

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Novel process for organic peroxides synthesis

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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Ce mémoire intitulé :

Novel process for organic peroxides synthesis

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en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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Igor CHERUBIN, membre

DEDICATION

For my family, my friends, and my director, thank you. . .

ACKNOWLEDGEMENTS

I want to begin by saying that everything is possible as long as we have ambition, faith and support. This journey was long, difficult but worth it. A long path is ahead full also of challenges, ups and downs but everything will be okay with the same support.

By this support I mean my family and boyfriend. They were and will always be here for me, with their encouragement, love and patience. My parents, my brother, my grandparents, my aunts and uncles, my boyfriend, and my cousins, THANK YOU ALWAYS.

To my parents especially, you've always been my inspiration all over the path. The pride and joy I see in your eyes after every success is my biggest motivation.

To my brother, my support system, you will always get my back during hard times even if we are miles apart.

To my grandparents, your prayers and blessings were and will always protect me.

To my aunts, uncles and cousins, your support means a lot to me!

To my boyfriend, without being next to me with your consistent support, I would never have done it. You endured my downs and lifted me always up to continue.

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Marie Therese El Kfoury

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RÉSUMÉ

On distingue différentes classes de peroxydes en fonction du groupe organique attaché à la liaison O-O du peroxyde d'hydrogène. On cite les hydroperoxydes, les diperoxydes où un ou les deux hydrogènes de H_2O_2 est substitué par un groupement aliphatique, les peroxyacides où un groupement acide carboxylique remplace un hydrogène de H_2O_2 , les peroxyesters, le peroxyde de cétone, etc. La consommation mondiale de peroxydes est principalement distribuée en Chine et Asie-Pacifique où les peroxydes de cétone et les hydroperoxydes sont les mieux classés.

Dans les années 1950, l'industrie du plastique a connu une accumulation de développements comme le polypropylène, le polyéthylène (basse et haute densité), le polystyrène, etc. Certains de ces procédés nécessitaient des peroxydes organiques comme initiateurs. Lors de leur décomposition, les peroxydes génèrent des radicaux utiles qui peuvent former des résines polymères. Les peroxydes sont également utilisés comme accélérateurs, activateurs, catalyseurs, désinfectants, durcisseurs et promoteurs. Toutes ces applications ont entraîné une évolution rapide de l'industrie des peroxydes et un taux de production croissant.

Plusieurs entreprises ont breveté des procédés de synthèse de peroxyde. Soit le type de réacteur, soit la charge, soit les conditions opératoires (température, pression) diffèrent d'un mode opératoire à l'autre. Mais les voies homogènes d'oxydation des alcanes sont les plus abondantes. L'inconvénient ici est la séparation difficile du catalyseur du mélange et la neutralisation nécessaire. En raison des lacunes, les chercheurs tentent de faire évoluer le processus vers une chimie durable en appliquant les catalyseurs hétérogènes.

L'objectif de ce travail était d'optimiser le procédé de synthèse de l'hydroperoxyde de tert-butyle (TBHP). Nous l'avons produit à partir d'alcool tertbutylique et de peroxyde d'hydrogène dans un réacteur à piston. Nous avons étudié l'effet de la température (40 °C à 70 °C), du débit (1 mL min⁻¹ et 2 mL min⁻¹) et du catalyseur (Amberlyst-15, Nafion, carbone activé, hétéropolyacide sur silica, carbon, et Amberlyst-15 support) sur le rendement du produit principal. De plus nous avons étudié la cinétique de la réaction et identifié tous les sous-produits. Nous avons constaté qu'une température de 70 °C et un débit de 1 mL min⁻¹ en présence de sites Bronsted d'Amberlyst-15 donnaient le rendement le plus élevé en TBHP. Dans l'autre partie, nous cherchions à produire le peroxybenzoate de tert-butyle par un couplage de l'acide perbenzoïque et de la matière sulfatée du catalyseur. Mais, nous avons

prouvé que la réaction entre l'acide benzoïque et H_2O_2 sur le catalyseur choisi ne produisait pas l'acide perbenzoïque souhaité et a limité notre travail à cette étape.

ABSTRACT

We distinguish different classes of peroxides depending on the organic group attached to the O-O bond of hydrogen peroxide. This includes hydroperoxides, dialkyl peroxides, peroxy acids, peroxy esters, ketone peroxide, etc. The peroxides global consumption is mainly distributed in China and Asia Pacific where ketone peroxides and hydroperoxides are the top ranked.

In the 1950s, the industry of plastic witnessed an accumulation of developments as polypropylene, polyethylene (low and high density), polystyrene, etc. Some of these processes needed organic peroxides as initiators. When decomposing, peroxides generate useful radicals that can initiate polymerization to form polymer resins. Peroxides are also applied as accelerators, activators, catalysts, cross-linking agents, curing agents, disinfectants, hardeners, and promoters. All these applications led to a fast evolution of the organic peroxide industry and growing production rates.

Several companies patented processes for peroxide synthesis. Either the reactor type, the feed or the operating conditions (temperature, pressure) differ between one procedure and another. But homogeneous pathways of alkane oxidation are the most abundant. The disadvantage here is the difficulty of removing the acid catalyst from the mixture and the neutralization needed. Due to the shortcomings, researchers are trying to shift the process toward sustainable green chemistry by applying heterogeneous catalysts.

The aim of this work was to optimize the process of tert-butyl hydroperoxide (TBHP) synthesis. We produced it from tert-butanol and hydrogen peroxide in a plug flow reactor. We studied the effect of temperature (40 °C to 70 °C), flow rate (1 mL min⁻¹ and 2 mL min⁻¹) and catalyst (Amberlyst-15, Nafion, activated carbon, heteropoly acids impregnated on silica, carbon, and Amberlyst-15) on the yield of the main product. Moreover, we studied the kinetics of the reaction and identified all the by-products. We found that a temperature of 70 °C and a flow rate of 1 mL min⁻¹ in presence of Bronsted sites of Amberlyst-15 gave the highest yield of TBHP. In the second part, we were focused on the synthesis of tert-butyl peroxybenzoate by a coupling of peroxybenzoic acid and the sulfated material from the catalyst. Unfortunately, we discovered that the reaction between benzoic acid and hydrogen peroxide over the selected catalyst did not yield the desired peroxybenzoic acid which limited our work at this step.

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LIST OF SYMBOLS AND ACRONYMS

Abbreviations

TBHP	Tert-butyl hydroperoxide
DTBP	Di-tert-butyl peroxide
TBA	Tert-butanol
HPA	Heteropoly acids
TAHP	Tert-amyl hydroperoxide
DSC	Differential scanning calorimetry
NMR	Nuclear magnetic resonance
GC	Gas chromatography
MTBE	Methyl tert-butyl ether
HPLC	High performance liquid chromatography
MS	Mass spectrometry
PDVB	Poly divinylbenzene
FID	Flame ionization detector
TCD	Thermal conductivity detector
ECD	Electron capture detector
PID	Photoionization detector
FPD	Flame photometric detector
UV	Ultra violet
PHR	Process hazard report
PPE	Personal protective equipment

Symbols

$F_{\text{calibration}}$	Calibration coefficient
A_{exp}	Measured peak area
n_{dilution}	Dilution coefficient
k	Reaction rate constant
E_{a}	Activation energy
R	Gas constant
T_0	Reference temperature
X_{TBA}	Conversion of TBA
S_{i}	Selectivity of the product

$n_{\text{TBA in}}$	Moles of TBA entering
$n_{\text{TBA out}}$	Moles of TBA flowing out
C	Concentration
V_{eq}	Volume at equivalence
m_{cat}	Catalyst mass
AC	Activated carbon
[TBHP]	Concentration of TBHP
[TBA]	Concentration of TBA
[H ₂ O ₂]	Concentration of H ₂ O ₂

CHAPTER 1 INTRODUCTION

1.1 Context

Peroxides are an important class of chemicals characterized for their weak covalent O-O bond [1]. Unlike other species, peroxides are designed to decompose. So, both formation and decomposition of O-O bond are crucial in many sectors [2].

On the commercial scale, peroxides are efficient as cross-linking and polymerization initiators, disinfectants, and bleaching agents. By this, they are used for surface coating formulations, plastics, and rubber manufacture. Also, many medicines for acne treatment, teeth whiteners, and antimalarial drugs integrate peroxides in their formulation [1, 3, 4]. The market of peroxides is expected to increase by 3.7% per annum until 2027 and much of the growth is attributable to these applications [5]. Many companies including United Initiators, Arkema, Nouryon, NOF Corporation, Lyondell-Basell, and Pergan Marshall lead the organic peroxide industry. The top two, Arkema and Nouryon, have the highest shares currently [5, 6].

Hydroperoxides are gaining much interest as cheap radical sources. The polymer industry is the biggest to employ them as initiators. They generate useful radicals that can form polymer resins, such as polyethylene and polyvinylchloride. For example, the tert-butyl radical is ideal initiator because the three methyl functional groups polarize the carbon on the side. Between 2017 and 2027, hydroperoxides are in second place between other peroxide families scoring 100 kt in the global production market (Figure 1.1) [5].

Although their commercial interest is high, the peroxides are hazardous. Some decompose and give off flammable vapour when exposed to heat, friction or shock. Several reports study the safety, handling, and storage of peroxides [7, 8]. For instance, concentrated hydrogen peroxide ignites when in contact with oil, resins, and fabrics. It strongly decomposes when any metal catalyst is present [1, 3, 9–11]. Aqueous tert-butyl hydroperoxide (TBHP) is more hazardous than TBHP solutions with acids/alkalis; it causes thermal explosion with a sharp self-heating rate ($T_{\max} = 336^{\circ}\text{C}$) under adiabatic conditions [7, 8]. At 49.5°C , TBHP with p-toluene sulphonic acid decomposes via a radical mechanism. The presence of acetone affects the stability of the mixture and decreases the decomposition temperature to 31°C [9]. Many kinetic studies exist on the thermal hazards and decomposition of both hydroperoxides and other organic peroxides. The homolytic cleavage of the peroxy bond in TBHP is first order according to Willms differential scanning calorimetry (DSC) study [10]. Di-tert-butyl

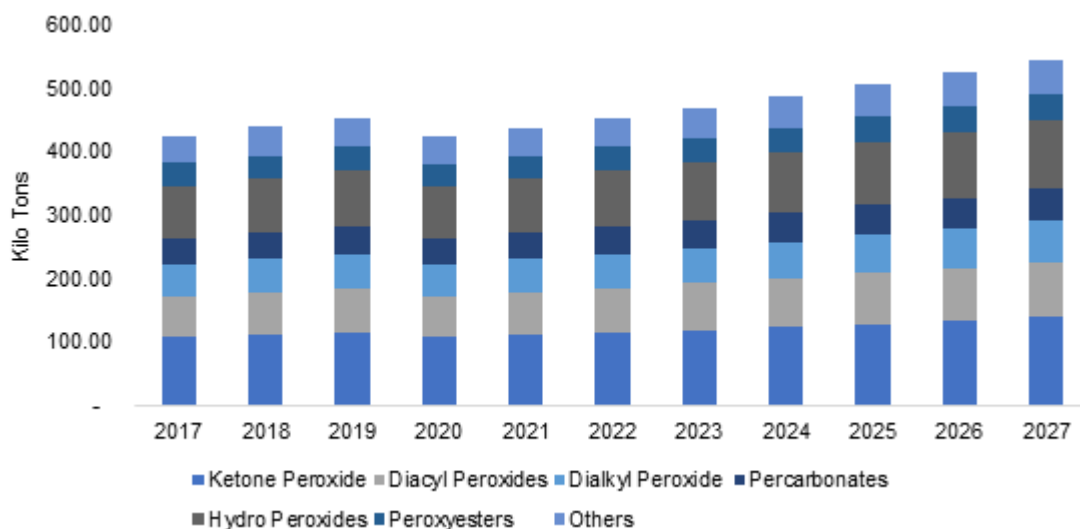


Figure 1.1 The organic peroxides global market between 2017 and 2027 [5].

peroxide (DTBP) decomposes via the O-O weak bond scission to two tert-butoxy radicals with the lowest barrier of 44 kcal mol^{-1} [11].

There have been many industrial incidents over the years due to improper storage or handling of organic peroxides [12]. Since these chemical compounds are thermally unstable, vulnerable to destabilization by contamination, and may be flammable or friction sensitive, care should be exercised to properly use organic peroxides on an industrial scale. This includes ensuring that these products be stored at the correct temperature, not be allowed to mix with incompatible materials, and exposure to ignition sources be prevented.

From existing literature, it exists a big gap in the industry of peroxides. In the 1900's, companies like Shell and Texaco patented several processes for hydroperoxide synthesis [13–16]. In fact, the alkane oxidation is the most applied and commercialized. Many configurations as the reactor type or the feed composition differ between approaches but most of them rely on homogeneous systems. Sulfuric acid is the most powerful and efficient for the reaction. But these traditional homogeneous processes induce subsequent steps as the purification and neutralization of the product and incur costs for regeneration and disposal. Nowadays, with the increasing focus on green chemistry, the use of heterogeneous catalysts provide several advantages.

1.2 Objective

The main objective of the first part of this research was to determine the optimal conditions of tert-butyl hydroperoxide's production and study the reaction's kinetics. We synthesized tert-butyl hydroperoxide from tert-butanol and hydrogen peroxide in a plug flow reactor and assessed the effect of temperature, flow rate and catalyst type on the product yield.

In the second part, we were aiming to produce the tert-butyl peroxybenzoate or Luperox[®] P. The reaction depended on an intermediate step in which benzoic acid would react with hydrogen peroxide to give the peroxybenzoic acid which could then be reacted with tert-butyl sulfate to yield the peroxyester. Unfortunately, we found that benzoic acid did not yield peroxybenzoic acid when reacted with hydrogen peroxide over Amberlyst-15 which prevented our final synthesis of the peroxyester.

1.3 Plan

This master's thesis is divided into seven chapters. Chapter 2 presents the state of art already done in the field of organic peroxides and heterogeneous catalysis. Chapter 3 describes the experimental methodology and analytical procedures applied in this study. Chapter 4 discusses the main results of this work and chapter 5 shortly describes an attempt for peroxy ester synthesis. A general discussion links the methodology and results with the literature review in chapter 6. Finally, the conclusion and perspectives are presented in Chapter 7.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Substituting one or both hydrogen atoms of hydrogen peroxide (H_2O_2) with an organic compound produces an organic peroxide, including hydroperoxides, diperoxides, peracids, peroxy esters, peroxy ketals, etc (Table 2.1). Alkanes, acids, esters are among the most common compounds [3,17]. Due to the covalent bond between oxygen atoms, peroxides tend to change to more stable products.

Table 2.1 Different classes of peroxides and their formula.

Class	Formula
Hydroperoxides	$\text{R}-\text{O}-\text{O}-\text{H}$
Diperoxide	$\text{R}-\text{O}-\text{O}-\text{R}_1$
Peroxy acid	$\text{R}-\text{C}-\text{O}-\text{O}-\text{H}$
Peroxy esters	$\text{R}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{O}-\text{R}_1$
Peroxy ketal	$\text{R}_1-\text{O}-\text{O}-\overset{\overset{\text{R}_3}{\mid}}{\underset{\underset{\text{R}_2}{\mid}}{\text{C}}}-\text{O}-\text{O}-\text{R}_1$

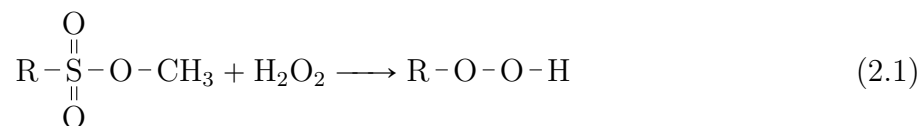
2.2 Organic Peroxides

Generally, organic peroxides can be synthesized by ozonolysis or by oxidation of alkyl halides, phosphides, sulfonates, alkenes, alkyl aromatics, alcohols, or ethers with hydrogen peroxide, singlet oxygen, or superoxide anion [17].

2.2.1 Synthesis

The most abundant method for hydroperoxide synthesis is the reaction between H_2O_2 and an electron-rich specie as alkenes and acids in the presence of H^+ , or halogen electrophiles. First the electrophile attacks the double bond or the alcohol to form a carbocation by water elimination. Then, H_2O_2 dissociates and both the anion and the carbocation form the hydroperoxide [3].

Although the attack of H^+ on alcohols gives a strong leaving group, mesylates and halides are also good candidates as nucleophilic groups in the substitution. The hydroperoxyl radical substitutes the SO_2OR functional group to give the primary or secondary alkyl hydroperoxides as shown in the reaction 2.1. By-products are alcohol and dialkyl peroxide. Yields of 38 % to 45 % of hydroperoxides are obtained in case of primary group. While, for a secondary radical, the yields are higher ranging between 43 % to 83 % [17].



On the other hand, autoxidation is also a hydroperoxide synthesis way. It includes three steps: initiation when carbon radical is formed, propagation with molecular oxygen and termination when the stable product forms (Figure 2.1). Substrate, including enols, phenols, alkanes, alkenes, dienes, and polyenes should be present in high concentrations to promote the autoxidation. For alkenes, propagation takes two routes, either abstraction, or addition of peroxy radical to the double bond [18,19]. In the presence of Cobalt (II) catalysts and triethylsilane solvent, alkenes produce silylated hydroperoxide. With two-step desilylation or with addition of alcohol as co-solvent, the alkyl hydroperoxide are obtained [17]. Also, trialkylboranes oxidize with O_2 to give dialkylperoxyalkylboranes. These, at their turn, are split into two equivalents of alkyl hydroperoxides and one equivalent of alcohol. The separation is difficult and gives low yield of peroxide [17].

Moreover, oxidative decarbonylation of aldehydes with hydrogen peroxide catalyzed with Cobalt is a recent synthetic route of alkyl hydroperoxides. Finally, monoperoxyacetals transform to alkyl hydroperoxide via hydrolysis in presence of acetic acid [17].

On a commercial scale, Texaco Chemical Inc. is the assignee of the isobutane oxidation process. In liquid phase, without any catalyst, isobutane reacted with oxygen to produce TBHP. The reaction was initiated with 0.05wt % to 0.08wt % DTBP. Isobutane contacted oxygen in continuous, semi-continuous or batch reactor at a temperature between 135 °C to 155 °C. Since the reaction is exothermic, heating was stopped at the point when the temperature rose. To purify the products, they introduced it to distillation, extractive distillation column, or solvent extractor. TBHP was recuperated in combination with tert-butanol (TBA) as by-product. Unreacted isobutane recirculated back to the inlet line. The reaction lasted for 2 h to 5 h to reach steady state conditions with a yield of 10 % TBHP [13].

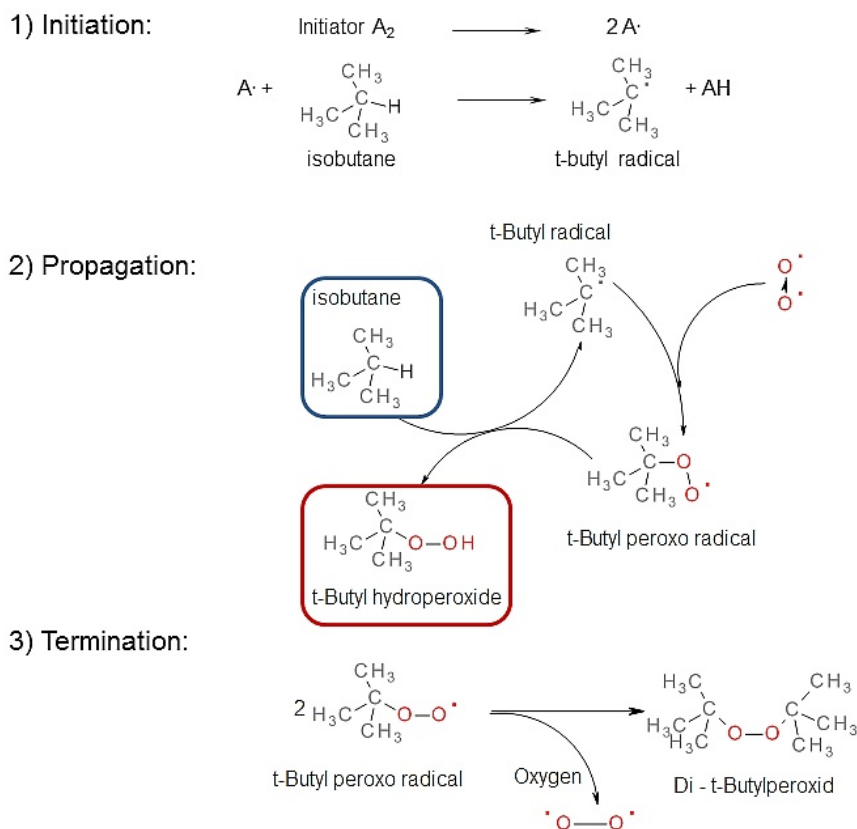


Figure 2.1 Mechanism of isobutane's oxidation [19].

Another configuration was introduced by Shell in 1946. The invention consisted of obtaining tertiary alkyl hydroperoxide from saturated aliphatic hydrocarbon containing tertiary carbon, in the presence of hydrogen bromide as catalyst and at elevated temperature. An example of process produced TBHP from vaporous isobutane and oxygen at super-atmospheric pressure and a temperature between 150 °C to 200 °C, in the presence of 2 mol % hydrogen bromide. An inert diluent was employed as a carrier to keep reactants in vapour phase. All the reactions endured for a sufficient period of time to cause the oxidation of oxygen [14].

Contrarily, Shell Canada claimed a process for liquid dense phase oxidation of isobutane. The operating conditions (140 °C to 170 °C and 55 bar) allowed the single, dense, quasi-liquid phase. An example stated the presence of 8 reaction zones, each consisted of a mixing mean as nozzle that directed the flow toward an eductor placed before the reactor. The eductor and the draft tube in the reactor assured a high mixing effect of the mixture dense phase. The outlet of the reactor was then cooled and introduced back to the nozzle to pass

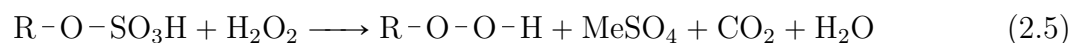
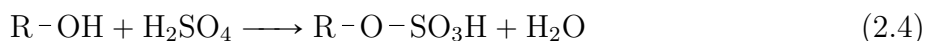
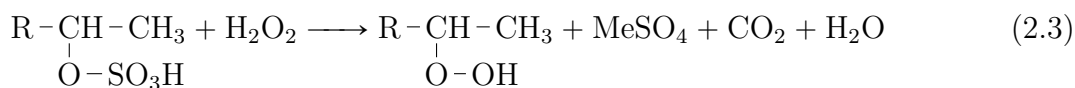
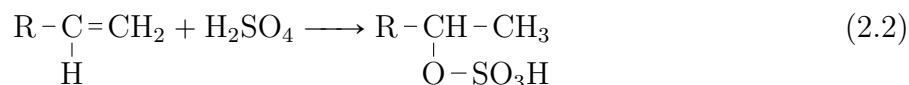
again by the whole process. The flow of the last zone can be distilled to get pure TBHP. The conversion of isobutane ranged from 5 % to 25 % [16].

By changing the feed, Shell in corporation with Delaware invented a process for the production of high amounts of tertiary alkyl hydroperoxide from TBA and H_2O_2 in 1953. They tried various reagents' ratios (stoichiometric amounts, excess H_2O_2 or excess TBA). Higher was the amount of H_2O_2 , higher was the yield of the main product, ranging from 90 % to 95 %. They stated that employing an excess of H_2O_2 from 40 % to 90 % over the theoretical stoichiometric value enhanced the selectivity toward the desired product.

They employed different types of catalysts: heteropoly acids (HPA), Friedel Crafts halide, and inorganic acids. Heteropoly acids are inorganic complexes with a nuclear element like phosphor, silicon, boron, or arsenic surrounded by a coordinated group of metal oxides such as tungsten, molybdenum, vanadium, chromium, sulfur, selenium, and tellurium.

Cited catalysts include silicotungstic acid $\text{H}_4[\text{SiO}_4\text{W}_{12}\text{O}_{18}(\text{OH})_{36}]$, phosphotungstic acid $\text{H}_4[\text{PO}_4\text{W}_{12}\text{O}_{18}(\text{OH})_{36}]$, borotungstic acid $\text{H}_5[\text{BO}_4\text{W}_{12}\text{O}_{18}(\text{OH})_{36}]$. Friedel Crafts halides include boron halides, especially boron trifluoride and boron trichloride, and the halides of amphoteric polyvalent metals like aluminum trichloride, ferric chloride, antimony trichloride, stannic chloride, and antimony tetra chloride. Another group of catalysts included carboxylic or inorganic acids, as sulfuric or metaphosphoric acid, etc. Small amounts of heteropoly acidic catalysts were capable of producing hydroperoxides [15].

On another side, Research Corporation studied the production of alkyl hydroperoxide from mono-alkyl salt. This salt was obtained by either reacting the unsaturated hydrocarbon with the inorganic acid (eq. 2.2, 2.3) or the alcohol with the acid (eq. 2.4, 2.5) [20]. We note that R is an organic radical and Me represents a metal:



Examples stated in this patent showed that the yield of alkyl hydroperoxide did not exceed the 45 % at temperatures below 0 °C [20].

Via one step reaction, Frenkel et al. isolated the hydroperoxide or diperoxide from the mixture containing n-alkyl or t-alkyl ether, a RO_2H compound, and an acid catalyst [21]. Depending on R, whether it is hydrogen or tert-alkyl, they obtained tert-alkyl hydroperoxide or di-tert-alkyl peroxide.

Most recently, Willms et al. studied the oxidation of isobutane into TBHP in micro reactor at different reaction conditions [22]. They were the first to study the reaction as a Taylor-Flow process. They checked the influence of two initiators, TBHP and DTBP, on the selectivity of products. Other than the main product (TBHP), by-products as TBA, DTBP, acetone were formed. TBHP as initiator increased the selectivity toward the main product, while DTBP decomposition needed higher temperature and longer time. A high ratio of surface to volume in this case enhanced the heat transfer and safety minimizing runaway reactions.

In case of isobutane oxidation, separation of TBHP was possible via distillation column knowing that the boiling points of both TBHP and isobutane are widely different. But, TBHP and DTBP have close boiling points and can be separated only by azeotropic distillation. In presence of an alcohol, DTBP formed an azeotrope and TBHP kept intact and separated from the mixture [23]. Isopropyl alcohol in presence of water was an example that formed ternary azeotrope with DTBP [24]. Also, methanol worked in case of tert-amyl hydroperoxide (TAHP) and produced high purity product [25].

2.2.2 Detection and determination

Several detection methods for hydroperoxides are present. Some are simple as titration, other are more advanced as nuclear magnetic resonance spectroscopy (NMR).

Iodometric titration with starch as indicator detects hydroperoxides after oxidation with hydrogen peroxide. This latter should be destroyed by catalase after the first titration which gives the total peroxides concentration while the second titration will be specific to hydroperoxides. The difference of both will give the concentration of remaining hydrogen peroxide. To get more accurate results, the UV-visible spectrophotometry is used instead of the colour indicator. For example, after titration with iodide in presence of the catalyst, I_3^- is detected at 290 nm. Also, hydroperoxides oxidize the iron Fe(II) into Fe(III) characterized at 305 nm [26].

Infrared spectrophotometry is used for the characterization of the hydroperoxides produced with O_2 . NMR is also a characterization and quantification technique of hydroperoxides generated during the thermal or radiative decomposition of polymers [26].

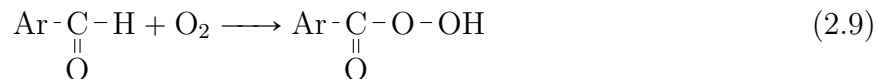
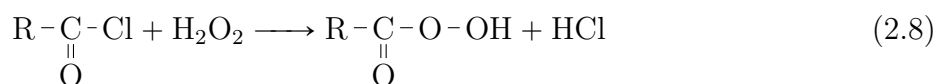
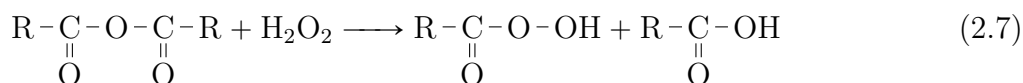
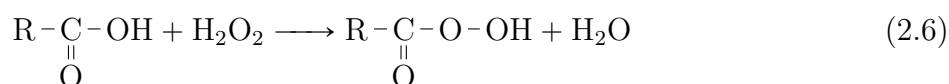
Finally, gas chromatography (GC) is applied as long as there is no thermal decomposition. So, GC with cold or low temperature on-column injection and slow heating rates is suitable for aliphatic hydroperoxides [26].

2.3 Peroxy Acids

Peroxy acids or peracids are known as strong oxidizers applied in disinfecting and chemical synthesis reactions. We distinguish organic and inorganic peracids. The inorganic ones are derived from conventional acids as the sulfuric and phosphoric acids. For instance, the peroxy phosphoric acid is electrophilic used in organic synthesis as oxidation of alkynes, alkenes, aromatic compounds and amines [1, 26].

2.3.1 Synthesis

Organic peracids are synthesized by one of the following methods: either by reacting their corresponding carboxylic acid or anhydride or acid chlorides with hydrogen peroxide (eq. 2.6, 2.7, 2.8) or by autoxidation of aromatic aldehydes with air or oxygen (eq. 2.9) [3]:



Shell Oil Company patented a process for the preparation of carboxylic peracids from the lower alkanolic acids and their substitution (chloro, fluoro and bromo) with hydrogen peroxide [27]. This invention presented advantageous modifications compared to previous work [28]. In summary, carboxylic acid reacted with hydrogen peroxide over an acid ion exchange resin in the presence of an appropriate solvent having a limited miscibility with water.

The amount of resin should be enough to play both roles: catalyst for oxidation of carboxylic acid and desiccating agent. Different cation-exchange resins having functional acidic groups as sulfonic, phosphonous, sulfuric or combination of such groups were appropriate for this process. The resin should be sufficiently cross-linked to resist peroxide attack but not so

high in order to adsorb water also. The amounts of resin depended on the water adsorption capacity; it varied between 10 % to 100 % by weight of acid fed. Moreover, a resin of 20 to about 50 mesh was the most suitable for a fixed bed in this process. The catalyst should be pretreated with a peroxygen-containing solution to minimize the hydrogen peroxide decomposition loss. Then, it should be washed with deionized water before drying to effectively adsorb water.

As previously mentioned, the solvent should be incompletely miscible in water to recover the carboxylic acid and peracid. It should have a solubility in water and for water below 10 %. Further, the solvent diluted the peracid below detonatable concentrations and should have lower boiling point than the peracid in order to be removed. Examples of appropriate solvents included hydrocarbons (toluene, benzene, ethers, etc.), halohydrocarbons (chloroform, dichloroethane, etc.), ethers (MTBE, etc.).

Unsubstituted aliphatic saturated acids were preferable starting acids. In general, the temperature varied between 10 °C to 60 °C. Stoichiometric proportions of reagents were the most advantageous but sometimes the proportions had one reactant in excess. In this case, the reaction should be done until completion; the reaction times varied between 0.5 h to 15 h.

An example of this process stated the use of 4 reactors with fixed bed, one for main reaction, second for elution of catalyst, third for regeneration of the resin and last for finishing reaction. Another configuration can only use one reactor, or suspended resin in the liquid with suitable agitation.

More specifically, peroxybenzoic acid is commercially synthesized by the reaction of benzoic acid and hydrogen peroxide over methanesulfonic acid [29, 30]. Also, another route known by Braun's procedure produced peroxybenzoic acid from benzoyl peroxide. At 0 °C, sodium methoxide reacted with benzoyl peroxide in chloroform to give the sodium perbenzoate. This product got acidified in sulfuric acid to liberate the peroxybenzoic acid. Another route introduced the sodium ethoxide instead of methoxide but it was not preferred since the perbenzoate will precipitate directly [31].

When coming to mechanism, the formation of peracids takes two different routes, where the carbonyl carbon of the acid is the electrophilic site and the hydrogen peroxide oxygens are the nucleophilic sites. In route A, the hydrogen peroxide attacks the carbonyl carbon to form a tetrahedral transitional state from which a water molecule is removed giving the peracid. On the other hand, route B is done in acidic media where the H^+ activates the carbonyl carbon. Then, hydrogen peroxide is added, water and H^+ are removed. Based on Rubio et al., route B is more feasible due to the fact that the intermediary formed has higher

energy that the reagents [32].

The formation of peracid is reversible, where the forward reaction is promoted by increasing the carboxylic acid or hydrogen peroxide molar ratio relative amount. Also, the reaction can occur without any catalyst and be auto-catalyzed by the acidity of the feed [33].

2.3.2 Analytical Methods

Redox, acid/base titration, spectrophotometry and chromatography (GC and HPLC) are all suitable methods for the analysis of peracids. The application of one versus the other is function of the type of peracid (long/short chain, aliphatic/aromatic, etc). They present both strengths and weaknesses.

Due to its power, peracid oxidizes the iodine I^- into I_2 , which is then titrated by thiosulphate. But, before this step, the hydrogen peroxide should be removed, either by scavenging it with potassium permanganate or excess chlorine, either by complexing it with potassium titanyl sulfate. Knowing that hydrogen peroxide reacts slowly with iodide, the peracids will first react alone without any catalyst. Then by the addition of a molybdenum catalyst, the hydrogen peroxide will react to be titrated. Due to the difference of the spectra in the UV region for acids and their peracids, we can apply spectrophotometric methods for their detection [34].

Acid-base titration is only feasible for peracids that are weaker than their parent acids. We cite peracetic acid, performic acid, perpropionic acid. [35].

Nowadays, chromatography is more convenient. Because aliphatic peracids do not absorb in the UV-Vis area, pre-column derivatization should be applied in case of UV-HPLC. On the other hand, mass spectrometry (MS) detector is suitable as long as the fragmentation patterns are known. Finally, GC separates well aliphatic peracids and flame ionization detect them [34, 35].

2.4 Catalysis

Homogeneous catalysts showed a good activity while applied to many reactions as oxidation, esterification, acylation etc. But aqueous acids possess many drawbacks as the corrosion, toxicity, environmental problems, difficult separation from the mixture, neutralization, and high-cost regeneration. All of these led to a shift toward sustainable green chemistry catalysis. Liquid heterogeneous catalytic processes circumvent some of these limitations. Heterogeneous catalysts are easily separable from the mixture, highly selective and active. Superacids are

one of a kind in their activity defined as stronger acids than 100 % sulfuric acid. Solid superacids include zeolites, polymeric resin sulfonic acids, perfluorinated polymer resin acids, acid metal oxides, and graphite-intercalated acids [36].

Zeolites are crystalline aluminosilicates, showing good activity by their alkali cations. These cations present in matrix's cavities are mobile and exchanged in chemical reactions. Zeolites have shown rapid growth in chemical processes after rendering the involved reactions milder and more selective. Acid-catalyzed and redox reactions involve zeolites the most as catalysts [37]. Because of their sorption to smaller organic molecules and their non-degradation in presence of hydroxyl radicals, zeolites are interesting adsorbents in water treatment processes and catalysts for wet peroxide oxidation of organic contaminants [38]. Also, they catalyze the carboxylic acid perhydrolysis and Baeyer Villiger reactions involving peracids as oxidants [39,40].

Ion exchange resins are gaining interest as catalysts for organic synthesis. The chlorination, fluorination, and nitration of benzene rings improve the stability and acidity of these sulfonated resins [41]. Dowex, Amberlite, Amberlyst constitute the biggest family of sulfonic acid resins. Active sulfonic acids mounted on the macro-reticular styrene divinylbenzene matrix make the acidity of Amberlyst-15 catalyst comparable to sulfuric acid [36]. Dowex acidity is moderate, comparable to the one of chloric acid [36]. Aside being applied in esterification, transesterification, halogenation, Friedel-Craft alkylation, acylation, and nucleophilic substitution reactions, they are effective for peroxy carboxylic acid synthesis [42]. Leveneur et al. showed that gel resin with 8 % cross-linking degree are resistant toward deactivation in peroxy propionic acid synthesis reaction [43].

Similarly, the poly-tetrafluoroethylene backbone with perfluorovinyl ether sulfonate end groups make Nafion a very strong acid with $pK_a \approx -6$ [44]. It was first developed by DuPont in the 1970's. Its low price, high proton conductivity, good chemical and mechanical stability make it efficient in fuel cells, energy storage devices and dryer membranes [45,46]. On the contrary, its high swelling capacity and water sorption limited its applications in certain areas [47].

The short side chain resins have a certain crystallinity compared to the amorphous Nafion. This has some drawbacks including small surface area and prohibited accessibility of active sites leading to low number of reacting molecules per unit weight of amorphous Nafion [36]. For this, Harmer and al. increased the surface area by developing Nafion silica nano-composite solid acid catalyst by sol-gel method [48]. Nano-composites have four times larger surface area than the one of Nafion polymer matrix. Modified Nafion membranes meet the

requirements (high proton conductivity, stability) for their employment in various applications as the direct alcohol fuel cells [49].

On the other hand, graphite consists of carbon sheets highly anisotropic. Highly oriented pyrolytic graphite is synthetically attractive due to its high crystallinity. Lewis superacids intercalated in graphite have showed mild catalysts compared to pure Lewis acids. But an inconvenience occurred when the Lewis acid leached out during organic reactions. Better activity was shown when intercalating Lewis acid to fluorinated graphite [36]. Besides being supports for acids intercalation, graphite nano-filters and carbon nanotubes are stable, active and selective when employed as direct heterogeneous catalysts for organic reactions [50].

Activated carbon is also a good heterogeneous catalyst and catalytic support for various reactions. Due to its stability in both acidic and basic media, it is applied for oxidation, reduction, acid catalyzed, basic catalyzed reactions, and C-C bond formation reactions as polymerization of cycloalkenes and dehydrogenation of alcohols [51].

Driven by environmental constraints, heteropoly acids (HPA) have found more attention in the last decades. They are recyclable, insoluble in apolar solvents, and highly stable toward air and humidity. HPA showed higher selectivity and yields with low reaction times than conventional H_2SO_4 , HCl and Lewis acid catalysts [52]. Four types of HPA exist where the Keggin type (of formula $\text{H}_x\text{A}_y\text{PW}_{12}\text{O}_{40}$) is frequently applied in oxidation reactions [53].

Finally, metal oxides are limited in their applications as catalysts due to their low acid density and low surface area. This is due to the high calcination temperature which reduces the number of acidic active sites. But some overcame the poor porosity of based oxide-acid catalysts by synthesizing a layered transition metal oxide solid acid. This nanostructure enhanced the mass transfer of certain molecules between the layers [54, 55].

Properties of heterogeneous catalysts were always a center of interest of scientists. Surface area, pore size, active site density and ease of accessibility are the main factors affecting the activity and stability of such systems. Many scientists tried to improve the activity of such catalysts by modifying different properties. For example, Magnotta and co improved acidity of Dowex by treating it with the Lewis acid halide AlCl_3 [56].

Finally, water is a contaminant to most of catalysts. It adsorbs on the catalyst's active sites or hydrolyzes the matrix leading to deactivation and lower activity. Many attempts were done to increase the hydrophobicity and control the wettability of solid acid catalysts

especially porous polymers.

Liu et al. improved the hydrophobicity of polydivinyl benzene PDVB-SO₃H by copolymerizing the divinylbenzene in sodium p-styrenesulfonate under solvothermal conditions. Moreover, they grafted strong-electron withdrawing groups on PVDB-SO₃Hs. This increased the exposure of acid sites to reagents and decreased the contact angle showing good wettability [57]. Zhang et al. improved the hydrophobicity and acidity of solid acids in nanoscale morphology. They synthesized polystyrene sulfonic acid catalysts with core-shell structure via macromolecular self-assembly within a confined nano-space. By this the sulfonic groups are closer to each other enhancing the H-bond interactions between acid sites [58].

CHAPTER 3 EXPERIMENTAL METHODOLOGY

3.1 Chemicals

We employed tertbutanol ($(\text{CH}_3)_3\text{COH}$, puriss p.a, ACS reagent, ≥ 99.7 wt%), hydrogen peroxide (H_2O_2 , 50 wt.% in H_2O), 2-propanol ($(\text{CH}_3)_2\text{CHOH}$, laboratory reagent, ≥ 99.5 vol%), ethanol (ACS spectrophotometric grade, 95 vol%), benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, ACS reagent, ≥ 99.5 %), Amberlyst-15 hydrogen form, and Nafion NR50 for the reactions. For the in-house synthesized catalysts, the precursors include tungstophosphoric acid (reagent grade), cesium carbonate (99 %), silica gel and activated carbon. All the reagents were purchased from Sigma Aldrich. We used them without further purification.

3.2 Catalysts

To test the hypothesis of Bronsted acid sites, we chose Amberlyst-15, Nafion, activated carbon, heteropoly acid salts impregnated over carbon and silica matrices (Table 3.1) as catalysts for the hydroperoxide synthesis.

Table 3.1 Catalysts' characteristics.

Name	Particle Size	Composition
Amberlyst-15	$d_p < 300 \mu\text{m}$	Sulfonic acid on styrene-divinylbenzene matrix
Nafion	Pellets	Sulfonic acid on tetrafluoroethylene matrix
HPA/Carbon	$63 \mu\text{m} < d_p < 106 \mu\text{m}$	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{C}$
HPA/Silica	$63 \mu\text{m} < d_p < 106 \mu\text{m}$	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$
HPA/Amberlyst-15	$d_p < 300 \mu\text{m}$	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Amberlyst-15}$
Activated carbon	$d_p < 300 \mu\text{m}$	Charcoal derived

3.2.1 Catalysts synthesis

We applied the incipient wetness impregnation technique for supporting the cesium salt of tungstophosphoric acid ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) on silica gel, carbon and Amberlyst-15. In the first step of the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ synthesis, we impregnated the tungstophosphoric acid on silica powder, dried it at 110°C for 4 h and calcined it at 300°C for 6 h. Then, in the same way, we impregnated the cesium carbonate on the $\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$, dried it at 110°C , and calcined it at 300°C [59].

For the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{C}$ catalyst, we followed the method reported by Yang et al [60]. First, we impregnated the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ salt for 6 h. Then, the black solid was washed in distilled water and dried at 105°C for 24 h.

We applied the same impregnation method for the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Amberlyst-15}$ catalyst without prior treatment of Amberlyst-15 [61].

3.2.2 Amberlyst-15 characterization

We measured the acidity of Amberlyst-15 by determining the concentration of its Bronsted acid. We titrated 0.05 g Amberlyst-15 suspended and stirred in 5 mL of distilled water and 0.5 mL of NaOH (0.1 M) with HCl (0.1 M) in presence of phenolphthalein as indicator. We stopped the titration when the solution changes from red rose to colourless [62].

We also performed the absorption test on Amberlyst-15, where we left 1 g in 10 g distillate water overnight. After this, we filter and weighed the water remaining to calculate the amount absorbed by the resin.

3.3 Analytics

3.3.1 Hydroperoxide

Gas chromatography (GC) separates volatile and semi-volatile compounds due to their retention on a stationary phase while being carried by a gaseous mobile phase. Two types of separation exist; either by boiling point in case of non-polar stationary phase or by varying structures in case of polar column [63].

Nowadays, capillary columns are most applied versus packed ones. In the former column, the stationary phase only coats the interior wall while in the latter case, the stationary phase fills all the volume.

Different types of detectors couple the GC including flame ionization detector (FID), thermal conductivity detector (TCD), mass spectrometry (MS), electron capture detector (ECD), photoionization detector (PID) and flame photometric detector (FPD). In case of FID, it ionizes eluted samples with a hydrogen-oxygen flame and then measures the ionization current.

In the scope of the reaction, gas chromatography is widely applied for peroxide analysis with close control on thermal conditions. Low injection temperature and slow heating rates

are suitable parameters for hydroperoxides [26, 63]. The final solution consisting of remains of tert-butanol and hydrogen peroxide, TBHP and other by-products, was analyzed by GC-FID CP-3800 over the Agilent ultra-stable, ultra-inert DB-1ms column. Table 3.2 shows the characteristics of the column.

Table 3.2 DB-1ms column’s specs.

Parameter	Specification
Capillary tubing	Fused Silica
Stationary phase	Dimethylpolysiloxane
Interior diameter (mm)	0.25
Film thickness (μm)	0.25
Length (m)	15

The auto-sampler injected 10 μL in a split mode where the sample was heated up to 77 °C (Table 3.3). The oven temperature should be higher than the molecules’s boiling point to vaporize the compounds. Knowing that the boiling temperatures of TBA , TBHP, and DTBP are 82 °C, 89 °C, and 111 °C respectively [64–66], the temperature in the oven ramped up to 200 °C during 16 minutes (Table 3.4).

Table 3.3 Injector operating parameters.

Parameter	Specification
$V_{\text{injection}}$ (μL)	10
R_{split}	1:100
$T_{\text{injection}}$ (°C)	77

Table 3.4 GC-FID ramp conditions.

	Step 1	Step 2	Step 3
Rate ($^{\circ}\text{C min}^{-1}$)	n/o	20	20
T_{oven} (°C)	35	100	200
t_{hold} (min)	3	1	4

Helium passed through the column at a rate of 1.3 mL min^{-1} . The detector’s temperature should be higher than the one in the column to minimize condensation. We set the FID at 250 °C.

We have used GC-MS in later steps because of technical problems in GC-FID. We applied the same method with some modifications to the Agilent GC (7880A) equipped with ultra inert DB Wax column and connected to mass spectrometer (5975C VL MSD) (Tables 3.5, 3.6).

Table 3.5 DB Wax column's specs.

Parameter	Specification
GC tubing	Fused Silica
Stationary phase	Polyethylene glycol
Interior diameter (mm)	0.25
Length (m)	30

Table 3.6 MS parameters.

Parameter	Value
Mass source temperature	230 °C
Quad temperature	150 °C
Transfer line temperature	250 °C
Full scheme range	29 to 500

Helium passed through the column at 0.7 mL min^{-1} . The auto-sampler injected $0.2 \mu\text{L}$ in split mode (Split ratio 50:1) where the sample heated up to 77°C . The temperature in the oven ramped up to 200°C during 27 minutes (Table 3.7).

Table 3.7 GC-MS ramp conditions.

	Step 1	Step 2	Step 3
Rate ($^\circ\text{C min}^{-1}$)	n/o	5	20
T_{oven} ($^\circ\text{C}$)	40	110	200
t_{hold} (min)	4	0	5

In order to quantify the reaction products, we calibrated the GC-MS with external standards (TBA, TBHP, DTBP) in ethanol. Before injection, we further diluted the samples with ethanol. We calculated the concentrations of the products as Eq. 3.1:

$$C = F_{\text{calibration}} \cdot A_{\text{exp}} \cdot n_{\text{dilution}} \quad (3.1)$$

3.3.2 Peracid

High performance liquid chromatography (HPLC) separates and quantifies compounds in a mixture. It relies on the interaction with the column stationary phase that retains and the mobile phase that elutes the species. There are different types of interactions: ionic bonding, hydrogen bonding, ion-dipole, dipole-dipole, hydrophobic interactions, etc. Reverse phase HPLC uses a polar mobile phase and a non-polar stationary phase. The suitable columns for this case retain non-polar or slightly polar analyte. For example, butyl, octyl, and octadecyl functional groups are the ones associated to the reverse phase chromatographic mode [67].

A polar mobile phase is a mixture of organic and inorganic solvents. Generally, acetonitrile or methanol is the organic solvent, while water is the inorganic one. The choice of organic solvent affects the compound's selectivity and its percentage alters the retention factor.

In the analysis of carboxylic acids by HPLC, it is important that ion-suppression agents must be used to keep the acid protonated as it elutes through the column. If ion-suppression is not used the acid peak can become very broad.

The stability of the silica-based stationary phase forces that the pH of the mobile phase should be maximum 7.5. The addition of strong acids (phosphoric or trifluoroacetic acid) maintains low pH during the analysis and suppresses the ionization of the acidic groups of the compounds. In addition, it avoids the ionizable silanol groups remaining on the underlying silica surface [68].

The liquid mixture, consisting of benzoic acid, H_2O_2 and peroxybenzoic acid, was analyzed by HPLC in isocratic mode. The mobile phase consisting of 50 vol%-50 vol% acidified water-methanol passed at 1 mL min^{-1} . I added 6 g of phosphoric acid (85 % H_3PO_4) to the 1 L of Milli-Q water for ion suppression. The auto-sampler injected $10 \mu\text{L}$ each time. Microsorb MV 100-5 C18 column from Varian with the following specs was employed (Table 3.8).

Table 3.8 HPLC column's specs.

Parameter	Specification
Adsorbent material	Octadecyl-Silica
Length (mm)	250
Diameter (mm)	4.6
Stationary phase particles (μm)	5
Pore size (nm)	10

Rings absorb very well with UV. So a UV detector with 254 nm was suitable for the case of benzoic and peroxybenzoic acid.

3.4 Setup

3.4.1 Hydroperoxide

Hydrogen peroxide reacted with tert-butanol in a plug flow reactor to form TBHP as the primary product and DTBP, acetone, and peroxy-ketals as by-products. Before initiating the reaction, H_2O_2 solution was diluted to 30 wt% with distilled water. Then melted TBA (at 50°C) was mixed with the solution of hydrogen peroxide in an equimolar ratio. A J-Kem dual syringe pump fed the reagents to the bottom of the plug flow reactor loaded with 0.3 g of catalyst. Reagents passed through the reactor immersed in hot water from bottom to top where the reaction took place on the catalyst surface. The reaction products accumulated in the condenser filled with the solvent (isopropanol) and cooled down in an ice quench (Figures 3.1, 3.2).



Figure 3.1 Lab-scale setup. 1: TBA+ H_2O_2 solution, 2: Pump, 3: thermometer, 4: water bath, 5: heating plate, 6: ice quench.

The 3.5 ml reactor was made of stainless steel for fast heating and met safety and material

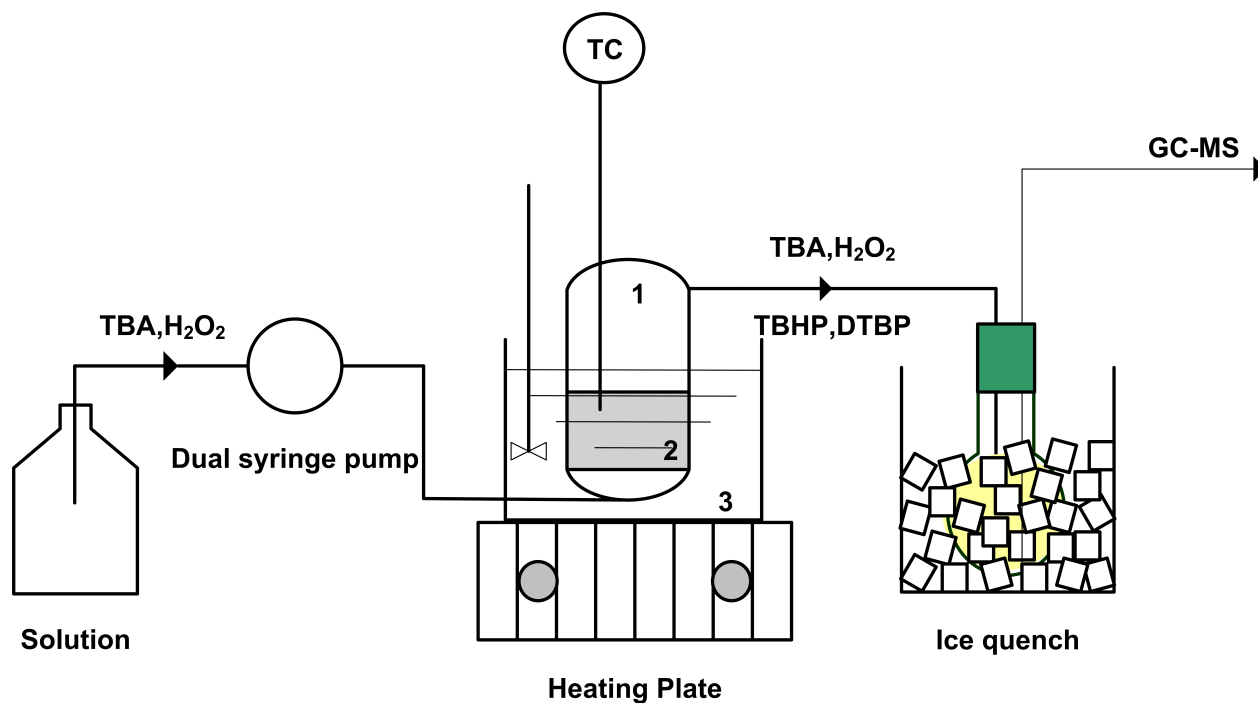


Figure 3.2 Scheme of lab-scale process; 1: plug flow reactor filled with 2: Amberlyst -15 is immersed in 3: magnetically stirred, heated water bath.

compatibility requirements (Figure 3.3).

3.4.2 Peracid

We tested two configurations for the synthesis of peroxybenzoic acid. The first one is the same as employed for hydroperoxides. A solution of benzoic acid and hydrogen peroxide passed at 1 mL/min through the plug flow reactor filled with 0.3 g of Amberlyst-15. The reactor was immersed in a water bath maintained at 50 °C. The outlet of the reactor was quenched and cooled down with ice bath to avoid thermal decomposition.

The second configuration consisted of just mixing the reagents together over Amberlyst-15 at room temperature. First, I dried 15 grams of the catalyst at 70 °C for two hours. Then, in 500 mL round flask, I added 1 mol of benzoic acid over Amberlyst-15. I dropped the hydrogen peroxide over the mixture during 20 mins. The mixture was left stirring over the weekend.



Figure 3.3 Reactor configuration: 3.5 mL plug flow reactor.

3.5 Design of experiment

To identify optimum reaction conditions, experiments were conducted at three temperatures (40, 55, 70 °C) and two flow rates (1, 2 mL min⁻¹). And finally Amberlyst-15, Nafion, Cs_{2.5}H_{0.5}PW₁₂O₄₀/SiO₂, Cs_{2.5}H_{0.5}PW₁₂O₄₀/C, Cs_{2.5}H_{0.5}PW₁₂O₄₀/Amberlyst-15, and activated carbon were examined at the optimum temperature and flow rate chosen.

3.6 Apparent kinetic measurements

To derive the apparent kinetic parameters of the reaction, we designed a set of experiments in a batch reactor in the temperature range 30 °C to 70 °C. For this, we mixed TBA and hydrogen peroxide in a 500 mL round flask containing 4 g of Amberlyst-15. In each run, the magnet stirrer homogenized the solution at the set temperature. To derive the reaction rate, sampling was conducted at 0 min, 15 min, 30 min, 45 min, and 60 min.

The kinetic model was based solely on the analysis of TBA. We carried out two sets of experiments with excess H_2O_2 at a molar ratio of H_2O_2 to TBA: 1.1 and 2. We derived the reaction rate constant k and activation energy E_a based on minimizing the sum of the square error applying a Levenberg-Marquardt algorithm:

$$k = k_0 \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (3.2)$$

By giving an initial guess of k_0 and E_a , the algorithm varies the values, calculate the square error on the concentration of TBA, and does several iterations to finally give the best values of k_0 and E_a that corresponds to the minimum sum of square error.

3.7 Safety measures

In the scope of the process hazard report (PHR), we have defined all the hazards that may occur when doing this reaction. Briefly, they occur in case of shock, friction or heat sensitivity. In order to minimize it, we had always cleaned any spills, stored peroxides at low temperatures far from incompatible materials and heat sources, and kept lids on containers when not in use. In case of impending runaways as reactor blocking, we had to directly turn off the pump and the heating plate and moved the reactor to the ice bath.

When handling the diluted solutions of peroxides, we wore the regular personal protective equipment (PPE) as the coat, gloves, safety glasses and face shield. All manipulations had been done under the hood.

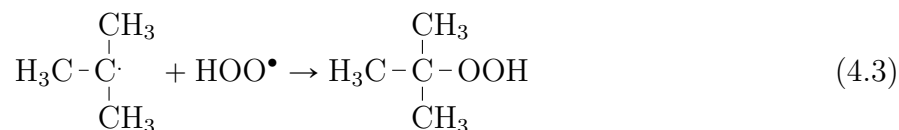
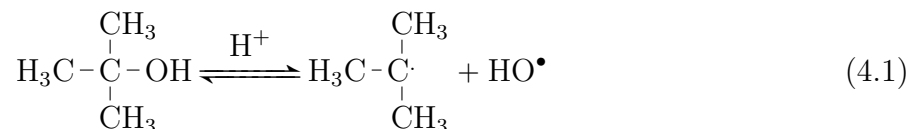
For the waste, we have disposed the solid used catalyst in a labeled plastic jar and the liquid waste in a sealed, labeled bottle in the flammable storage cabinet.

CHAPTER 4 RESULTS AND DISCUSSION

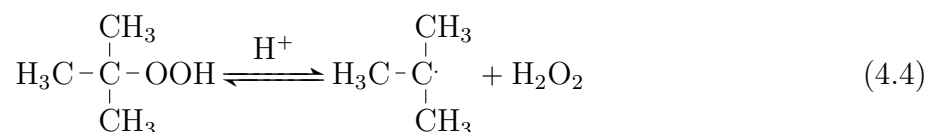
4.1 Mechanism

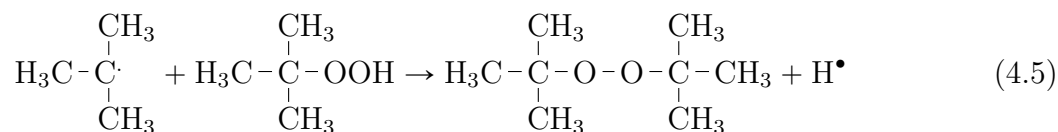
Any surface reaction, in case of heterogeneous catalysts, occurs via one or combination of the following three mechanisms. In case of Langmuir-Hinshelwood mechanism, both molecules A and B adsorb on the surface of the catalyst, collide and form a new molecule A-B which will desorb later. Another case is based on Rideal-Eley mechanism when only A adsorbs on the surface and B, without being adsorbed, meets A on the surface to form A-B. Finally the precursor mechanism occurs if A adsorbs on the surface and B collides with the surface to give a mobile precursor state that will facilitate the formation of the new A-B molecule [69].

In the case of this study, the main reaction between TBA and H_2O_2 occurs via the Rideal-Eley mechanism. TBA adsorbs on the catalyst surface where it forms with the Bronsted acid site a strong leaving group and give the tert-butyl radical. On the other hand, H_2O_2 in water is more likely to dissociate by the O-H bond than by the O-O bond with a low energy barrier of $34.52 \text{ kJ mol}^{-1}$ [70]. Both hydroperoxyl and tert-butyl radicals then collide and form the TBHP (Eq. 4.1 - 4.3).

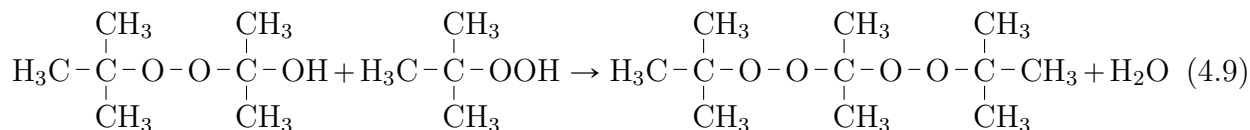
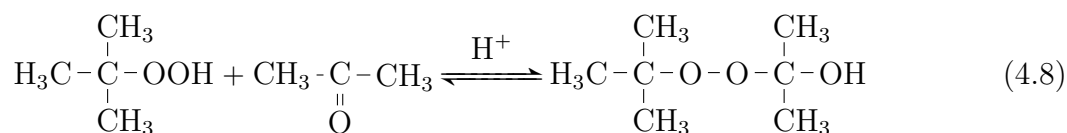
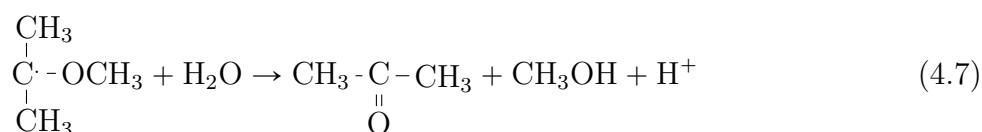
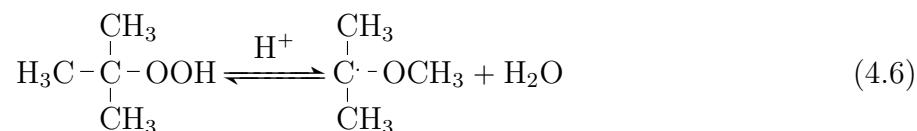


For the other by-products, TBHP in presence of H^+ dissociates in two different mechanisms to give either DTBP or acetone. In fact, H^+ can react with the first oxygen of the hydroperoxide functional group and create the H_2O_2 leaving group. This forms the tertbutyl radical which reacts again with TBHP to give DTBP [9]:





Also, H^+ can attack the second oxygen and creates a reactive intermediate inducing the 1,2 rearrangement to give acetone (Eq 4.6, 4.7). But acetone also reacts with two equivalents of TBHP to form the 2,2-bis(tertbutylperoxy) propane or the peroxyketal (Eq 4.8, 4.9) [9,71].



4.2 Chromatogram

The chromatogram (Figure 4.1) demonstrated the narrow symmetric peaks of DTBP (2.6 min), TBA (4.0 min), TBHP (15.5 min) and an undefined product eluted at 5.5 min from GC-MS. For GC-FID chromatogram (Figure 4.2), the shift in retention time of all the compounds is due to the following factors. The difference in columns' stationary phases, lengths, and the carrier gas flow rates shorten the retention time in case of GC-FID. DB-1ms column is 15 m shorter than the DB wax column. Also, the helium flow rate is 1.3 mL min^{-1} , higher than the one for GC-MS, meaning that the analytes are being swept faster from the column and their retention time decreases. Coming back to the mechanism, we presume that the undefined product in GC-MS chromatogram is the peroxyketal as acetone elutes between 0 min to 2 min in the case of DB Wax column not at 5.5 min.

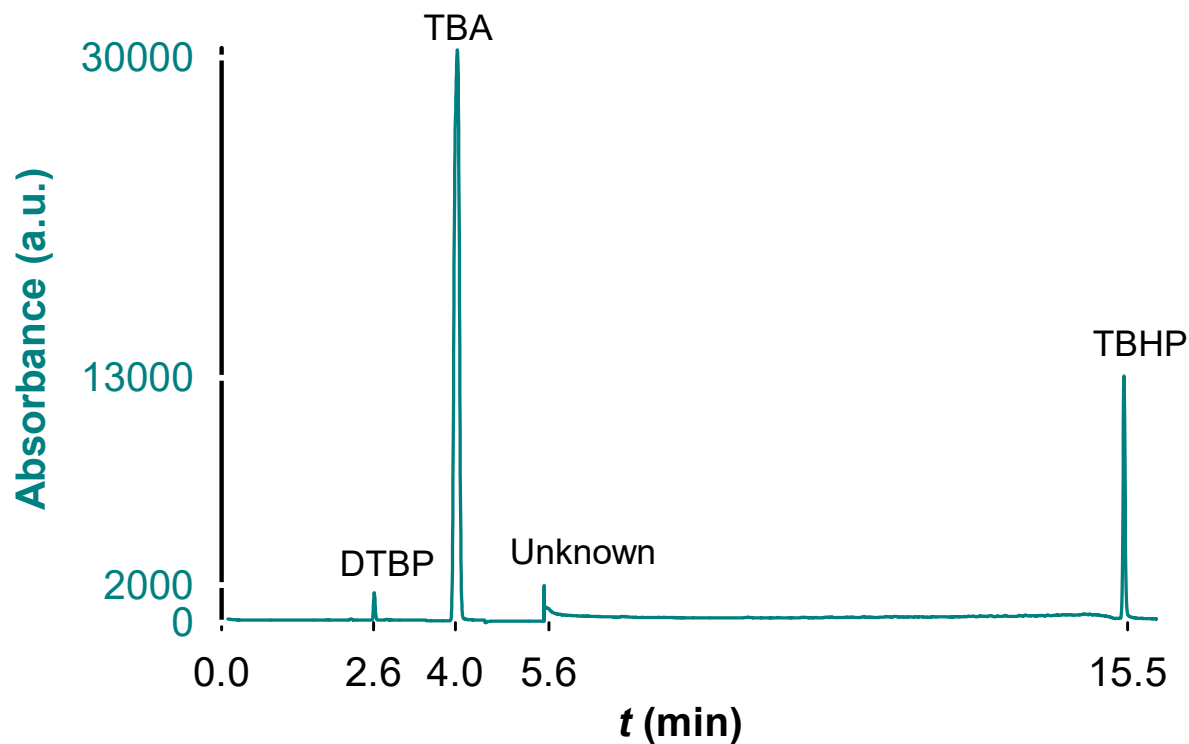


Figure 4.1 GC-MS chromatogram for the sample at 1 h and 50 °C with a molar ratio H_2O_2 :TBA of 2.

4.3 Mass balance

Table 4.1 summarizes the conversion of TBA and the selectivity of both products TBHP and DTBP at different operating conditions. The expressions for the conversion and selectivity are:

$$X_{\text{TBA}} = \left(1 - \frac{n_{\text{TBA out}}}{n_{\text{TBA in}}}\right) \cdot 100 \quad (4.10)$$

$$S_i = \frac{n_i}{n_{\text{TBA in}} - n_{\text{TBA out}}} \cdot 100 \quad (4.11)$$

4.4 Temperature and flow rate effect

We studied the TBHP synthesis over a range of 40 °C to 70 °C. The upper temperature was constrained by the decomposition temperature of TBHP that ranges from 77 °C to 110 °C based on the material [72]. The yield of TBHP at 1 h increased from 0.5 % to 3 % and 16 %

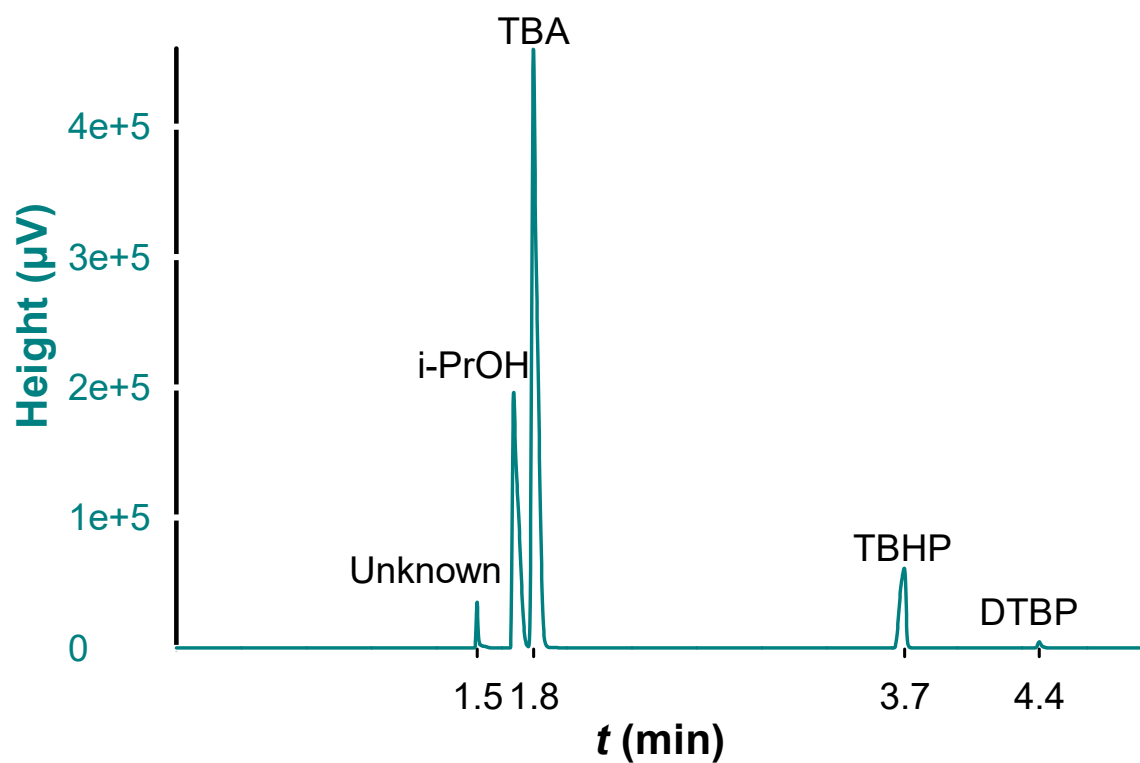


Figure 4.2 GC-FID chromatogram for the sample at 1 h and 70 °C with a flow rate of 1 mL min⁻¹. The solvent isopropanol elutes at 1.73 min

Table 4.1 Experimental results.

Catalyst	T , °C	Q , mL min ⁻¹	X , %	S_{TBHP} , %	S_{DTBP} , %
Amberlyst-15	40	1	9.6	4.6	0.2
Amberlyst-15	55	1	25.3	11.7	0.2
Amberlyst-15	70	1	51.5	30.3	6.4
Amberlyst-15	55	2	9.3	6.6	0.1
Amberlyst-15	70	2	24.2	22.3	0.4
Nafion	70	1	21.9	1.6	0.1
HPA/C	70	1	7.7	9.1	0.3
HPA/SiO ₂	70	1	11.5	1.6	0.1
HPA/Amberlyst-15	70	1	11.1	43.8	0.7
Activated carbon	70	1	28.3	1.1	0.1

when the temperature increased from 40 °C to 55 °C and 70 °C respectively at 1 mL min⁻¹. As expected for a first order reaction, the TBHP yield at a flow of 1 mL min⁻¹ was higher than

at 2 mL min^{-1} . We selected then 70°C and 1 mL min^{-1} as the optimum working conditions for TBHP synthesis (Figure 4.3).

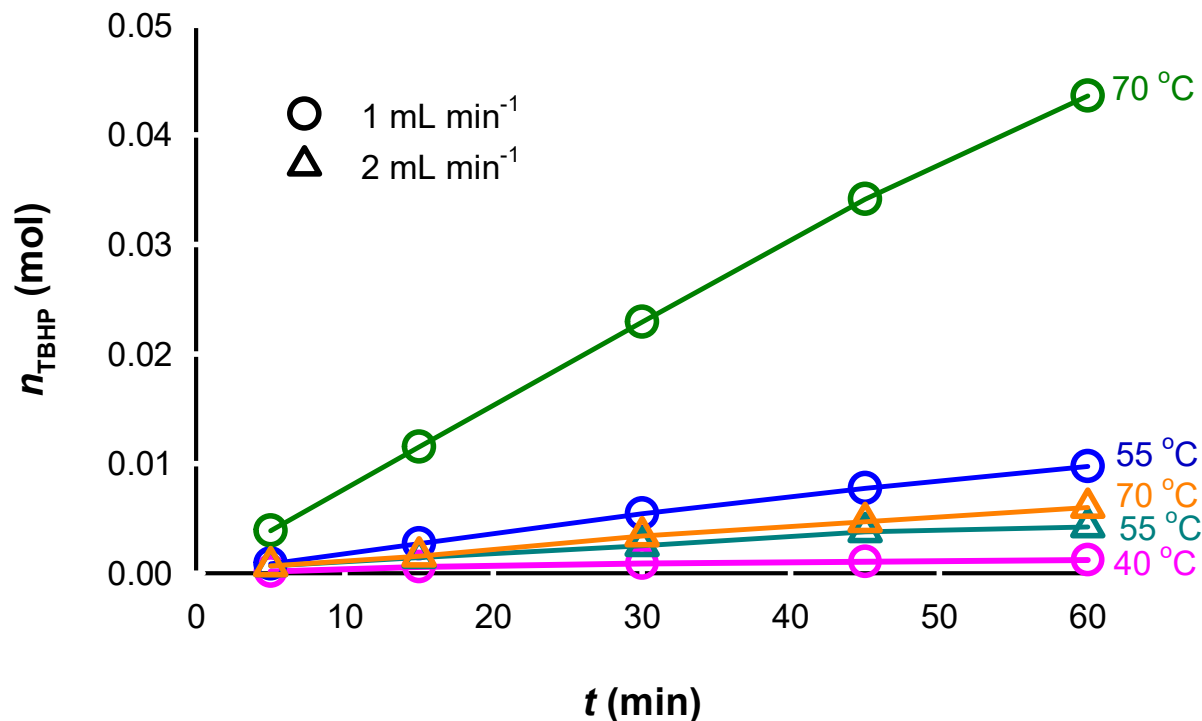


Figure 4.3 Moles of TBHP formed function of time at different temperatures and flow rates.

4.5 Catalyst type effect

From the volumetric titration reported above (section 3.2.2), we obtained the equivalence at V_{eq} of 2.4 mL and calculated the Amberlyst-15 acidic concentration to 4.8 mmol g^{-1} as follows:

$$C_{\text{Bronsted acid}} = \frac{C_{\text{HCl}} \cdot V_{\text{eq}}}{m_{\text{cat}}} \quad (4.12)$$

The value agrees approximately with the one reported in the literature (4.3 mmol L^{-1}) [73,74]. This high acidic concentration in addition to the macro-porous matrix and hydrophilic sites explain the activity of Amberlyst-15. Amberlyst-15 is hydrophobic due to the styrene-based structure but the SO_3H functional group makes it hydrophilic with affinity to polar molecules [73]. TBA, due to the polar hydroxyl group, adsorbs to the catalytic sites. But, Amberlyst-15 is also hygroscopic and adsorbs water [75]. This hinders the adsorption of TBA, by

diluting the sulfonic groups, thereby limiting the conversion to 52 % and the TBHP yield to 16 % at 70 °C (Figure 4.4).

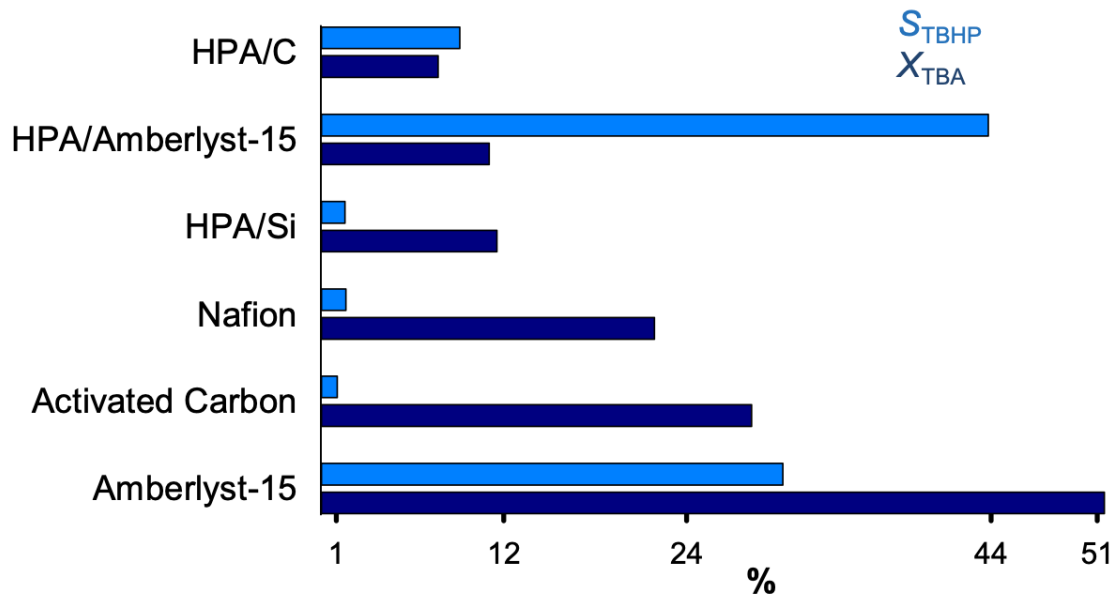


Figure 4.4 Distribution of the TBA conversion and TBHP selectivity for the different tested catalysts at 1 h.

The Nafion catalyst exhibited only 22 % TBA conversion due to the preferential alcohol adsorption compared to water. However, once adsorbed, TBA produces the $HO^\bullet$ radical that degrades Nafion. $HO^\bullet$ decomposes the support by removing a hydrogen from the carboxylic acid end group or from the hydrofluorocarbon. This will dissociate and shorten the backbone releasing HF molecules [45].

The cesium salts of HPA are hydrophobic and adsorb water readily which deactivates the catalyst [52]. In our case, the reagent solution had a H_2O mass fraction of 43 %. Consequently, TBHP yield in case of $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ was only 0.2 % (Figure 4.4).

Carbon was chosen also as support for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ acid because it entraps HPA in water [51]. Even though, HPA is considered a super acid and is active in several organic reactions because of the high active Bronsted sites, but the synthesized $Cs_{2.5}H_{0.5}PW_{12}O_{40}/C$ was inactive for this chemistry (TBA conversion and TBHP selectivity of 8 % and 9 % respectively (Figure 4.4)) . We attribute this to the alkaline nature of the catalytic support and the uneven distribution of the HPA over the support surface due to high HPA concentrations [76] (Figure 4.5).

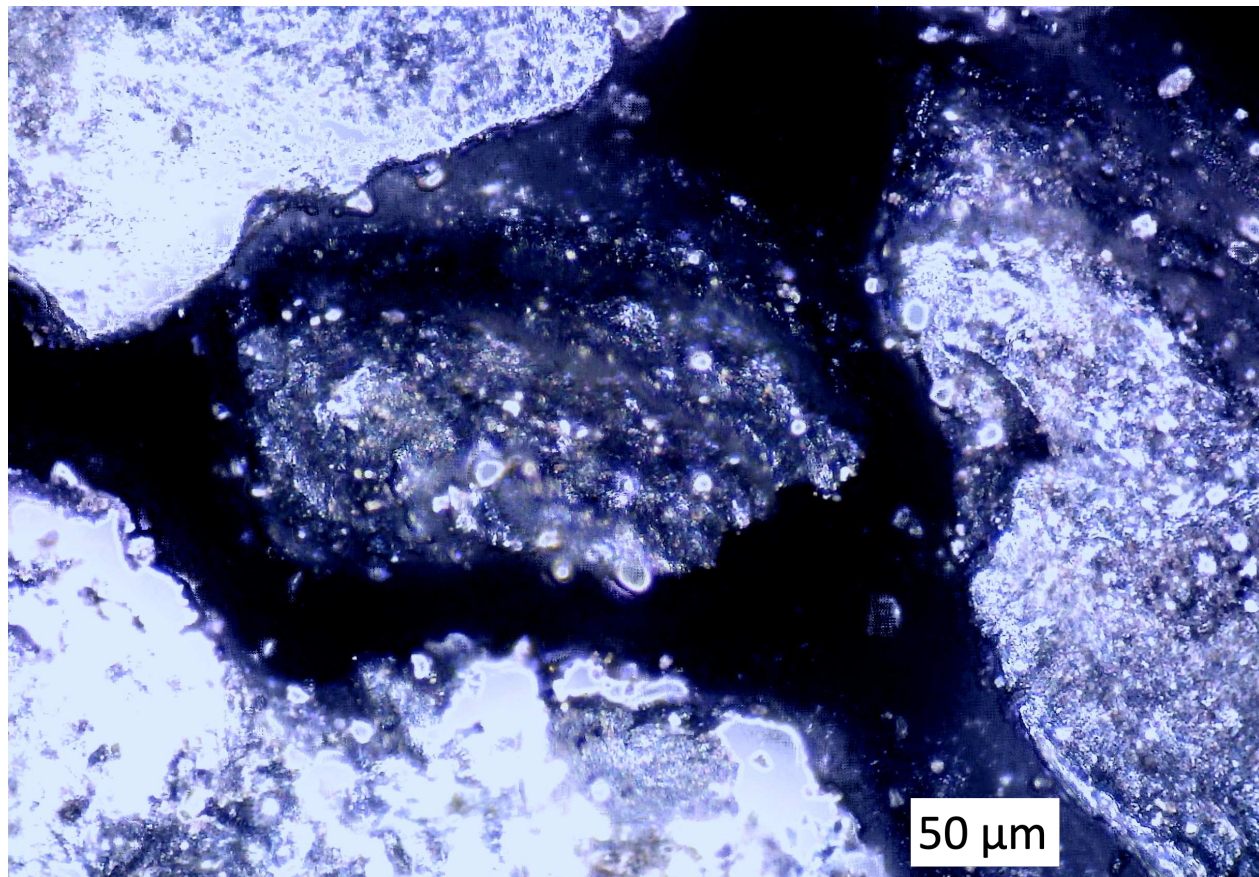
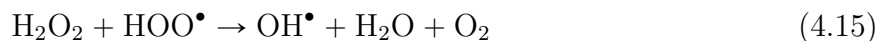
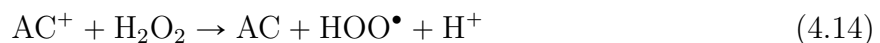


Figure 4.5 Microscope picture of the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{C}$ catalyst. The glossy points represent the heteropoly acid salt while the black particles are the carbon support.

Powder activated carbon is more active than granule particles as the high surface availability is capable of adsorbing more H_2O_2 and creating $\text{HOO}^\bullet$ [69, 77]. But, the non-dissociated H_2O_2 reacts again with the $\text{HOO}^\bullet$ radical and degrades to water and oxygen [78]:



However, because of the limitations in the fixed bed reactor, our design was constrained to the larger granules. The low selectivity/activity was due in a part to the larger particles bed also to the degradation of H_2O_2 to H_2O and O_2 (Eq. 4.15). TBA did adsorb to the activated carbon but the concentration of the $\text{HOO}^\bullet$ radicals was insufficient to form TBHP.

Finally, the combination of both HPA and Amberlyst-15 was predicted to have higher activ-

ity than Amberlyst-15 due to the double interaction and strength of Bronsted acidic sites. Unfortunately, this was not the case and the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /Amberlyst-15 yielded 6 % of TBHP (Figure 4.4). Since we did not wash away the sulfonated groups before impregnation of HPA, the HPA and sulfonic groups were both present on the support and competed on the TBA adsorption, instead of just having the stronger HPA.

4.6 Kinetics

We can express the reaction of TBHP as the function of the concentrations of TBA and H_2O_2 raised to the power α and β respectively:

$$\frac{d[\text{TBHP}]}{dt} = -\frac{d[\text{TBA}]}{dt} = k' \cdot [\text{TBA}]^\alpha \cdot [\text{H}_2\text{O}_2]^\beta \quad (4.16)$$

where k' is the rate constant. Since H_2O_2 was in excess, its concentration remained approximately constant and gave a new effective equation rate constant $k = k' \cdot [\text{H}_2\text{O}_2]^\beta$ and a new equation:

$$\frac{d[\text{TBHP}]}{dt} = -\frac{d[\text{TBA}]}{dt} = k \cdot [\text{TBA}]^\alpha \quad (4.17)$$

We tested the model of the first order rate equation ($\alpha=1$). To test its accuracy, we plotted the concentration obtained from the kinetic model versus the experimental concentration of TBA measured by the GC-MS and found that the model agrees with the experimental data between 30 °C to 50 °C (Figure 4.6). At 60 °C and 70 °C, the experimental data deviated at longer time (Figure 4.7). The mass balance was not achieved because other by-products formed but were not detected with the GC. Once formed, DTBP undergoes thermal and acid-catalyzed decomposition at high temperatures to give stable radicals and molecules like methane, ethane, water, 2-methyl propane, ethene, etc [11, 79].

We derived the activation energy from the model (Eq. 4.18) between 30 °C to 50 °C and obtained a value of 32 kJ mol⁻¹:

$$k = 0.003 \exp \left[-\frac{32000}{R} \left(\frac{1}{T} - \frac{1}{323} \right) \right] \quad (4.18)$$

When applying the steady state approximation on tert-butyl radical and knowing that the decomposition of TBA (Eq. 4.1) is the rate determining step, we obtained that the rate of the reaction is $r = k_1 \cdot [\text{TBA}]$. This expression conforms with the obtained kinetic results that show the pseudo-first order in TBA. If the first reaction is slow (Eq. 4.1), that means the contribution of tert-butyl radical and $\text{HO}^\bullet$ toward TBA can be neglected in front of TBHP

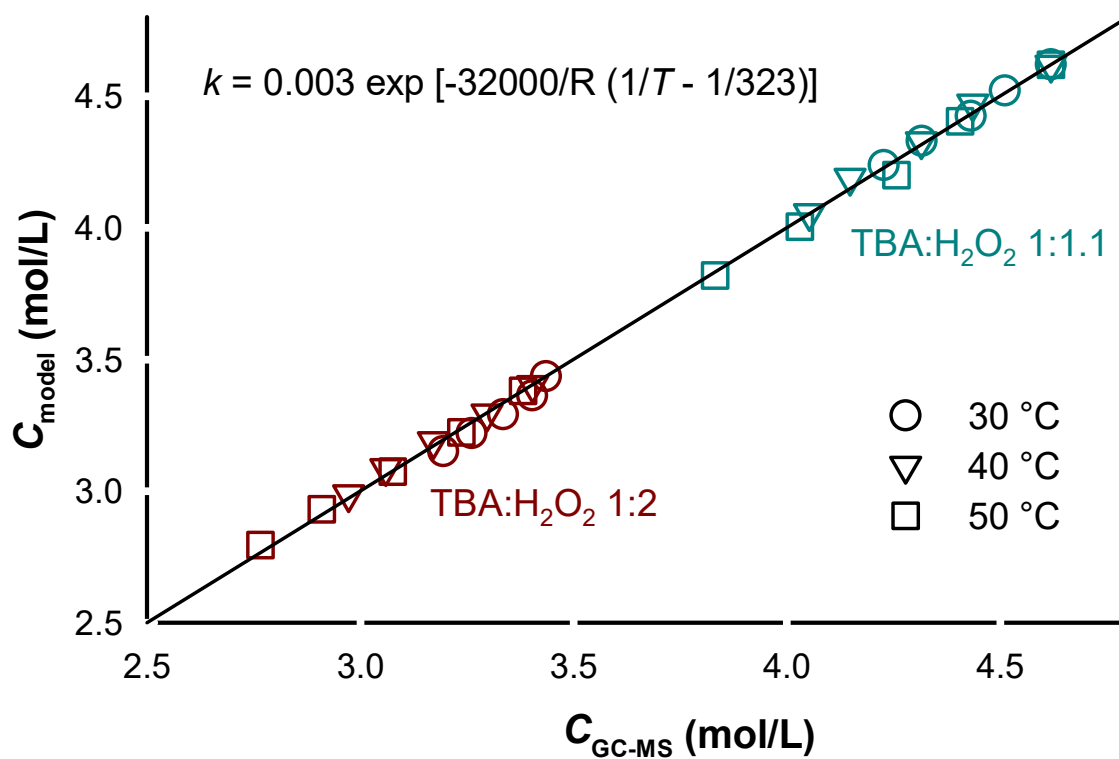


Figure 4.6 Parity plot showing the extent of model's accuracy.

synthesis. And, the tert-butyl radical is more likely to react with $\text{HOO}^\bullet$ and produces TBHP than with $\text{HO}^\bullet$ to yield TBA.

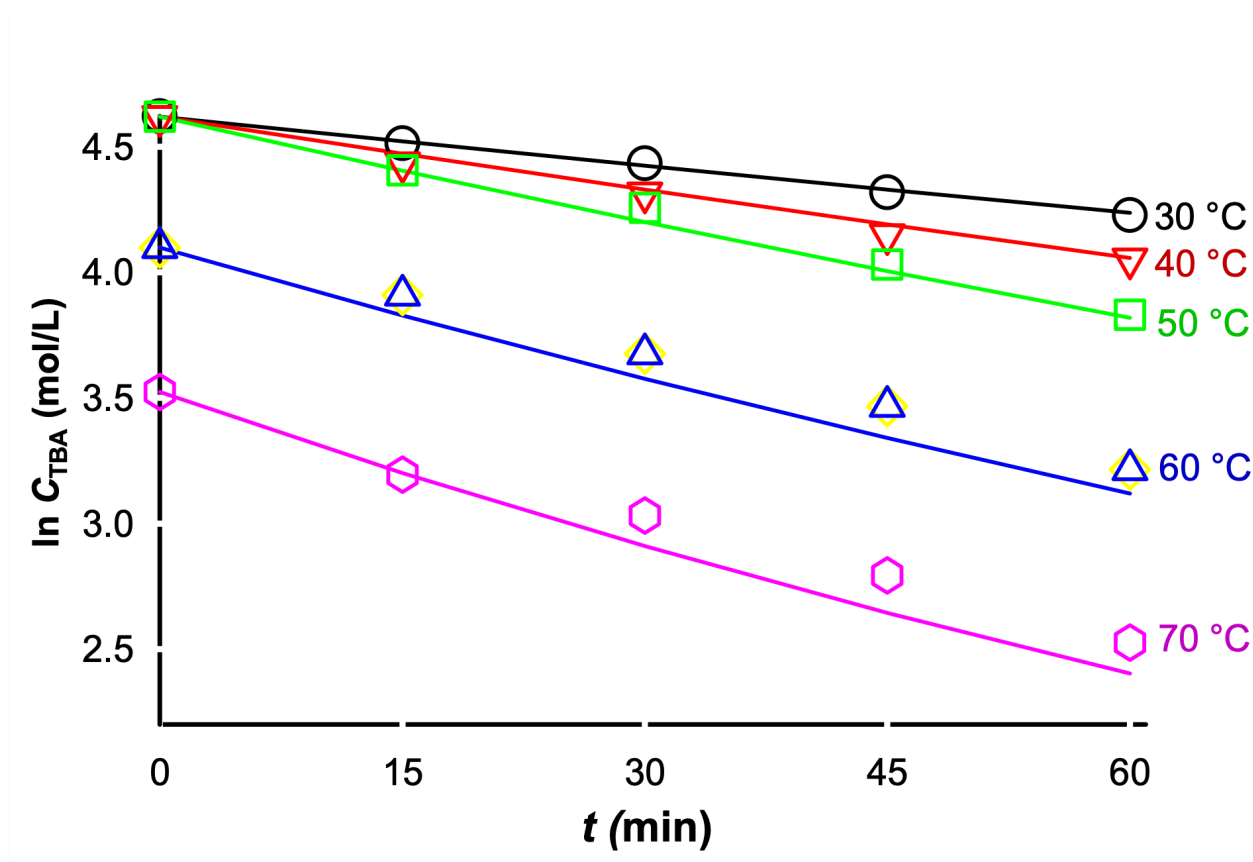


Figure 4.7 Plot of $\ln(C_{TBA})$ versus time at T between 30 °C to 70 °C and molar ration of 1.1.

The line represents the model.

CHAPTER 5 ADDITIONAL RESULTS: COUPLING PATH FOR PERESTER SYNTHESIS

5.1 Introduction

Due to their labile O-O bond, peroxy esters or peresters are valuable products as initiators for polymerization, cross-linking agents, and pharmaceutical additives [80,81]. Under heat or ultraviolet radiation, they generate radicals that serve as precursors to oxidative degradation of biological molecules and petroleum products [82]. They are also a source of electrophilic oxygen applied in reactions as C-H activation and C-O formation [83].

The main synthesis route consists of reacting alkyl hydroperoxides with acid chlorides under basic conditions. Milder and simpler conditions were introduced by Baj et al. with phase transfer catalysts [81]. Acid-promoted esterification of carboxylic acids, alkylation of peracids by highly stabilized cation sources, and oxidation of activated carbon bonds in presence of copper catalysts are also peresters producing methods [83,84].

Specifically, tert-butyl ester is commercially popular because of its strength toward nucleophilic attack. The simplest production way is the reaction of isobutylene with carboxylic acid over acidic catalyst. Isobutylene was either fed directly or obtained via dehydration of tert-butanol. Only sulfuric acid on powdered magnesium sulfate succeeded compared to other catalysts including Nafion, Dowex, potassium bisulfate, and methane sulfonic acid. The reaction remained successful with aliphatic, aromatic, olefinic, amino or heteroatomic acids [85].

Among tert-butyl esters, Luperox[®] P (tert-butyl peroxybenzoate) is between the most produced in the industrial plastic sector [1]. Recently, the reaction between benzoyl chloride and the sodium salt of TBHP produced stable tert-butyl peroxybenzoate in presence of liquid alkali and magnesium sulfate as stabilizer [86].

This chapter discusses a new coupling path to produce Luperox[®] P. It describes both reactions: the first one forms a sulfated material from isobutylene and Amberlyst-15, the second one gives peracid form corresponding carboxylic acid and hydrogen peroxide also over Amberlyst-15. Both reactions' products then mix to yield the perester.

5.2 Process

First, the benzoic acid reacts with H_2O_2 in an acidic media to give the peroxybenzoic acid. The isobutylene then reacts either with the same bed or another one. The peracid is finally introduced over this last bed to generate the perester (Figure 5.1). Only one bed, over which isobutylene and benzoic acid are added, may not be sufficient for the two reactions to occur. In fact, all the Bronsted sites of the catalyst can attack the isobutylene and won't be sufficient to produce the peroxy acid. But, it can still be possible if the reaction between benzoic acid and H_2O_2 is faster than the one with isobutylene. Being uncertain about the kinetics of both reactions, two beds are preferable.

Going back to Chapter 3, we tried two configurations for peroxybenzoic acid synthesis over Amberlyst-15 and stopped at this stage.

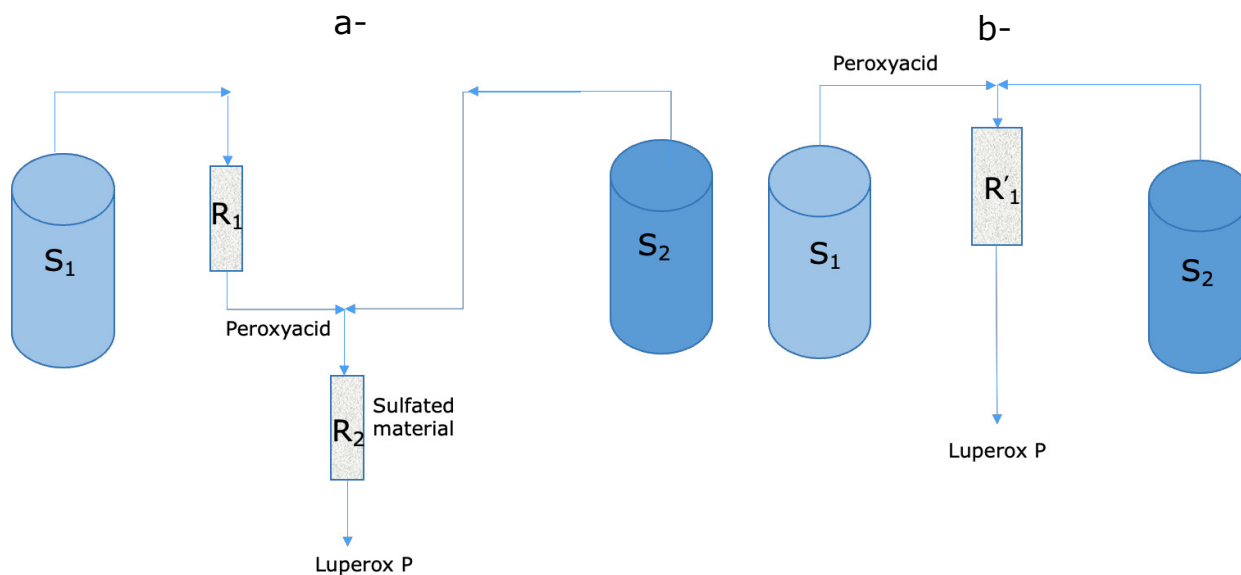


Figure 5.1 Coupling process scheme: a-2 beds, b-1 bed. S₁: solution of benzoic acid and H_2O_2 , S₂: solution of isobutylene, R-R': beds of Amberlyst-15.

5.3 Results and discussion

In case of aliphatic acids and in presence of acidic catalyst, the mechanism of peracid's formation occurs by the activation of the carbonyl carbon, the addition of hydrogen peroxide, the loss of water molecule, and finally the generation of the catalyst [32].

We expected the synthesis of peroxybenzoic acid in the same way. But as seen in the HPLC chromatograms, there was no reaction occurring. The heights of both benzoic acid and

hydrogen peroxide peaks were the same before and after reaction time and no other products were seen (Figure 5.2).

As stated in the literature, the addition of sulfuric acid to benzoic acid in presence of hydrogen peroxide carbonizes and transforms the solution to brown. This was seen in the case of the second configuration after we left the solution mixing for 48 h over Amberlyst-15 (Figure 5.3) [30].

5.4 Conclusion

The coupling path to produce perester is promising in case of any other aliphatic acid or with methane sulfonic acid instead of Amberlyst-15 [28,30] . It is a substituent for the perester traditional synthesis methods and advantageous due to the heterogeneous catalyst. The success of this route depends on several extra variants as replacing isobutylene by TBHP and applying ultra-sonication. This will help overcome the solubility issue of isobutylene and ensure the mixing of streams [87].

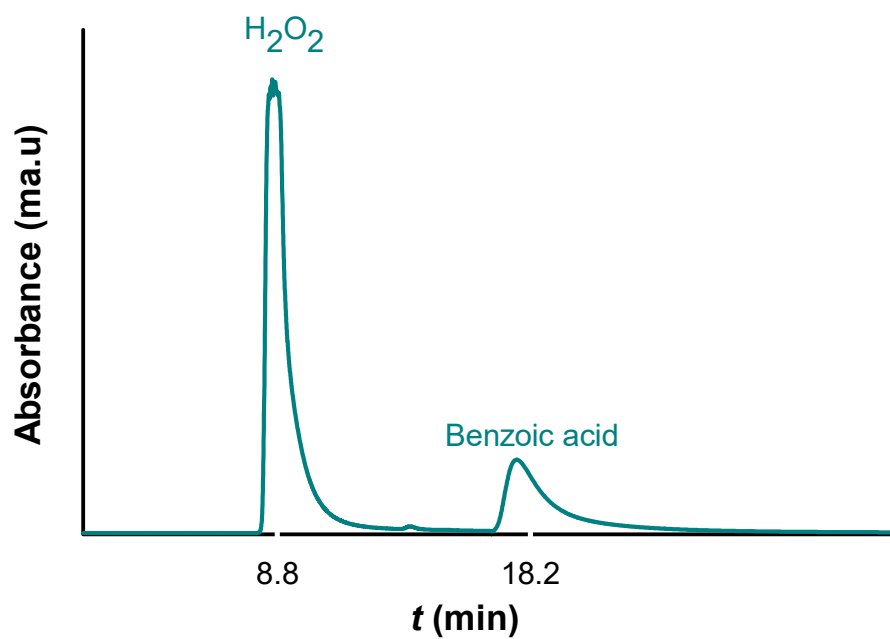
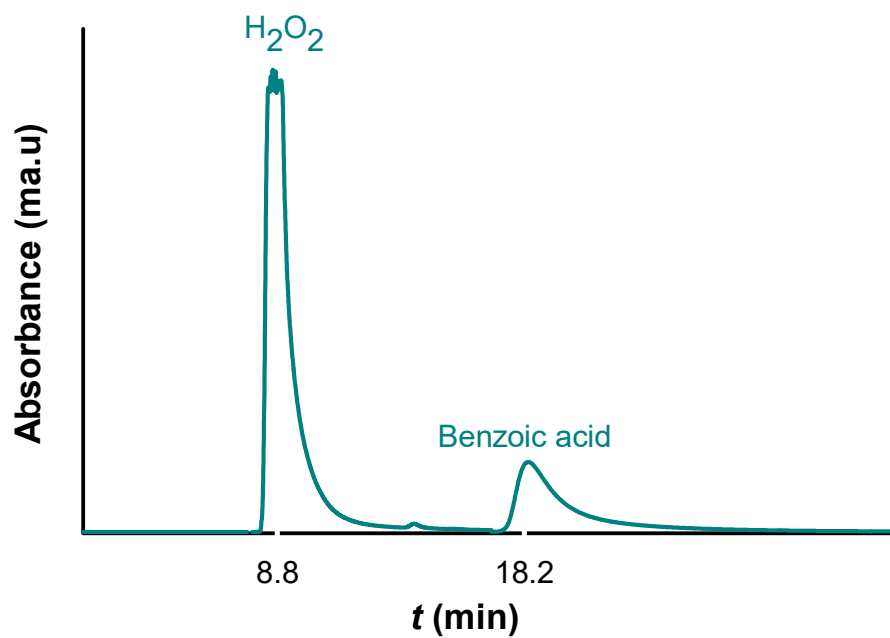
(a) S_0 (b) S_{final}

Figure 5.2 HPLC chromatograms of both solutions before and after reaction.

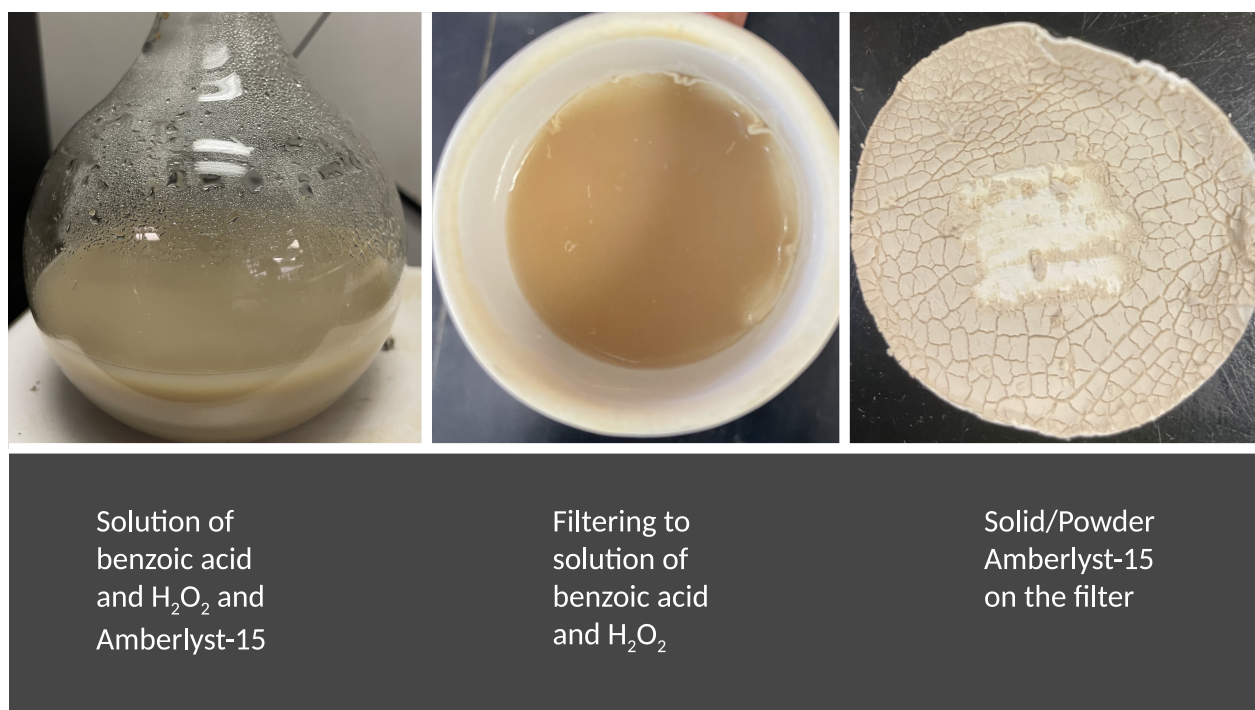


Figure 5.3 Filtering steps of the benzoic acid and H_2O_2 solution after 48 h.

CHAPTER 6 GENERAL DISCUSSION

This study made an attempt in flow chemistry to produce tert-butyl hydroperoxide from tert-butanol and hydrogen peroxide over heterogeneous catalyst. The research objective was to find the optimal conditions for this reaction. We tested two hypothesis: Bronsted acid sites trigger the mechanism and high temperature limits the by-product reactions. For this, we tested a temperature range of 30 °C to 70 °C and six catalysts including Amberlyst-15, Nafion, activated carbon, HPA over carbon, silica, and Amberlyst-15 support.

The Amberlyst-15 showed the best activity with a yield of 16 % due to its sulfonic acid sites that attack TBA and create the $\text{H}_2\text{O}^\bullet$ strong leaving group but also its hygroscopy that lets water competitively adsorb.

We applied the Levenberg-Marquardt algorithm, estimated the apparent kinetic parameters by minimizing the sum of the square error, and prove that the reaction is pseudo-first order in TBA with an activation energy of 32 kJ mol⁻¹ between 30 °C to 50 °C. Above 50 °C, the by-product DTBP can thermally decompose to stable radicals and molecules as methane, ethene, acetone, etc [11].

Although the yield here was not as high as the one achieved by traditional homogeneous processes, this approach is cleaner and omits the need for product purification and neutralization. It is also economic knowing that the catalyst is reusable and recyclable. If commercially scaled up, this process helps to meet the predicted increasing demand on peroxides in several areas as in environmental monitoring, pharmaceutical industry [88], in chemistry as radical precursors [89], in rubber vulcanization, radical polymerization [79,90,91], in coating applications [92], in energy-efficient fuel cells, rockets and as cathode material in Li batteries [93].

Finally, we tried a coupling path to produce the Luperox[®] P from peroxybenzoic acid and sulfated material over Amberlyst-15. Although the first reaction did not give peroxybenzoic acid but this path can still be prosperous to yield another perester. The second reaction occurs between the isobutylene and the Amberlyst-15 with tert-butanol as a solvent. Excess tert-butanol shifts the reaction toward more isobutylene that will react with the sulfonic

end groups of Amberlyst-15 to produce the molecule $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{SO}_2-\text{O}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$. The latter sulfated molecule and peracid mix together and generate the perester.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

In conclusion, this study prove the synthesis of tert-butyl hydroperoxide from tert-butanol and hydrogen peroxide over heterogeneous catalyst in a plug flow reactor. The carbocation, produced from the adsorption of tert-butanol on the catalyst surface, reacted with hydrogen peroxide and generated the hydroperoxide.

A design of experiment with three factors was developed to optimize the reactions conditions. We tried three temperatures (40 °C, 55 °C, and 70 °C), two flow rates (1 mL min⁻¹ and 2 mL min⁻¹), and six catalysts (commercial and in house synthesized). The factor that has the highest impact is the catalyst type (support/active sites). Bronsted acid sites with enough concentration were capable of triggering the mechanism but to continue the reaction, the support should be stable enough and resistant toward radicals and water generated.

GC-FID and GC-MS were able to detect and quantify the main and by-products to be tert-butyl hydroperoxide, di-tert-butyl peroxide, and peroxyketal. H⁺ from the catalyst dissociated the tert-butyl hydroperoxide to give di-tert-butyl peroxide and acetone. At its turn, acetone reacted with tert-butyl peroxide to form the peroxyketal. The highest TBHP yield obtained was 16 % in case of Amberlyst-15 because of the competitive adsorption of water.

We further studied the kinetics of the reaction by designing two sets of experiments in a batch reactor between 30 °C to 70 °C at two H₂O₂:TBA molar ratios of 1.1 and 2. By applying the Levenberg Marquardt algorithm, we showed that the reaction is pseudo-first order in tert-butanol with an activation energy of 32 kJ mol⁻¹ below 50 °C. The incapability of the GC method to detect other by-products between 60 °C to 70 °C limited our model to 50 °C. At 60 °C and 70 °C, DTBP may decompose and generate by-products as acetone, ethene, etc.

To conclude, the flow chemistry with heterogeneous catalyst is an approach to oxidize the tert-butanol to tert-butyl hydroperoxide. Commercially, this process is promising since it is less polluting than traditional homogeneous routes.

7.2 Recommendations

For future work, we recommend the following:

- Although this approach is new but the yield is still not as high as the industry wishes.

We anticipate higher yields in larger reactors with larger amounts of catalysts. Recycle mode is a way to increase the conversion as well. The recyclability and reusability of Amberlyst-15 are favorable for the unconverted tert-butanol to recirculate back and get adsorbed.

- The reaction yielding TBHP is bi-molecular. Big pore volumes and pore diameters are essential for the tert-butyl and the hydroperoxyl radicals to meet and form TBHP. Finding a catalyst with these properties is a way to increase the yield. Heteropoly acids over Amberlyst-15 is a promising catalyst if the loading concentration of heteropoly acids is exact. For this, it's necessary to find the suitable procedure to impregnate the heteropoly acids over Amberlyst-15 support.
- The coupling path to produce perester can be satisfactory with an aliphatic acid. Also, finding an active heterogeneous catalyst to replace Amberlyst-15 in the peroxybenzoic acid synthesis is a solution to still produce the Luperox[®] P.

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