed that the process developed for the electrochemical oxidation of phenols, yields mainly the para-isomers of the respective hydroquinones and benzoquinones in good yields and selectivities, with fair current efficiencies and good mass balances at high conversions. For example:

- Phenol (batch) 8 F: 34 % current efficiency, 70 % hydroquinone, 6 % catechol, 9 % benzoquinone, 9 % phenol and 94 % mass balance.
- 2-T*ert*-butylphenol (flow) 10 F: 37 % current efficiency, 65 % hydroquinone, 33 % benzoquinone, 2 % phenol and 100 % mass balance.
- 2,6-Di-*tert*-butylphenol (flow) 11 F: 23 % current efficiency, 92 % hydroquinone, 6 % benzoquinone, 1 % phenol and 99 % mass balance.

In view of the promising results (in terms of product yields and isomer purity) obtained for the electrochemical oxidation of phenols in an aqueous medium, it is quite likely that this methodology may be developed further to form the basis of an economically viable process for the production of the respective hydroquinones. However a lot of work is still needed in order to accomplish this and only some of the more important aspects are highlighted below.

- To test long term integrity and stability of the reactor and its components. The reaction medium is not extremely corrosive, but the stability of the electrodes could be a problem.
- It is also deemed necessary to further investigate specifically the anode identity and composition using different lead dioxide formulations in order to increase electrode lifetime and stability as well as reaction efficiency.
- To investigate flow cell design and introduce micro reactor technology which should significantly increase electrode area.
- To further confirm the proposed mechanism.
- To achieve long term operation with consistent performance and no lead contamination of the final product.
- To optimize the overall processes and rationalize the sensitivity of reactor performance to economics, technological, environmental and safety factors.
- To define other unit processes and their integration with the electrochemical reactor.

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# MECHANISTIC ASPECTS OF THE ELECTROCHEMICAL HYDROXYLATION OF 2*tert*-BUTYLPHENOL

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### ABSTRACT

The electrochemical oxidation of 2-tert-butylphenol is investigated in an aqueous / organic mixture at a PbO<sub>2</sub> and a Pt anode using cyclic voltammetry, divided cell electrolysis and undivided constant current electrolysis using a flow cell, where product distribution profiles are obtained as a function of input electrical charge per mole of substrate, and potential monitoring during the oxidation. The mechanism of the oxidation at a PbO<sub>2</sub> anode differs from that at a Pt anode and two separate mechanisms are proposed, based on the experimental results obtained. In addition another mechanism is proposed which may explain the formation of an intermediate during electrolysis in a flow cell; this intermediate breaks up later in the electrolysis to form 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone, giving near 100 % mass balance. The formation of the intermediate is more pronounced with the Pt anode than with the PbO<sub>2</sub> anode.

### **1 INTRODUCTION**

The electrochemical hydroxylation of phenol in an aqueous electrolyte is shown in Scheme 1 below and takes place in two well-defined steps: firstly oxidation to the dihydroxybenzenes, followed by further oxidation to the benzoquinone. Of the possible dihydroxybenzenes, hydroquinone (para isomer) and catechol (ortho isomer) are the two most abundant products, whilst resorcinol (meta isomer) will not be formed to a great extent due to the deactivation of the meta position on the ring and the resulting instability,<sup>1</sup> since the hydroxyl group is electron donating. Further oxidation leads predominantly to the p-benzoquinone.



Upon substituting a bulky group, like a tertiary butyl group, in the 2 position on the aromatic ring, the formation of the corresponding catechol compound is prevented, due to the inductive effect of the bulky group and the para-directing effect of the hydroxyl group on the ring. Further oxidation leads exclusively to the 2-*tert*-butylbenzoquinone



Scheme 2 : Oxidation of 2-*tert*-butylphenol to 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone

Not shown in the scheme is the formation of oligomeric and polymeric products during electrolysis due to O-C and C-C coupling reactions between primary oxidation products and substrate and / or oxidation products. Such coupling reactions are particularly problematic during electrolytic oxidation reactions if primary oxidation intermediates are allowed to accumulate at the electrode surface. Polymer formation on the anode surface can often be observed with phenol during these oxidation reactions. When one or more positions adjacent to the phenolic hydroxyl group is substituted, especially with a bulky substituent such as a tertiary butyl group, the tendency to form C-O coupled oligomers is reduced.

The electrochemical oxidation of phenol has been investigated largely from a point of view of the destruction of the phenol in waste streams.<sup>2,3,4,5,6</sup> Preliminary work in the authors laboratories using a PbO<sub>2</sub> anode and a Ni cathode showed that phenol and especially 2-*tert*-butylphenol can be readily converted to the respective hydroquinones and benzoquinones in good yields with high selectivity and high conversions : for example after 10 F of electrical charge, 2-tert-butylphenol was converted in a flow cell to : 65 % 2-*tert*-butylhydroquinone, 33 % 2-*tert*-butylbenzoquinone, with 2 % of the substrate remaining ( % values given as mole % ) and 37 % current efficiency.

From the product distribution diagrams obtained as a function of input charge per mole it was found that a noted drop in mass balance always occurred indicating the formation of an unknown species; however later during the electrolysis, this unknown compound is further oxidized to the respective hydroquinone and benzoquinone, restoring the mass balance of the system back to near 100 %.

Further investigations showed that the mechanism of the oxidation is also highly dependent on the anode material used, with PbO<sub>2</sub> giving a different mechanism from Pt.

This work will study the electrochemical oxidation of 2-*tert*-butylphenol on PbO<sub>2</sub> and Pt in order to investigate the mechanism of the oxidation.

# 2 **EXPERIMENTAL**

### 2.1 Materials

Chemicals used in the oxidation, synthetic procedures and analytical methods were purchased from either Merck or Aldrich, and were all of analytical grade and used as received. Phenol was dried in a vacuum oven.

Pt on niobium, Ni and PbO<sub>2</sub> electrodes were obtained from Electrosynthesis in the USA. The electrode area was 5  $cm^2$ .

### 2.2 Synthetic procedures

### 2.2.1 2-Tert-butylbenzoquinone

Was produced from the corresponding phenol through electrochemical oxidation in a divided cell, which was equipped with a nafion membrane. The anode was  $PbO_2$ and the cathode a Pt electrode. The electrolyte in each compartment was a mixture of acetonitrile (53 cm<sup>3</sup>) and an aqueous solution of 5 % v/v sulphuric acid solution (22 cm<sup>3</sup>). A current of 800 mA was used and twice the theoretical amount of charge (8 F) was passed through. After electrolysis, the product was extracted with ethyl acetate, and the 2-*tert*-butylbenzoquinone separated and purified. Analysis using GC-MS, IR, DSC and TLC showed the product to be min 99 % pure.

### 2.2.2 2-Tert-butylhydroquinone

Was prepared from the corresponding benzoquinone, synthesized above by electrochemical reduction in a divided cell. The anode was a carbon electrode and the cathode a nickel electrode. The experimental details were the same as for the benzoquinone above. After electrolysis, the product was extracted as before, purified and analysed giving a purity of 99 %.

### 2.3 Oxidation procedures

### 2.3.1 Divided cell electrolysis

The electrochemical cell used consisted of two glass compartments equipped with heating jackets and separated with a nafion membrane. Constant current electrolysis was carried out using an Amel 2051 General Purpose galvanostat.

### 2.3.2 Undivided batch recirculation micro flow cell electrolysis

This consisted of a double-walled reactor flask, 150 cm<sup>3</sup> in volume, equipped with a heating jacket, which was connected to a Labcon circulator in order to affect either heating or cooling. The reactor lid was designed with quikfit and screw top adapters for the insertion of flow inlet and outlet tubes, thermometer and condenser. The flow outlet from the reactor was connected to an Iwaki model WD-15FY-220N impeller pump which forced the liquid through a flow indicator into the Electrosynthesis Micro-01 flow cell whose electrodes were connected to an Amel galvanostat. The flow cell outlet fed back into the double walled glass reactor in order to complete the loop.

### 2.4 Analytical procedures

### 2.4.1 HPLC analysis

This was carried out on a Hewlett Packard 1100 series HPLC chromatograph with a dual pump system (G 1312A), equipped with a variable UV – Visible detector (G 1314A) and an auto sampler unit (G 1313A). Data was acquired with a personal computer loaded with HP Chemstation for LC software (ver A.06.03). All solvents were HPLC grade and were degassed prior to analysis with a Millipore vacuum-degassing unit. A 3.9 x 300 mm Waters µBondapak C18 (serial no. WAT027324) column fitted with a Supelco Discovery C18 guard column was used for the analysis of the reaction samples. Response factors for the compounds of interest were determined by means of a five-level calibration using standard solutions containing known amounts of the analytes and internal standards.

The sampling procedure for HPLC analysis from the electrochemical reactor, consisted of taking 0.50 cm<sup>3</sup> aliquot samples, followed by dilution with 7.0 ml of acetonitrile containing 6.5478 mmol/L of p-dichlorobenzene as internal standard. Table 1 summarises the HPLC conditions for the analysis of the 2-*tert*-butylphenol oxidation mixtures.

Injector Volume	10 µl
Column	µBondpak C <sub>18</sub> 3.9 x 300 mm (Waters)
Wavelength	220 nm
Flow Rates	$1 \text{ cm}^3 \text{ min}^{-1}$
Mobile Phases	55% MeCN : 45% $H_2O$ buffered to pH = 3
	with H <sub>3</sub> PO <sub>4</sub>
Internal Standard	p-di-chlorobenzene

Table 1: HPLC conditions for 2-tert-butylphenol oxidation

### 2.4.2 GC-MS analysis

This was carried out on a Thermo-Finnigan Trace GC coupled to a Quadropole Trace MS plus detector. Separation was achieved with the aid of a Restek-RTX 5 MS column (15 m x 0.25 mm i.d.). Helium was used as the carrier gas, with a flow rate of 40 cm<sup>3</sup> min<sup>-1</sup>. Data acquisition, manipulation and instrumental control were carried out with Excalibur ver. 1.3 software using a DELL personal computer. Use was made of a split / splitless injection mode using a GC syringe (supplied by Hamilton). Other important chromatographic conditions used are summarized in Table 2.

Initial column temperature	70 °C
Initial column hold time	5 min
Heating rate	10 ºC min⁻¹
Final column temperature	270 °C
Final column hold time	5 min
Injector temperature	250 °C
Detector temperature	300 °C
Detector solvent delay	2 min

#### Table 2: GC-MS analysis conditions

### 2.5 Cyclic voltammetry

CV studies were performed on a BAS CV50 cyclic voltammetry system. A Gateway 2000 personal computer, running CV50 software, was used for both instrumental control and data acquisition. The electrochemical cell was equipped with platinum, glassy carbon and lead dioxide working electrodes, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. The potential of the working electrode was scanned over potential ranges permitted by the working electrode. The scan rates used ranged from 10 to 1000 mV s<sup>-1</sup> and sensitivities were varied as needed according to the sample concentrations and scan rate. Cyclic voltammograms were recorded for the substrates, intermediates and final products, so as to determine their oxidation potentials and the mechanistic pathway. The same solvent / supporting electrolyte systems used for the reactions was used as the analysis medium.

# 3 RESULTS

### 3.1 Cyclic Voltammetry

Cyclic voltammerty was used to elucidate the electro-organic mechanism at the Pt and PbO<sub>2</sub> anodes. This work was performed using 50 mmol dm<sup>-3</sup> analyte solutions in the reaction medium consisting of 70% v/v acetonitrile and 27 % v/v water and 3 % v/v sulphuric acid. The analytes were 2-*tert*-butylphenol and its respective hydroquinone and benzoquinone.

In these experiments the scan rate was varied from 10 to 1000 mV s<sup>-1</sup>. By varying the scan rate, different species in the mechanism can be investigated, even short-lived ones. Reverse sweep and multiple sweeps also allow further investigation of the species formed at the electrode during the electrochemical reaction.

#### 3.1.1 Platinum as working electrode

As suggested above the oxidation of 2-t-butylphenol should follow the same route as for phenol, leading first to the corresponding hydroquinone and then to the relevant benzoquinone. Figures 1 and 2 compare the voltammogram for phenol with that for the 2-*tert*-butylphenol. Both the voltammograms show the oxidation peak for the respective phenol in the anodic sweep. Two important points are observed :

- Peak potential: The peak potential for 2-*tert*-butylphenol is slightly lower than for phenol, since the tertiary butyl group will increase the electron density on the ring, and therefore cause easier oxidation as compared to phenol.
- Peak shape: The shape of the oxidation peak for 2-*tert*-butylphenol is distorted compared to that of phenol. This is due to the stability which the tertiary butyl group imparts on 2-*tert*-butylphenol and its oxidation intermediates through the stabilization of both the radicals and the cations formed during the process.<sup>7,8</sup> Since the increased stability of the intermediates increases their residence time in the reaction medium, they can be observed during the scan.



Figure 1: Cyclic voltammogram of a 50 mmol dm<sup>-3</sup> phenol solution

(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; 100 mV s-1 scan rate; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)




(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; 100 mV s<sup>-1</sup> scan rate; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

Figure 3 shows the cyclic voltammograms for the supporting electrolyte carried out at four different scan rates.



Figure 3: Cyclic voltammograms: Supporting electrolyte solution

(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

The window range for the specific supporting electrolyte solvent system ranges from -200 to 2200 mV vs. Ag/AgCl (3 mol dm<sup>-3</sup>). Two electrochemical processes are observed: these are the anodic oxidation of water and the cathodic reduction of protons.

Figure 4 shows the cyclic voltammograms for 2-tert-butylbenzoguinone carried out at four different scan rates. As indicated there are no peaks in the first anodic sweep indicating that there are no oxidisable species present initially besides the water. On the cathodic sweep there is a reduction peak at approximately -26 mV due to reduction of 2-tert-butylbenzoquinone to the 2-tert-butylhydroquinone. On the second anodic sweep there is now an oxidation peak at about 730 mV due to the oxidation of the 2-tert-butylhydroquinone to the 2-tert-butylbenzoquinone, showing that the 2-tert-butylhydroquinone is produced by the reduction of 2-tertbutylbenzoquinone in the previous sweep. As the cycles continue the peaks reoccur and the peak size decreases; this decrease is due to the depletion of the analytes surrounding the working electrode. Increasing the scan rates indicates that there are no short lived species present in either the reduction of 2-tertbutylbenzoquinone or the oxidation of the 2-tert-butylhydroquinone. It is also noted that as the scan rate increases, the ratio of the 2-tert-butylbenzoquinone reduction peak to the 2-tert-butylhydroquinone oxidation peak decreases. This can be ascribed to the reduction being performed on the 2-tert-butylbenzoquinone which is present in the solution, but the oxidation being performed on the 2-tertbutylhydroquinone which is only formed on the surface of the electrode: the longer it takes for the reverse sweep to occur, the more of the 2-tert-butylhydroquinone diffuses from the electrode surface into the bulk of the solution, thus giving smaller peaks. As the scan rate increases, 2-tert-butylhydroquinone diffuses to a lesser extent from the electrode into the bulk of the solution, hence peak size increases the reduction of the respective 2-*tert*-butylbenzoquinone.





(50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

As seen from the voltammogram there is an electrochemical equilibrium between the 2-t-butylhydroquinone and the 2-t-butylbenzoquinone, shown by Equation 1.



 $R_1$  and  $R_2 = H$  or  $C(CH_3)_3$ 

Superimposed on the reduction of the benzoquinone is the production of hydrogen gas from the acid present.

$$2 H^{+} + 2 e^{-} \Longrightarrow H_2(g)$$
 (eq 2)

Although the reduction of the benzoquinone requires protons, reaction 2 is the only reaction that physically consumes protons as the oxidation of the hydroquinone to the benzoquinone will supply the protons required during reduction.

Figure 5 shows the cyclic voltammograms for 2-*tert*-butylhydroquinone carried out at four different scan rates. The same trends are visible as in Figure 4, except that there is no peak present which corresponds to the reduction of 2-*tert*-butylbenzoquinone in the first cathodic sweep. After the first anodic sweep and the oxidation of 2-*tert*-butylhydroquinone, a peak resulting from the reduction of 2-*tert*-butylbenzoquinone appears on the next cathodic sweep, indicating that the 2-*tert*-butylbenzoquinone is produced by the oxidation of 2-*tert*-butylhydroquinone. The 2-*tert*-butylhydroquinone shows the same peak ratio phenomena observed in the 2-*tert*-butylbenzoquinone study and this can be explained in a similar manner.



Figure 5: Cyclic voltammograms: 2-tert-butylhydroquinone

(50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

#### Figure 6: Cyclic voltammograms: 2-tert-butylphenol



(50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; Pt working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

Figure 6 represents the cyclic voltammetry studies performed on a 50 mmol dm<sup>-3</sup> 2-*tert*-butylphenol solution at the four different scan rates. The first anodic sweep shows a group of peaks at approximately 1075 mV relating to the oxidation of 2-*tert*-butylphenol. The first cathodic sweep shows a peak at approximately 55 mV relating to 2-*tert*-butylbenzoquinone reduction. The second anodic sweep shows a peak at approximately 670 mV relating to 2-*tert*-butylhydroquinone oxidation, followed by the peaks observed in the first anodic sweep.

The grouping of peaks relating to 2-*tert*-butylphenol oxidation is as a result of the oxidation of the phenol to intermediates which are stable enough for the duration of the analysis to produce the respective peaks. The stability is caused by the presence of the tertiary butyl group, which imparts some stability to the primary oxidation intermediates of 2-*tert*-butylphenol.<sup>7,8</sup> When the scan rate is increased, additional anodic peaks appear after those of 2-*tert*-butylphenol. The intensity of these peaks increases relative to the other peaks with an increase in scan rate.

This is an indication that these peaks can be associated with short lived species in the reaction mixture.

#### 3.1.2 Lead dioxide as working electrode

The results discussed in this section were obtained with a lead dioxide working electrode and scan rates ranging from 10 to 1000 mV s<sup>-1</sup>. Higher scan rates show the same trends. Figure 7 shows the cyclic voltammograms for the supporting electrolyte solution at four different scan rates.

The lead dioxide electrode was made by the anodic electrolysis of a lead surface in aqueous sulphuric acid. This oxidised the lead surface to lead sulphate and the lead sulphate to lead dioxide, it is thus clear that the electrode surface will contain some lead sulphate and this is demonstrated in the cyclic voltammograms. From Figure 7 it can be seen that in the first anodic sweep there is a peak at approximately 1965 mV corresponding to the oxidation of lead sulphate to lead dioxide, followed by a rise resulting from the oxidation of water. On the first cathodic sweep a peak at approximately 1300 mV, corresponding to the reduction of lead dioxide to lead sulphate is observed.





(reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid;  $PbO_2$  working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

Figure 8 shows the cyclic voltammograms for 2-*tert*-butylbenzoquinone and for 2*tert*-butylhydroquinone carried out at two different scan rates using a lead dioxide working electrode. It is important to note that there are no extra peaks present due to the oxidation or reduction of the substrate. Figure 9 shows the cyclic voltammogram for 2-*tert*-butylphenol at two scan rates using the lead dioxide working electrode. As before there are no extra peaks present that can be ascribed to the oxidation of the substrate. This therefore suggests strongly that a different mechanism is at play at a lead dioxide surface as compared to that acting on a Pt surface.



(50 mmol dm<sup>-3</sup> analyto: reaction modium: 70% y/y acotonitrilo. 27 % y/y water and 3 % y

# (50 mmol dm<sup>-3</sup> analyte; reaction medium: 70% v/v acetonitrile, 27 % v/v water and 3 % v/v sulphuric acid; PbO<sub>2</sub> working electrode; Ag / AgCl (3 mol dm<sup>-3</sup>) reference electrode)

## 3.2 Reaction potential scan

The anodic potential at a platinum and lead dioxide electrode was monitored as a function of time in an undivided, constant current batch cell during electrolysis

using the reaction conditions shown in Table 3 with the addition of an Ag/AgCl (3 mol dm<sup>-3</sup>) reference electrode to the reaction set-up. The results (Figure 10) show that at a lead dioxide working electrode, the potential remains relatively constant throughout the reaction. At the platinum working electrode, however, there are noticeable variations in the potential throughout the electrolysis. This strongly suggests that at a lead dioxide electrode, one single reaction dominates during the electrolysis of 2-*tert*-butylphenol. With platinum as working electrode, however, it would appear as if several processes having different oxidation potentials, lead to variations in the anodic potential. This suggests that there are different oxidation mechanisms at play at each anode.

Variable	Value
Acetonitrile (% v/v)	70
Acid conc. (% v/v)	3
Substrate loading (% m/v)	2.5
Current density (A/m <sup>2</sup> )	2000
Temperature (°C)	50
Anode	Lead dioxide on titanium mesh
Cathode	Nickel

Table 3 : Standard conditions: undivided batch cell electrolysis





## 3.3 Divided cell electrolysis

Divided cell electrolysis was performed on 2-*tert*-butylphenol using lead dioxide as the anode and nickel as the cathode material. The reactions were performed using the reaction conditions shown in Table 4.

Variable	Value
Acid conc. (% v/v)	4.9
Organic solvent (% v/v)	70
Current density (A/m <sup>2</sup> )	2000
Organic solvent	Acetonitrile
2- <i>tert</i> -butylphenol loading (% m/v)	4.0
Temperature (°C)	50
Anode	Lead dioxide on titanium mesh
Separator	Nafion
Cathode	Nickel

Table 4 : Standard conditions for the divided batch cell electrolysis

Figure 11 shows the product distribution diagram for the anodic compartment (oxidation of 2-*tert*-butylphenol) and Figure 12 shows the product distribution for the cathodic compartment (reduction of 2-*tert*-butylbenzoquinone). These figures show the percentages of the 2-*tert*-butylphenol, 2-*tert*-butylhydroquinone, 2-*tert*-butylbenzoquinone, mass balance (sum of 2-*tert*-butylhydroquinone, 2-*tert*-butylbenzoquinone and 2-*tert*-butylphenol) and current efficiency as the reaction proceeds.

Figure 11 : Product distribution diagram for the anodic electrolysis of 2-tertbutylphenol in a divided cell



Figure 12 : Product distribution diagram for the cathodic electrolysis of 2-*tert*-butylbenzoquinone in a divided cell



The most important observations from these two diagrams are as follows:

- During the anodic oxidation of 2-*tert*-butylphenol in a divided cell, the substrate is oxidised rapidly, and with high selectivity to produce mainly 2-*tert*-butylbenzoquinone. While small amounts of 2-*tert*-butylhydroquinone may be detected in the anodic compartment, it is not clear whether such 2-*tert*-butylhydroquinone is the result of the oxidation of 2-*tert*-butylphenol at the anode, or whether it is as a result of the slow diffusion of the 2-*tert*-butylbenzoquinone or 2-*tert*-butylhydroquinone between the anodic and cathodic compartments. It is, however, more likely to be the result of the former, the oxidation of the 2-*tert*-butylphenol. The very low concentration of the hydroquinone is an indication of its low oxidation potential.<sup>1</sup>
- The current efficiency is remarkably high up to ~ 4 Faradays of charge per mole of substrate. This is in sharp contrast to the oxidation in an un-divided cell where the current efficiency is normally significantly lower.
- The cathodic reduction of 2-*tert*-butylbenzoquinone at a nickel cathode produces 2-*tert*-butylhydroquinone exclusively. This process is very rapid, and is probably the source of most of the 2-*tert*-butylhydroquinone normally detected during oxidation reactions in undivided cells.

## 3.3.1 Typical product distribution profiles

In this section the flow cell electrolysis of 2-*tert*-butylphenol is carried out using two different anodes, namely lead dioxide and platinum on niobium. Table 5 shows the conditions used for this electrolysis and Figures 13 shows the product distribution diagram obtained for lead dioxide, whilst Figure 14 shows the results obtained for the platinum electrode.

Variable	Value
Anode material	Lead dioxide on lead or platinum on
	niobium
Cathode material	Nickel
Electrode separation (mm)	6
Flow rate setting	2
Substrate loading (% m/v)	4.0
Current density (A/m <sup>2</sup> )	2000
Acid conc. (% v/v)	3
Organic solvent (% v/v)	70
Organic solvent	Acetonitrile
Temperature (°C)	50

#### Table 5: Standard conditions: 2-tert-butylphenol micro-flow cell electrolysis

#### Figure13: Product Distribution Diagram: Lead dioxide on Lead Anode



Figures 13 and 14 clearly show distinctly different behaviours for a platinum anode and a lead dioxide anode. The main features of these product distribution diagrams are as follows:

- In both cases, the substrate 2-*tert*-butylphenol (2-tbPhOH) is smoothly oxidised to reaction products over the range 0 – 12 Faraday's of charge per mole of substrate.
- In the case of a lead dioxide anode, the reaction products are essentially 2tert-butylhydroquinone (2tbHQ) and 2-tert-butylbenzoquinone (2tbBQ) as is indicated by the smooth and continuous increase in the sum of these two products, as well as the relative constant mass balance.
- For the platinum anode, however, the formation of reaction products (up to ~ 8 F of charge per mole of substrate) cannot be explained in terms of the formation of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone. As the substrate is consumed the sum of 2-*t*-butylhydroquinone and 2-*tert*-butylbenzoquinone increases only very slowly, and the overall mass balance shows a steady decrease. After ~ 8 Faradays of charge per mole substrate, however, there is a rapid increase in 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone formation, which is accompanied by a sudden increase in the overall mass balance of the reaction. Interestingly, this rapid formation of 2-*tert*-butylhydroquinone and 2-*tert*-butylbenzoquinone always seems to be accompanied by a small, yet noticeable decrease in the rate of substrate oxidation.

Figure14: Product Distribution Diagram: Platinum on Niobium Anode



- Additional observations regarding the above behaviour, and which are not shown by the product distribution diagrams are:
  - The observed mass balance drop for the platinum anode may also be observed for lead dioxide electrodes where lead dioxide is formed on a supporting metal plate (eg. titanium) and where some part of the supporting metal is also exposed to the reaction medium.
  - The observed mass balance drop is much more pronounced in a flow cell than in a batch cell.
  - The observed mass balance drop is more pronounced at lower temperatures.
  - The observed mass balance drop is more pronounced for 2-*tert*butylphenol than for phenol itself.

## 4 Discussion

## 4.1 General

The results described in the preceding section strongly suggest the existence of different mechanisms for the oxidation of 2-*t*-butylphenol at a lead dioxide anode on the one hand, and platinum on the other. Any proposed mechanism for the anodic process must be able to explain several important observations. These are:

- Cyclic voltammetry shows no peaks that can be ascribed to the oxidation of substrate and oxidation intermediates when using a lead dioxide electrode, but clear distinct peaks when using a platinum electrode.
- The observed variation in the potential of a platinum anode during an oxidation reaction as compared to the very constant potential of a lead dioxide anode.
- The observed differences in the behaviour of the reaction mass balance when using a lead dioxide anode and when using a platinum anode. In the case of lead dioxide the reaction mass balance typically remains quite high while for platinum a distinct drop in the reaction mass balance occurs that is rapidly restored towards the end of the oxidation.
- The remarkable selectivity of the electrochemical oxidation of the substituted phenol to the respective hydroquinone and benzoquinone.

The difference in the cyclic voltammetry results can possibly be explained by proposing two distinct reaction mechanisms for the oxidation of the substituted phenol at a lead dioxide anode on the one hand, and for platinum on the other. It is therefore proposed that for lead dioxide there is no direct electron transfer between the anode and the substrate, and oxidation must therefore involve the oxidation of the substrate by some form of activated species on the surface of the electrode, which is subsequently regenerated electrochemically.

In the case of platinum there is clearly a direct transfer of electrons between the substrate and the anode and the mechanism is probably a typical ECE type mechanism. This would also explain the observation of peaks in the cyclic

voltammogram that results from the oxidation of oxidizable intermediates, such as the 2-*tert*-butylhydroquinone.



 $R_1 = H \text{ and } R_2 = C(CH_3)_3$ 

The observed mass balance behaviour can only be explained in terms of the formation of an intermediate compound that cannot be detected by simple GC-MS, or HPLC (UV) analysis as used during this investigation. It was initially suspected that the observed mass balance deviation was as a result of the formation of a quinhydrone-type complex (Figure 15) between the 2-*t*-butylbenzoquinone and 2-*t*-butylhydroquinone present simultaneously in the reaction mixture, but this was discarded due to the following considerations:

- i Quinhydrone-type complexes will not readily form the *tertiary* butylsubstituted hydroquinone and benzoquinone due to the interference of the large *tertiary*-butyl group with hydrogen bonding.
- ii The fact that the decreasing mass balance phenomena is especially noticeable with the substituted phenols.
- iii The fact that the intermediate at some stage during the oxidation process decomposes to produce both hydroquinone and benzoquinone. A quinhydrone-type complex will always be present (as long as both the benzoquinone and the hydroquinone is present in the same solution) and will thus not give the observed rapid increase in mass balance towards the end of the oxidation reaction.

Careful analysis of reaction mixtures during oxidation reactions of 2-*tert*butylphenol by means of GC-MS revealed the presence of small amounts of the dimer 1,1'-biphenyl-4,4'-diol (Figure 16). Dimer and higher oligomer formation is a well documented phenomena during electrochemical (also catalytic and stoichiometric) oxidation of phenols.<sup>9,10,11</sup> It is not unfeasible for such dimeric species to undergo further oxidation to the respective biphenoquinones (see Scheme 5). Such biphenoquinones are not easily analyzed by means of GC-MS and UV / HPLC analysis, and could explain the "loss" in the reaction mass balance in the middle part of the oxidation reactions.



Before presenting the proposed reaction mechanisms the exceptional selectivity to the corresponding hydroquinone and benzoquinone needs some comment. The catalytic hydroxylation of phenol with hydrogen peroxide (using acid catalysis) produces both hydroquinone and catechol in a roughly 1:2 statistical ratio.<sup>12</sup> In contrast, the electrochemical oxidation of phenol and 2-*t*-butylphenol produces only trace amounts of catechol. This observation clearly indicates a different reaction mechanism to that at work during catalytic hydroxylation. One way of introducing such high regioselectivity during the electrochemical oxidation of phenols is through the intermediate cyclohexa-2,5-dienone cation and cyclohexa-2,5-dienone radical (Figure 17).

Figure 17: cyclohexa-2,5-dienone cation structure



 $R = H \text{ or } C(CH_3)_3$ 

While it is possible to form the cyclohexa-2,4-dienone cation and radical, it is known to be considerably less stable than cyclohexa-2,5-dienone cation and radical and hence, more difficult to generate. The instability of the cyclohexa-2,4-dienone cation and radical, relative to the cyclohexa-2,5-dienone cation and radical accounts for the preferential formation of the respective hydroquinones instead of the catechols.

### 4.2 Reaction mechanisms

Taking the preceding considerations into account, two reaction mechanisms are proposed for the selective electrochemical oxidation of phenols to their respective hydroquinones and benzoquinones. For convenience we will refer to these two mechanisms as the "Direct Electrochemical Oxidation Mechanism" and the "Indirect Electrochemical Oxidation Mechanism".

#### 4.2.1 Indirect electrochemical oxidation mechanism

As discussed above, the electrochemical oxidation of phenols at a lead dioxide electrode probably does not involve the direct transfer of electrons between the substrate and the electrode. It is, instead, believed that the oxidation is achieved by the interaction of an electrochemically formed activated species on the lead dioxide electrode surface and substrate molecules. One possible way by which such activated species may be formed is through the formation of surface bound hydroxyl-radicals. Scheme 3 shows the proposed mechanism and each step of the mechanism is explained.

Scheme 3 : Indirect hydroxylation of phenols at a lead dioxide electrode

 $2 \text{ MO}_{x}[\text{OH}^{-}] \xrightarrow{\text{Viii}} 2 \text{ MO}_{x}[] + \text{O}_{2} + 2 \text{H}^{+} + 2 \text{e}^{-}$ 

( R = relevant phenol and  $MO_x$  = lead dioxide; for simplicity the substituted phenol is shown as a phenol structure )

- i The movement of the phenolic molecule (R) from the bulk of solution to the electrode solution interface followed by the adsorption of the molecule onto the electrode.
- ii The movement of the adsorbed phenolic molecule onto an active site on the metal oxide electrode.
- iii The adsorption of water onto an active site on the metal oxide electrode, followed by the oxidation of the water molecule to a hydroxyl radical which remains bonded on the active site.

- iv The reaction between the bonded hydroxyl radical and the adsorbed phenol molecule on adjacent active sites leading to the formation of the hydroxylated product through oxidation.
- v The reaction between the hydroquinone and the electrode bonded hydroxyl radical leading to an organic radical.
- vi Reaction of the organic radical with the electrode bonded hydroxyl radical leading the respective 4,4-dihydroxycyclohexa-2,5-dien-1-one.
- vii Rearrangement of the respective 4,4-dihydroxycyclohexa-2,5-dien-1-one by the loss of water to the respective benzoquinone.
- viii A side reaction resulting in the electro-generated hydroxyl radical oxidation to molecular oxygen.

This suggested mechanism up to hydroquinone production is in line with is in line with that suggested by literature.<sup>2,3,4,5,6</sup>

### 4.2.2 Direct electrochemical oxidation mechanism

In this mechanism direct electron transfer takes place between the electrode surface and the phenolic substrate, resulting in a radical cation which then undergoes further reaction to form the hydroxylated products. Scheme 4 shows this proposed mechanism with all the steps explained.

Scheme 4 : Direct electrochemical hydroxylation of phenol



The mechanism can be broken down into the following steps:

i E: Anodic oxidation of the aromatic substrate at the electrode surface in order to produce the radical cation, followed by resonance stabilization of this radical. The extent to which this occurs depends on the oxidation potential of the phenolic compound. The lower the oxidation potential the greater the extent of the reaction.

- ii C: The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical. The location from which this proton is lost depends on the acidity of the phenolic group and the reaction medium.
- iii E: The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- iv C: Nucleophilic attack of water on the cation, resulting in a highly unstable structure, which is then rapidly rearranged, with the loss of a proton.
- v C: Rearrangement of the compound to hydroquinone.
- vi E: Anodic oxidation of the hydroquinone at the electrode surface in order to produce the radical cation.
- vii C: The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical.
- viii E: The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- ix C: Nucleophilic attack of water on the cation, resulting in an unstable structure, which is then rapidly rearranged, with the loss of a proton in order to produce the 4,4-dihydroxycyclohexa-2,5-dien-1-one.
- x This 4,4-dihydroxycyclohexa-2,5-dien-1-one then loses water in order to produce the benzoquinone.

The above mechanism (Scheme 4) is a widely accepted direct electron transfer mechanism. The problem is that this mechanism does not explain the pronounced mass balance change observed during the product distribution diagrams. It is well known that phenol undergoes dimerization and polymerization at a platinum anode, and one of the dimers (the respective 1,1'-biphenyl-4,4'-diol) was detected in trace amounts.<sup>9,10,11</sup> Scheme 5 shows a mechanism which proposes to explain the mass balance change.

Scheme 5 : Proposed direct electrochemical mechanism (dimer route)



 $R_1$  and  $R_2$  = H or C(CH<sub>3</sub>)<sub>3</sub> (from step iv to step xi the R groups are not displayed due to space limitation)

The mechanism can be broken down into the following steps:

- i Anodic oxidation of the aromatic substrate at the electrode surface in order to produce the radical cation.
- ii The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical. The location from which this proton is lost depends on the acidity of the phenolic group and the reaction medium.
- iii Coupling of the radicals in order to produce the dimeric isomers of the respective 1,1'-biphenyl-4,4'-diols.
- iv The loss of an electron from the 1,1'-biphenyl-4,4'-diols in order to produce the radical cation, followed by resonance stabilization of this cation.
- The loss of a proton from the radical cation in order to produce the radical, followed by resonance stabilization of this radical.
- vi The loss of an electron from the radical in order to produce the organic cation, followed by resonance stabilization of this cation.
- vii The loss of a proton from the organic cation in order to produce the respective biphenoquinone.
- viii The loss of an electron from the biphenoquinone in order to produce the radical cation, followed by resonance stabilization of this radical cation.
- ix Nucleophilic attack of water on the radical cation, resulting in a hydroxylated radical.
- x Loss of an electron forming the hydroxylated radical leading to a organic cation.
- xi Nucleophilic attack of water on the organic cation, resulting in the respective 1,1'-dihydroxy-1,1'-bi(cyclohexa-2,5-dien-1-yl)-4,4'-diones.
- xii The addition of a proton to the respective 1,1'-dihydroxy-1,1'-bi(cyclohexa-2,5-dien-1-yl)-4,4'-dione, leading to its break up into the respective hydroquinone and organic cation.
- xiii A typical two electron oxidation of the respective hydroquinone to the respective benzoquinone.
- xiv The loss of a proton from the organic cation yielding the respective benzoquinone.

The electrochemical oxidation of phenolic compounds at a platinum anode probably occurs according to both the known mechanism shown in Scheme 4 and the proposed mechanism shown in Scheme 5. The latter mechanism would explain the mass balance change during the oxidation.

## 5 Conclusion

This study has shown that in a divided cell 2-*tert*-butylphenol is readily oxidized to 2-*tert*-butylhydroquinone, which rapidly oxidizes further to the 2-*tert*-butylbenzoquinone. In an undivided cell, such as a flow cell, the resulting benzoquinone can then be cathodically reduced at a Ni surface to the corresponding hydroquinone. Especially in the case of Pt as anode, there is an intermediate formed during the electrolysis, which later decomposes to form the relevant hydroquinone and benzoquinone. Using PbO<sub>2</sub> the formation of this intermediate is not as pronounced as with Pt.

It was also shown that a different mechanism takes place on a PbO<sub>2</sub> anode as compared to a Pt surface :

- Platinum anode : The results showed that electrochemical oxidation of 2-tertbutylphenols proceeds through two different direct electrochemical oxidation mechanisms: one of which is the well known ECE mechanism shown in Scheme 4 whilst the other being the proposed dimmer formation mechanism shown in Scheme 5.
- Lead dioxide anode: The results showed that electrochemical oxidation of 2tert-butylphenol at the lead dioxide anode proceeds through two different mechanisms. The indirect electrochemical oxidation mechanism utilizing the electrode bonded electro-generated hydroxyl radical shown in Scheme 3 and to a lesser extent the proposed direct dimer formation mechanism shown in Scheme 5.

This investigation also yielded a possible explanation for the increased ratio of the relevant hydroquinone to catechol observed during the electrochemical oxidation. The explanation for this is that both the mechanisms produce the products through either the cyclohexa-2,5-dienone cation or cyclohexa-2,5-dienone radical.

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