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EFFECT OF IONS ON THE HYDROXYLATION OF BENZENE TO PHENOL BY
HYDROGEN PEROXIDE OVER TS-1 CATALYST

Miss Rudemas Manosak

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

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 BENZENE TO PHENOL BY HYDROGEN PEROXIDE
 OVER TS-1 CATALYST
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ฤดีมาศ มโนศักดิ์: ผลของไอออนต่อการไฮดรอกซิไลซ์เบนซีนเป็นฟีนอลโดยไฮโดรเจนเปอร์ออกไซด์บนตัวเร่งปฏิกิริยาไททานเนียมซัลโฟนาไลต์-1 (EFFECT OF IONS ON THE HYDROXYLATION OF BENZENE TO PHENOL BY HYDROGEN PEROXIDE OVER TS-1 CATALYST) อ.ที่ปริกษาวิทยานิพนธ์หลัก: รศ.ดร.ชราชมงคลศรี, 99 หน้า.

งานวิจัยนี้ศึกษาปฏิกิริยาไฮดรอกซิเดชันของเบนซีนเป็นฟีนอลโดยไฮโดรเจนเปอร์ออกไซด์ในเครื่องปฏิกรณ์แบบสามเฟส ด้วยผลของไอออนต่างๆ (H^+ , NH_4^+ , NO_3^- , Cl^- และ CH_3COO^-) ในสารละลายโดยการใช้อุณหภูมิ 3 ชนิดและเกลือ 2 ชนิด (กรดไฮโดรคลอริก, กรดอะซิติก, กรดไนตริก, แอมโมเนียมไนเตรด และ แอมโมเนียมคลอไรด์) พบว่า ในสารละลายที่มีโปรตอน เบนซีนสามารถละลายได้เพิ่มมากขึ้นเนื่องจากความแข็งแรงของพันธะไฮโดรเจนในโมเลกุลของน้ำลดลง และในสารละลายที่มีไอออน NH_4^+ , NO_3^- และ Cl^- อัตราการละลายของเบนซีนจะเพิ่มขึ้นเนื่องจากการลดลงของแรงตึงผิวและความหนืดของสารละลาย ในกรณี CH_3COO^- ไอออนเนื่องจากโมเลกุลมีส่วนที่ไม่มีขั้วจึงช่วยในการละลายของเบนซีนได้มากขึ้น ในส่วนของการเกิดปฏิกิริยา พบว่า ความเข้มข้นสมมูลและอัตราการละลายของเบนซีนส่งผลต่อการเกิดปฏิกิริยาที่จุดเหมาะสมของความเข้มข้นสมมูลและอัตราการละลายของเบนซีน การเปลี่ยนแปลงของไฮโดรเจนเปอร์ออกไซด์ไปเป็นผลิตภัณฑ์จะเพิ่มขึ้น นอกเหนือจากนั้น พบว่า ปฏิกิริยานี้สามารถอธิบายได้ด้วยแบบจำลองแลงเมียร์-ฮินเชลวูดซึ่งสารตั้งต้นสองตัวจำเป็นต้องดูดซับลงบนพื้นผิวของตัวเร่งปฏิกิริยาเพื่อให้เกิดปฏิกิริยา

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RUDEMAS MANOSAK: EFFECT OF IONS ON THE HYDROXYLATION OF BENZENE TO PHENOL BY HYDROGEN PEROXIDE OVER TS-1 CATALYST. ADVISOR: ASSOC.PROF.THARATHON MONGKHONSI, Ph.D., 99 pp.

The direct hydroxylation of benzene to phenol by hydrogen peroxide over TS-1 catalysts is carried out in a three phase stainless steel reactor system. In this research, the effects of ions (H^+ , NH_4^+ , NO_3^- , Cl^- and CH_3COO^-) in solution by using three acids and two salts (hydrochloric acid, acetic acid, nitric acid, ammonium nitrate and ammonium chloride) are studied. It is found that the addition of H^+ in aqueous phase results in higher amount of benzene can dissolve into the aqueous phase due to the breaking of the extent and strength of hydrogen bonding of water molecule. The addition of NH_4^+ , NO_3^- and Cl^- ions can increase the solubility rate of benzene by the decreasing the surface tension and viscosity of aqueous solution. In case of CH_3COO^- , the molecule has a part of non-polar which can help benzene to dissolve. It is observed that the solubility rate and equilibrium concentration of benzene affect the hydroxylation of benzene to phenol. With the optimization of solubility rate and equilibrium concentration of benzene in aqueous phase, the reaction is able to reach high conversion. Furthermore, this reaction is explained by Langmuir-Hinshelwood model in which the adsorption of two reactants on the catalyst surface is necessary for the reaction to occur.

Department :Chemical Engineer.....

Student's Signature

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CHAPTER I

INTRODUCTION

Phenol is an organic compound which consists of a phenyl (-C₆H₅) group, bonded to a hydroxyl (-OH) group. It is widely used as a precursor to many materials and useful compounds. Moreover, phenol is also largely used in pharmaceutical industry such as antiseptic drugs, herbicides and detergents.

In industrial scale, phenol is mainly produced via the cumene process as shown in Figure 1.1. This process includes three steps beginning from the alkylation of benzene with propylene to cumene. The oxidation of cumene to cumene hydroperoxide follows by the decomposition of cumene hydroperoxide to phenol and acetone. The major disadvantages of this process are the multi-step reaction which needs a large amount of energy especially in the separation process and the exceed market demand of the co-product acetone. Moreover, the other disadvantage in this process are the formation of cumene hydroperoxide which is an explosive substance and using of hazardous sulfuric acid as catalyst for the decomposition of the intermediate cumene hydroperoxide that lead to the corrosive waste is produced, the catalyst can not be easily regenerated and negatively impact environment.

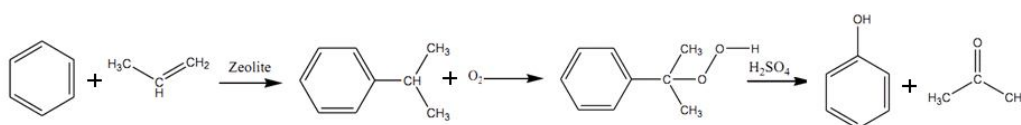


Figure 1.1 Cumene route process for phenol production.

The direct hydroxylation of benzene to phenol with hydrogen peroxide using titanium silicalite-1 (TS-1) catalyst is one of interested reaction because of several advantages as shown in Figure 1.2. For example, this reaction can produce phenol in only one reaction step under mild condition and avoid toxic waste or unwanted co-product. This develops new environmentally safer chemical transformations.

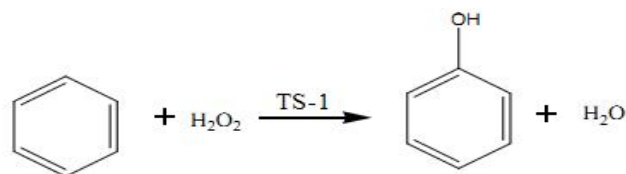


Figure 1.2 The hydroxylation of benzene to phenol.

A problem of this reaction is the phase separation of the two reactants due to benzene is non-polar phase but hydrogen peroxide solution is polar-phase and the low yield of phenol product. Some researchers have attempted to solve the above problem by trying to homogenise the mixture by using some organic solvents to combine the benzene phase and the aqueous phase together. This method is reported that the presence of solvent cause a diffusion hindrance of benzene molecule into catalyst's channel and the competitive absorption of solvent with Hydrogen peroxide to adsorb on TS-1 catalyst which suppresses the reaction. (Bhaumik et al, 1998; Bengoa et al., 1998; Kumar et al., 1999; Chammingkwan et al., 2009) Furthermore, this method also leads to solvent separation and solvent recycling problem.

From the drawback of the two phase system described above, the three phase system is preferred in this research. However, the conversion is still low as a result of the different phases of reactants and the catalyst. Benzene is on the top surface of the hydrogen peroxide phase (aqueous phase) while the solid catalyst stay at the bottom of the reactor. The solution to this problem is increasing the opportunity of benzene, hydrogen peroxide and catalyst contact together. Vigorous stirring can help for mixing. Nevertheless, this technique can use only in a laboratory reactor which has a small distance between the benzene layer on the surface of the hydrogen peroxide solution and the catalyst at the bottom of the reactor. For a larger system, the larger distance between the benzene phase and the catalyst causes difficulty mixing the mixture.

In one of our research (Mongkhonsi and Mitpapan, 2011) we have found that a better way than using solvent is to operate the reactor in the three phase system but increasing the system temperature. This reaction carried out in a pressurized autoclave reactor in order to raise the reaction temperature higher than the boiling point of benzene. The increase temperature leads to higher amount of benzene dissolves in the aqueous phase. This leads to higher benzene conversion. In another parallel research, the oxidation of toluene to cresol/benzaldehyde by hydrogen peroxide over TS-1 (Kasemsukphaisan, 2009; Saintapong, 2011) using the same reaction system, it is found that adding HCl in the aqueous phase can increase the solubility of toluene and the reaction between toluene and hydrogen peroxide. Therefore, it is the subject of interest of the research whether can we combine both techniques together.

In the present research the hydroxylation of benzene to phenol over TS-1 catalyst is carried out in the three phase system. Three acids and two salts (hydrochloric acid, nitric acid, acetic acid, ammonium nitrate and ammonium chloride) are used to adjust the pH of the aqueous phase. The solubility of benzene in different acidic ionic solutions, however, is measured at room temperature. The hydroxylation reaction is carried out in a pressurized autoclave reactor at 110°C which is higher than the normal boiling point of both benzene and water.

The purpose of this research is to study the effects of ion of solution on the solubility of benzene in aqueous phase and the reaction between benzene and hydrogen peroxide by using TS-1 catalysts. This research has been scoped as follows:

1. Preparation of TS-1 catalyst which has 50 Si/Ti molar ratios by using hydrothermal technique synthesis.
2. Characterization of TS-1 catalysts by using the following techniques.
 - Determination of chemical composition by using X-ray fluorescence spectroscopy (XRF)

- Determination of specific area by N₂ adsorption based on Brunauer-Emmett-Teller method (BET)
 - Determination of structure and crystallinity of the catalysts by using X-ray diffraction technique (XRD).
 - Determination of incorporation of Ti atoms into the framework structure by using Fourier transform infrared spectrometer (FT-IR).
3. Evaluated the solubility of benzene at room temperature in a variety of solution which consists of H⁺, NH₄⁺, CH₃⁺, Cl⁻, NO₃⁻ and CH₃COO⁻ using hydrochloric acid, nitric acid, acetic acid, ammonium nitrate and ammonium chloride.
4. Investigate the influence of ion type (H⁺, NH₄⁺, CH₃⁺, Cl⁻, NO₃⁻ and CH₃COO⁻) and the amount of ion in solution by carry out the reaction without and with different aqueous solution (hydrochloric acid, nitric acid, acetic acid, ammonium nitrate and ammonium chloride) at different concentration of acid in the aqueous hydrogen peroxide phase.

The present thesis is organized as follows:

Chapter I describes background and scopes of the research.

Chapter II reviews the current productions of phenol in commercial scale, the study of the hydroxylation of benzene reaction and literature on the catalytic activity of TS-1 catalysts in the direct hydroxylation of benzene by hydrogen peroxide and comments on previous works.

Chapter III consists of catalyst preparation, techniques which used in the characterization of catalysts, the solubility of benzene measurement and catalytic activity evaluation in the direct hydroxylation of benzene by hydrogen peroxide.

Chapter IV presents the experimental results of the characterization of catalyst, the solubility of benzene in a variety of solution (hydrochloric acid, nitric acid, acetic acid, ammonium nitrate and ammonium chloride) and the hydroxylation of benzene reaction in these solutions over TS-1 catalyst.

Chapter V contains the overall conclusion emerging from this research and some recommendations for future work.

Finally, the sample of calculation of catalyst preparation, the GC standard preparation and calibration curves from area to mole of benzene and phenol, the sample of solubility of benzene and conversion calculation, the calculation of amount of solvent required for homogenization the mixture, the data of these experiments which had emerged from this research and material safety data sheet of benzene, hydrogen peroxide, phenol and the variety of ionic solution used are included in appendices at the end of this book.

CHAPTER II

LITERATURE REVIEW

2.1 Production of phenol from benzene via cumene

At present, phenol in industrial section is mainly produced by cumene route which has three steps to proceed. First, the production of cumene by using the alkylation of benzene with propylene is followed by the oxidation of cumene with air to form cumene hydroperoxide. The final process is the decomposition of cumene hydroperoxide to phenol and acetone. The schematic of the whole cumene process is shown in Figure 2.1 below.

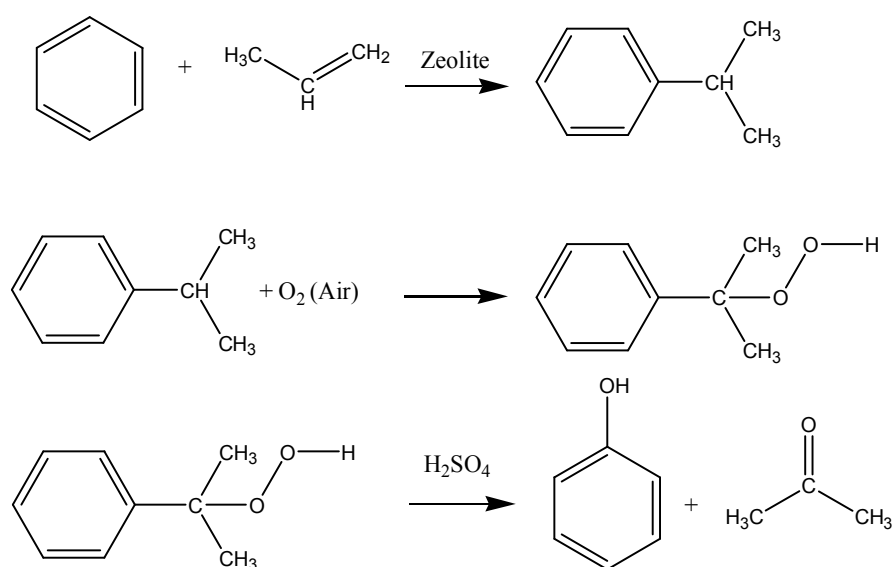


Figure 2.1 The production of phenol from benzene via cumene.

2.1.1 Production of cumene

Production of cumene process technology is available on a commercial basis with three major suppliers namely, UOP LLC, Badger/Raytheon, and CDTECH. However, these processes from four major suppliers are also similar therefore in this

place will only mention to the detail of the UOP Q-max process. From a company information, cumene is produced in form of isopropylenebenzene by using benzene and propylene as a raw material. First, proper amount benzene and propylene is feed to the alkylation reactor which contains Zeolitic catalyst QZ-2000 or QZ-2001TM. Then, the product which consists of benzene, propane, cumene, diisopropylenebenzene, and heavy aromatic from the alkylation reactor is send to a separation unit. Entering contaminate propane from propylene feed to reactor is removed by depropanizer column in vapor phase. The bottom of depropanizer is sent to benzene column to separate benzene and recycle to the alkylation reactor. Some vapor benzene is condensed by using water cooled exchanger and stored in storage to use later. The remained product from the benzene column is sent to the cumene column in order to separate cumene. The distillate cumene is condensed by using overhead exchanger and sent to phenol production unit. Finally, the bottom of cumene column is sent to the diisopropylenebenzene column where diisopropylbenzene is separated and recycled to the transalkylation reactor and combined with additional benzene to form additional cumene. The flow schematic of production of cumene unit by UOP Q-max process is shown in Figure 2.1.

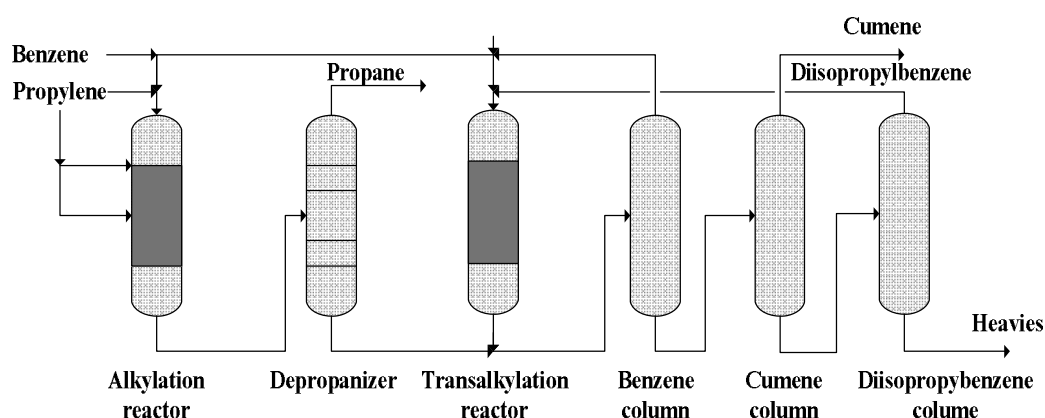


Figure 2.2 Schematic flow diagram of cumene production unit by UOP Q-max process.

2.1.2 Production of phenol

The reaction in phenol production is the oxidation of cumene with air to form cumene hydroperoxide and the decomposition of cumene hydroperoxide to phenol and acetone. In Sunoco/UOP technology the oxidation, starting from fresh cumene is sent to feed wash column to remove light acid using treated water. Afterward, cumene is heated and sent to an oxidizer reactor which the reaction condition is carried out at the temperature in the range of 90-130°C and pressure between 1-10 atm. This reaction requires to operate at low conversion per pass (typically 20%) due to explosivity of cumyl hydroperoxide. Then, the product is filtrated to remove organic salt and rust because rust causes the unneeded decomposition of cumene hydroperoxide. Then, the filtrated product is sent to deep vacuum distillation to increase the concentration from 25-40% to 80-84% which is appropriate concentration to decompose. Afterward, cumene hydroperoxide is decomposed in the decomposer using 2000-4000 ppm of sulfuric acid as a catalyst to get the high yield. The decomposed product is cooled down from 135 °C to 38 °C and neutralized. Finally, the product is sent to a dehydrator in order to transform the intermediate product, dicumyl peroxide, to alpha-methylstyrene (ASM), phenol and acetone and further hydrogenated to form cumene before recycling back to oxidation section again.

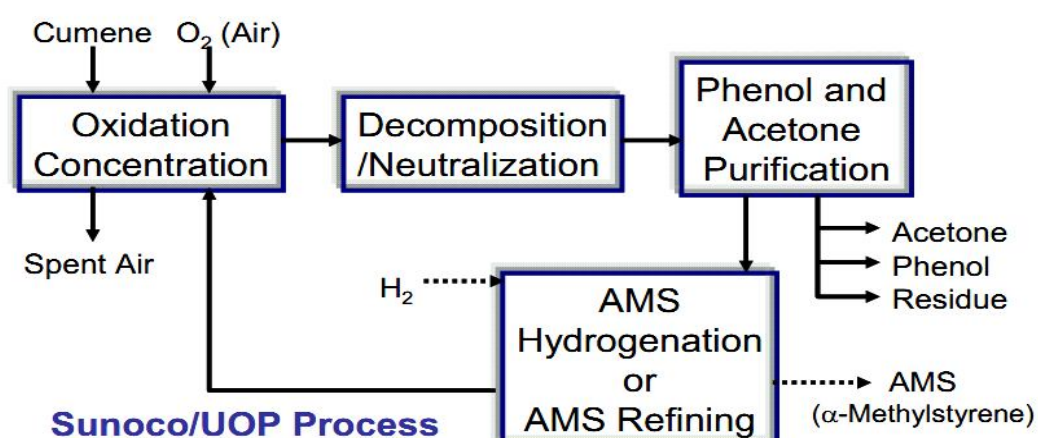


Figure 2.3 Schematic flow diagram of phenol production unit by Sunoco/UOP process.

2.2 Hydroxylation of benzene

One of interested reaction is the direct hydroxylation of benzene to phenol with hydrogen peroxide using titanium silicalite-1 (TS-1) catalyst because this reaction can produce phenol in only one reaction step under mild condition and this reaction avoids the co-production of acetone. The reaction of benzene and H_2O_2 produces water as the by-product as shown in figure 2.4 below;

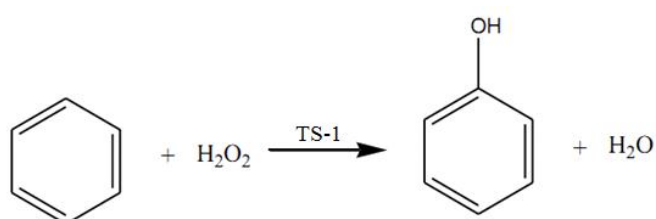


Figure 2.4 Hydroxylation of benzene to phenol.

The early study of the hydroxylation of benzene to phenol over various zeolites was reported by Thangaraj et al. in 1990. They found that benzene remained unreacted over silicalite-1, TiO_2 (both amorphous and crystalline), and also in the absence of catalysts. The conversion of hydrogen peroxide to hydroxyl benzene decreased in the order $\text{TS-1} > \text{Fe-TS-1} > \text{Al-TS-1} > \text{Fe-ZSM-5} > \text{Al-ZSM-5}$. On the contrary, the decrease of selectivity to phenol followed the reverse order. They reported that while phenol was the only product over pure acid zeolites (Fe-ZSM-5 and Al-ZSM-5) but the secondary product, para-benzoquinone, was formed in appreciable quantities over titanium-containing zeolites (TS-1, Fe-TS-1 and Al-TS-1). The selectivity for para-benzoquinone decreased in the order: $\text{TS-1} > \text{Fe-TS-1} > \text{Al-TS-1}$. The acid strength of these zeolites followed the reverse trend: $\text{Al-TS-1} > \text{Fe-TS-1} > \text{TS-1}$. Protonation of phenol over acid zeolites probably suppressed the further electrophilic reaction leading to dihydroxy benzenes.

The study of the influence of solvent conditions on benzene catalytic oxidation with hydrogen peroxide was reported by Bhaumik et al. (1998) and Kumar et al. (1999). The research carried out the liquid phase hydroxylation reactions in a glass batch reactor under atmospheric pressure at 50°C to 80°C and using different solvents namely water, methanol and acetonitrile. They reported that using a tri-phase system (solid-liquid-liquid), in the absence of an organic co-solvent, the conversion of benzene during the oxidation by the TS-1/H₂O₂ system could be achieved. Since the surface of titanium silicalite was relatively hydrophobic in nature. The presence of co-solvent (like acetone, acetonitrile or methanol) caused a diffusion hindrance of benzene molecule inside the catalyst channel and such hindrance was not occurred in solvent-free system. However, vigorous stirring was necessary for the tri-phase system in order to homogenize the mixture. The best value of conversion was reached 78% benzene conversion with 86% phenol selectivity at reaction temperature 70°C using benzene/H₂O₂ molar ratio of 1:1.

Although, Bhaumik et al. (1998) and Kumar et al. (1999) reported that the benzene conversion increased from 10.9% to 78.5% and the phenol selectivity increased from 85% to 89% when water was used as solvent instead of acetonitrile (benzene: solvent 1:5 (wt/wt)) and almost similar results were obtained when acetone or methanol was used as solvent in place of acetonitrile. Nevertheless, the repeated study under the same reaction system at solvent-free conditions by Bianchi et al. (2007) showed that the benzene conversion lower than that reported by Bhaumik et al. in 1998. The benzene conversion reported by Bianchi et al. (2007) was only at 4.5% with 42% phenol selectivity under the identical conditions. Moreover, several works after 1999 exhibited that nobody can repeat the result of Kumar's research team cause the problem on the confidence of the work of Kumar's research team.

Another study of the catalytic activity on the hydroxylation of benzene to phenol in three phase system was reported by Bengoa et al in 1998. The reaction was carried out in a 250 ml batch glass reactor at reaction temperature 30°C and atmospheric pressure over TS-1 catalyst. They found that conversion of hydrogen peroxide was around 17% with 74% phenol selectivity. The decrease in activity was

observed when methanol was used instead of water. They reported that the competitive absorption of methanol can compete with H_2O_2 to adsorb on TS-1 catalyst but this competitive adsorption did not totally prevent the H_2O_2 adsorption.

In 2001, He et al. studied the hydroxylation of benzene over Ti-MCM-41 catalyst using acetone as solvent. The liquid phase hydroxylation of benzene was performed in a 100 ml three necked glass flask batch reactor equipped with a magnetic stirrer, a reflux condenser stirred. The reaction was carried out under atmospheric pressure and reaction temperature at 65°C . They reported that the large pore of Ti-MCM-41 offered the great advantage of benzene substrate to diffuse and react on the active site and also phenol diffuse away from the active site to liquid reaction phase. Moreover, the hydrophilic property of the catalyst surface favored the hydroxylation of benzene with hydrogen peroxide over catalyst. The conversion of benzene increased when increased the titanium content and the introduction of Al. The maximum conversion was reported at 98% with more than 95% phenol selectivity for (Si, Ti, Al)-MCM-41 ($\text{Si/Ti} = 25$ and $\text{Si/Al} = \alpha$) while TS-1 catalyst gave 10% benzene conversion and 63% phenol selectivity. In the same reaction system using Ti-MCM-41 ($\text{Si/Ti}=100$) as the catalyst studied by Tanev et al. in 1994 was reported that the 68% conversion and 98% phenol selectivity.

Balducci et al. in 2003 and Bianchi et al. in 2007 studied the hydroxylation of benzene using different solvents namely acetone, acetonitrile, methanol, tert-butyl alcohol, acetic acid, dimethylformamide, N-methylpyrrolidone, dimethylsulfone, and sulfolane over a modification of titanium silicalite (TS-1) catalysts. The modification was done by catalyst treatment with $(\text{NH}_4)\text{OAc}$, $(\text{NH}_4)\text{HF}_2$, $\text{H}_3\text{PO}_4/\text{H}_2\text{O}_2$, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, $\text{HF}/\text{H}_2\text{O}_2$, $(\text{NH}_4)\text{F}/\text{H}_2\text{O}_2$ and $(\text{NH}_4)\text{HF}_2/\text{H}_2\text{O}_2$ in order to remove the less selective catalytic sites of the catalyst. The best result was obtained from treatment the catalyst with $(\text{NH}_4)\text{HF}_2$ and H_2O_2 . They reported that using nitrogen containing solvents, such as dimethylformamide and N-methylpyrrolidone, promoted the unproductive decomposition of hydrogen peroxide which depressed the catalytic activity of TS-1 results in low conversion. Co-solvents containing sulfone group, such as dimethyl sulfone and tetramethylene (sulfolane), exhibited the benzene conversion

around 8% and the phenol selectivity higher than 80% at 100 °C. Sulfolane was a solvent which molecule has high dipole moment (4.81 Debye) and dielectric constant (43.26). The peculiar property caused a sterically hindered species with phenolic compound which this complex could not enter the titanium silicalite pores lead to inhibiting the further oxidation of phenol to dioxygenated compounds.

The study of catalytic testing on the hydroxylation of benzene to phenol using acetic acid as co-solvent has been done by Lemke et al. (2003). The catalytic tests were carried out in a closed glass autoclave system which operated up to a pressure of 10 bar and the reaction temperature up to 70°C. This reaction used supported vanadium oxide as a catalyst which prepared by using various support materials such as MCM-41, MCM-48, SiO₂ and amorphous microporous mixed oxide. They reported that the site of isolated VO_x catalysts suppressed consecutive oxidation reactions. The best result was obtained from using VO_x/SiO₂ catalyst with low percentage of vanadium loading (0.14 wt.%) at 8.3% phenol yield which a benzene conversion more than 10% and phenol selectivities more than 40%. However, high conversion of benzene was achieved at low selectivity of phenol.

Another study on the influence of solvent conditions on the liquid-phase hydroxylation of benzene over vanadium-substituted heteropolyacids catalysts was reported by Zhang et al. (2005). The reaction was carried out in a 50 ml three-neck round bottom flask at condition of atmospheric pressure and room temperature. Various solvents, for example, formyl acid, glacial acetic acid, propyl acid, butyric acid and acetonitrile and different vanadium species such as NaVO₃, H₄PMo₁₁VO₄₀, H₅PMo₁₀V₂O₄₀ and H₆PMo₉V₃O₄₀ were tested in their study. They reported that all catalyst active for the hydroxylation of benzene with satisfying results and the best result was obtained by using glacial acetic acid at 91% phenol selectivity and yield of 26%.

The hydroxylation of benzene to phenol over vanadium oxide using acetic acid as solvent was studied by Gao and Xu (2006). The reaction was performed at reaction temperature 40°C and atmospheric pressure in a 100 ml four-neck flask stirred reactor under stirring over clay supported vanadium oxide. They reported that the physical mixture of clay and V₂O₅ catalyst exhibited lower activity than V₂O₅/clay prepared by impregnation method. The best result obtained at the optimum 2.5% vanadium loading with 94 % phenol selectivity and 14% benzene conversion. They also reported that the excessive of vanadium oxide decomposed H₂O₂ which resulted in low conversion.

The study of the catalytic activity of titanium silicalite-1 (TS-1) catalysts modified by Fe, Al, Co and V was carried out by Shenchunthichai in 2006. The reaction was performed in a batch reactor, a 250 ml, water jacketed, three-necked, glass flask fitted with a condenser under stirring at 70°C and atmospheric pressure. It has been reported that the addition of Fe, Al, Co and V could increase the catalytic activity of TS-1 on the hydroxylation of benzene in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. However, the decrease of strong acid site followed the mentioned order.

The direct hydroxylation of benzene with hydrogen peroxide over the titanium-silica based catalyst such as Ti-MCM-41, TS-1 and TS-PQTM (the trade mark of PQ Corporation) was studied by Chammingkwan et al. (2009). The three phase slurry reaction system was carried out in a batch glass reactor equipped with a condenser operated at atmospheric pressure and an autoclave reactor operated at 20 bar using N₂ to pressurize the system. Under the preliminary studied conditions, TS-PQTM exhibited the highest catalytic activity among the studied catalysts. The effect of pressure was studied at 60°C and 70°C at molar ratio between benzene:H₂O₂ was set at 5:1. They found that the system pressure did not have any significant effect on the H₂O₂ conversion to organic compounds. The temperature effect was also investigated at the range of 65°C to 75°C. They found that the conversion of H₂O₂ increased in a narrow range from 14.9% at 65°C to 19.4% at 70°C. The influence of various solvent namely methanol, ethanol, tert-butylalcohol, acetone and acetonitrile

was investigated. The results showed that the reaction in water (three-phase) exhibited higher H_2O_2 conversion to organic compounds than the reaction carried out in the presence of organic solvent. They reported that the presence of solvent caused a diffusion hindrance of benzene molecule inside the TS-1 channel and such hindrance is not encountered in solvent-free. Furthermore, the effect of additional water to the reaction mixture on H_2O_2 conversion to organic compounds and product selectivity was also studied. They reported that when increase the volume of additional water the conversion of H_2O_2 could reach 22% at 40 ml additional water. Thereby, phenol selectivity of 96% could be achieved from 80% selectivity at 10 ml additional water. However, at 60 ml additional water can increase phenol selectivity up to 98% but decreased the H_2O_2 conversion. They considered that water helped to strip phenol away from the catalytically active sites, thereby preventing further hydroxylation of phenol. Moreover, it enabled the formation of catalyst suspension and thereby the interaction of the three phases.

Effect of acidity on the oxidation of toluene to cresol/benzaldehyde by hydrogen peroxide over TS-1, was studied by Kasemsukphaisan in 2009 and Setthapong in 2011. The three phase system reaction is carried out at reaction temperature 70°C and 90°C in a stirred slurry reactor and at temperature 120°C in an autoclave reactor. They found that adding hydrochloric acid can increase toluene solubility rate and concentration in water. This is the reason why during the catalytic activity testing of hydroxylation of toluene it was found that the reaction added with hydrochloric acid has higher conversion than reactions which no acid.

Mongkhonsi and Mitpapan in 2011 studied the effect of elevated temperature on the liquid phase hydroxylation of benzene to phenol by hydrogen peroxide over TS-1 catalyst. The three phase system reaction was performed in an autoclave reactor operated at 2 bar using N_2 to pressurize with a reaction temperature higher than the normal boiling point of benzene and water. They reported that with the increase in system pressure, the reaction could be carried out at a higher temperature. However, the conversion of benzene decreased rather increased. At higher reaction temperature, though not all benzene vaporized, most of liquid benzene injected into the reactor

existed in the gaseous phase rather than the liquid phase. This loss could be minimized by reducing the volume of space above the liquid surface by increasing the volume of water used as solvent. Furthermore, they also found that benzene that really involves in the hydroxylation reaction was the benzene already dissolved into the liquid phase, not the liquid benzene on the top surface of the water layer. The best value of conversion was reached 35% hydrogen peroxide conversion with 100% phenol selectivity at reaction temperature 110°C using benzene/H₂O₂ molar ratio of 10:1.

Meng et al. (2011) reported the direct hydroxylation of benzene to phenol by hydrogen peroxide over TS-1 zeolite as a catalyst using ammonia, ammonium carbonate or urea as a solvent. The influences of key reaction parameters, including reaction temperatures and times, the catalyst amount, and the type of solvent on the reaction were also studied. Finally, the optimum reaction condition was determined. The maximum yield of phenol can reach 66.32% when the reaction time was 2 hours, the reaction temperature was 40 °C, and the molar ratio of ammonia: catalyst: hydrogen peroxide: phase transfer catalyst: benzene was 2.80: 0.10: 2.52:0.005: 1, respectively.

Hu et al. (2011) studied a new Fenton-like system in a medium of hydrophilic triethylammonium type of ionic liquid (IL) in the hydroxylation of benzene to phenol. They reported that the triethylammonium acetate ((Et₃NH)(CH₃COO)) IL exhibited retardation performance for the decomposition of H₂O₂ and protection performance for the further oxidation of phenol, thus the yield and selectivity to phenol were promoted greatly. The acidity of the system was proved to be an important factor for the selectivity to phenol.

2.3 Comment on previous works

From the above previous studies of the direct hydroxylation of benzene to phenol over TS-1 catalyst, it can be seen that the three phase system using water as solvent show higher activity of hydroxylation than the two phase system using co-solvent such as acetone, acetonitrile, methanol, ethanol and sulfolane (Bhaumik et al., 1998; Kumar et al., 1999; Balducci et al., 2003; Bianchi et al., 2007 and Chammingkwan et al., 2009). From the above reviewed literature of the selective oxidation of benzene to phenol over vanadium species catalyst, the result shows that using glacial acetic acid as solvent gives the high activity of oxidation the organic compounds (Lemke et al., 2003; Zhang et al., 2005 and Gao and Xu, 2006).

From the literatures reviewed above one can see that the methods normally employed are using organic solvent in TS-1 catalyst and using glacial acetic acid as solvent in vanadium species catalyst. In concurrent researches (Meng et al., 2011 and Hu et al., 2011), it is showed that using ammonia, ammonium carbonate or urea as a solvent and using the triethylammonium acetate ((Et₃NH)(CH₃COO)) ionic liquid greatly promoted the yield and selectivity to phenol. Furthermore, the acidity of the system is proved to be an important factor for the selectivity to phenol. The effect of elevated reaction temperature makes them more activity than a reaction temperature lower than the boiling point of benzene (Mongkhonsi and Mitpapan, 2011). The effect of acidity on the oxidation of toluene to cresol/benzaldehyde over TS-1 using three phase reaction system shows the high activity of oxidation the organic compounds after acidification by hydrochloric acid due to more amount of toluene can dissolve in aqueous phase (Kasemsukphaisan, 2009 and Setthapong, 2011)

However, there is no information about the effect of acidity of solution on the hydroxylation of benzene to phenol over TS-1 catalyst. Thus, the direct hydroxylation of benzene to phenol by hydrogen peroxide over TS-1 catalyst using hydrochloric acid, nitric acid, glacial acetic acid, ammonium nitrate and ammonium chloride as a solvent operated at 110°C is chosen to be studied in this research.

Nevertheless, our preliminary experimental result shows that using hydrochloric acid, nitric acid and acetic acid as solvent can increase the solubility of benzene in aqueous phase which the equilibrium concentration is finally equal. However, using ammonium nitrate and ammonium chloride as solvent does not affect the equilibrium concentration which is about the same as of in water. Moreover, the solubility rate in any acids solution is different. As above mentioned, the effect of acidity can not explain the whole phenomena but the effect of ion should be the answer. Up to present, we have noticed that there is no information about the effect of ions of solution on the solubility of benzene and the hydroxylation of benzene to phenol over TS-1 catalyst. This is the reason why they become the subject of our study.

CHAPTER III

EXPERIMENTAL

The experimental of this research consists of three sections. Section 3.1 describes the procedures of TS-1 catalyst preparations. Section 3.2 explains the composition, structure and surface properties of the catalyst characterized by various techniques such as XRF, XRD, FT-IR and N₂ adsorption-desorption isotherm. Finally, Section 3.3 illustrates the procedures of the investigation of the effect of ions of solution to the solubility of benzene and the catalytic reaction.

3.1 Catalyst preparation

3.1.1 Chemical for preparation of TS-1 catalyst

The detail of all chemicals used in the preparation procedure of TS-1 catalyst is shown in Table 3.1.

Table 3.1 The chemicals use in the catalyst preparation.

Chemical	Grade	Supplier
Titanium (IV) butoxide 97%	-	Fluka
Tetrapropylammonium bromide 98%	-	Aldrich
Sodium chloride	Analytical	Loba Chemie
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich
Sodium silicate solution	Extra pure	Merck

3.1.2 Preparation procedures

TS-1 catalyst is prepared by hydrothermal method which the reagents are summarized in Table 3.2 and the preparation procedure is shown in Figure. 3.1.

Table 3.2 The reagents use for the preparation of TS-1.

Solution for the gel preparation			Solution for decant-solution preparation		
<u>Solution A1</u>			<u>Solution A2</u>		
Ti(O(CH ₂) ₃ CH ₃) ₄	2.2970	g	Ti(O(CH ₂) ₃ CH ₃) ₄	2.2970	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
De-ionized water	60	ml	H ₂ SO ₄ (conc.)	3.4	ml
H ₂ SO ₄ (conc.)	3.4	ml			
<u>Solution B1</u>			<u>Solution B2</u>		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
<u>Solution C1</u>			<u>Solution C2</u>		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H ₂ SO ₄ (conc.)	1.55	ml			

Table 3.2 illustrates the amount of reagent to prepare TS-1 catalyst which atomic ratio of Silicon/Titanium is set at 50. The source of metals for catalyst preparation is Ti(O(CH₂)₃CH₃)₄ for Ti, and sodium silicate for Si. TPABr (Tetra-n-propyl ammonium bromide((CH₃CH₂CH₂)₄N)Br) is used as organic template.

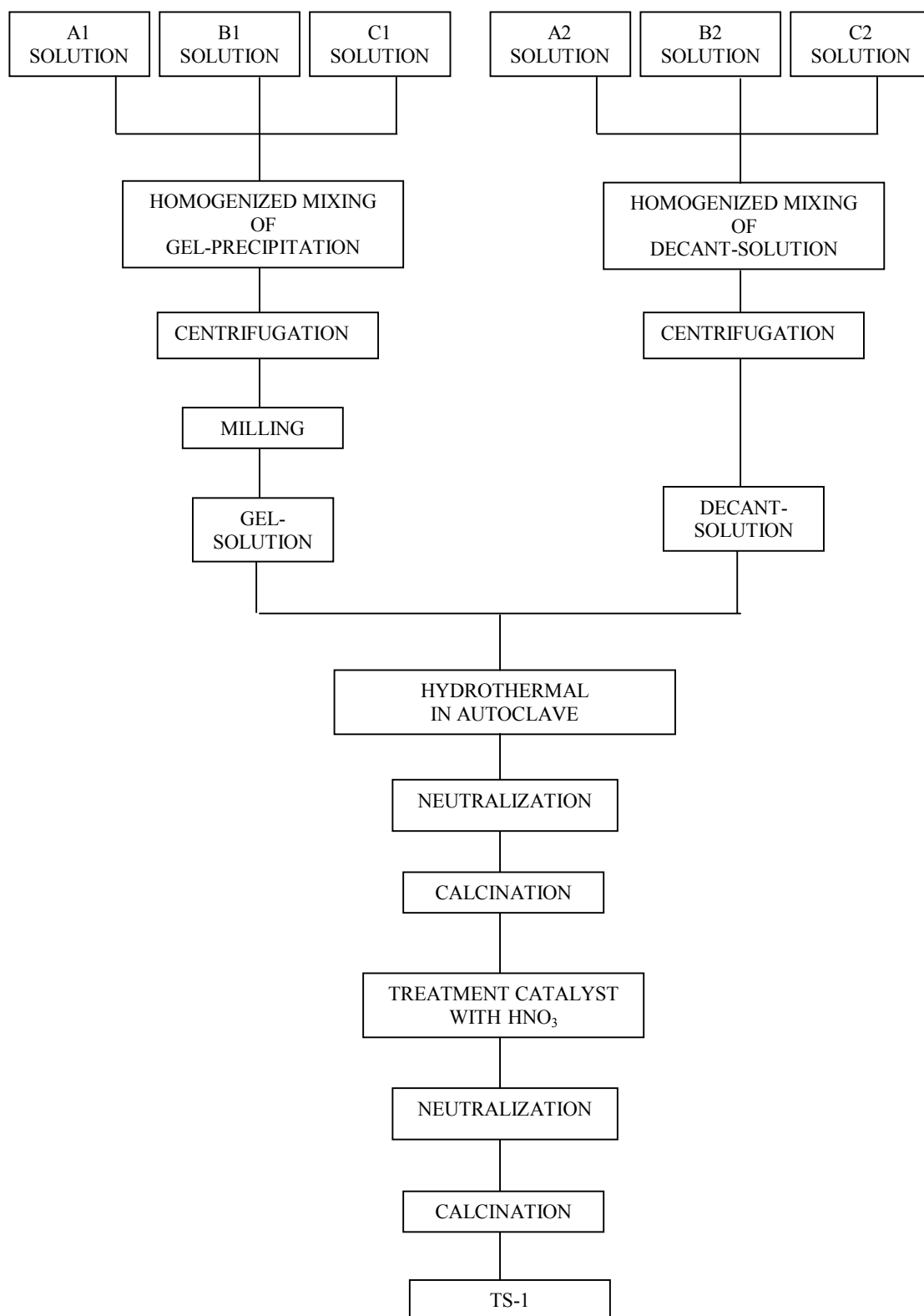


Figure 3.1 The preparation procedure of TS-1 by hydrothermal method.

3.1.2.1 Preparation of gel and decant solution

The TS-1 catalysts are prepared from the mixture of gel and decant solutions. For the gel solution, solution A1 and B1 are added dropwise into solution C1 with simultaneous stirring using a magnetic stirrer at room temperature. Whereas solution A1 is acidity and solution B1 is basic, the alternate dropwise of solution A1 and solution B1 is used to maintain the pH within the range 9-11 (appropriate pH for precipitation). H_2SO_4 (conc.) or NaOH solution are used to adjust pH of the gel mixture to an appropriate level if it is necessary. After that, the gel mixture is centrifuged at 3500 rpm for 15 minutes to separate the formed gel from the supernatant liquid. The precipitated gel mixture is milled for 15 minutes alternate with centrifuged for 15 minutes by totally 1 hour. The milling procedure is as follows: milled 15 min \rightarrow centrifuge (to remove liquid out) 15 min \rightarrow milled 15 min \rightarrow centrifuge 15 min \rightarrow milled 30 min \rightarrow centrifuge 15 min.

For the decant solution, solution A2 and B2 are added dropwise into solution C2, same as for the preparation of gel mixture. The colorless supernatant liquid is separated from the mixture by centrifugation.

3.1.2.2 Hydrothermal procedures

The gel solution is mixed together with the decant solution. However, before mixing, the pH of solution is maintained between 9-11. The mixture is filled in an autoclave which is pressurized to 3 barg by nitrogen gas and heated up to 180°C. The autoclave temperature is maintained at this temperature for 3 days. After crystallization time, the mixture is cooled down to room temperature in the autoclave.

In neutralization step, the obtained crystal is separated from the supernatant liquid by centrifugation. Then, some of hot de-ionized water is added into the crystal in order to remove chloride out of the crystal. Using centrifugation to separate the crystal from the supernatant liquid switch with adding hot water until the crystal is pH 7. After that, the crystal is dried in an oven at 110°C for at least 24 hours.

In calcination step, the dry crystal is calcined in an air stream at 550°C at a heating rate of 10 °C per minute and held at that temperature for 7 hours to burn off the organic template and leave the cavities and channels in the crystals. Afterward, the calcined crystal is finally cooled down to room temperature.

In treatment step, with the fraction of 10 g of the obtained TS-1 per 150 ml of 5M HNO₃ is placed into a reflux round bottom flask. Then, the mixture is heated up to 80°C and held at this temperature for 3 hours in order to removal of some species that block in the small pore. The treated catalyst is separated from the supernatant liquid by centrifugation.

Finally, the dry obtained TS-1 is neutralized and calcined again same as for the neutralization step and the calcinations step as describes above. The final product is obtained as white powder.

3.2 Catalyst characterization

3.2.1 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface is determined by FT-IR using Thermo Nicolet model Impact 6700. The sample is mixed with KBr with ratio of sample: KBr equal to 1:100 and milled thoroughly in a small quartz mortar to obtain a very fine powder in order to minimized the scattering of infrared radiation and provided a high quality of spectrum. Then, the sample is pressed into a thin wafer and analyzed which infrared spectra is recorded between 400 and 4000 cm⁻¹ on a microcomputer. The measurement is performed in transmission mode.

3.2.2 X-Ray Fluorescence Spectrometer (XRF)

The composition analysis of element in the bulk of the catalyst is determined by x-ray fluorescence spectroscopy (XRF). The analysis is carried out on X-ray fluorescence spectrometer (WDXRF) BRUKER AXS, Germany : Model S4 PIONEER

3.2.3 X-Ray Diffraction (XRD)

Crystal structure is identified using x-ray diffraction (XRD) technique. The analysis is performed with a SIEMENS D5000 using Cu K α radiation with Ni filter. The operating condition of measurement is shown below:

2 θ of detection:	6° to 30°
Resolution:	0.04°/sec.
Number of scan:	20

3.2.4 N₂ adsorption-desorption isotherm

The total surface area and pore volume are calculated using BET Micromeritics ASAP 2020. The sample cell which contained 0.2 g of sample is placed into BET Micromeritics ASAP 2020. Then the sample is heated up to 200 °C and held at this temperature for 2 hours to remove some species which exist in the pore. In the first of the measurement, the catalyst is adsorbed nitrogen until the equilibrium adsorption of nitrogen on the surface is reached. Afterward, the nitrogen-adsorbed sample is desorbed to remove the adsorbed nitrogen. After degassing step, the surface area of catalyst can be determined from the amount of adsorbed nitrogen and adsorption/desorption profile.

3.3 The study of the effect of ions

The effect of ions in the solutions to the solubility of benzene and catalytic reaction is studied in this research. Section 3.3.1 shows the chemicals used in this experiment. The procedure of the solubility of benzene in a varied solution measurement is described in section 3.3.2. Finally the details of the catalytic reaction procedures study is shown in section 3.3.3.

3.3.1 Chemicals

All chemicals used for the effect of the acidity study are summarized in table 3.3.

Table 3.3 Chemicals use for the effect of the acidity of solution study.

Chemical	Grade	Supplier
Hydrochloric acid	AR	QRëC
Nitric acid	AR	QRëC
Acetic acid	AR	QRëC
Ammonium nitrate	Analytical	Univar
Ammonium chloride	Analytical	Univar
Benzene	Analytical	Panreac
Hydrogen peroxide 30%	Analytical	Merck
Ethanol	Analytical	Merck

3.3.2 The solubility of benzene

The solubility experiment is studied in a 250 ml beaker which a 1/4" tube is vertically placed in the beaker at room temperature and atmospheric pressure. 160 ml of solvent which is completely covered with benzene on the top surface of the

solution is stirred at 1100 rpm by magnetic bar. The experiment is done when the solubility of benzene in aqueous phase constants.

The influence of various ion which consists of H^+ , NH_4^+ , CH_3^+ , Cl^- , NO_3^- and CH_3COO^- on the solubility of benzene is investigated using water, of 0.1M hydrochloric acid, 0.1M acetic acid, 0.1M nitric acid, 0.1M ammonium nitrate and 0.1M ammonium chloride as solvent.

Procedures

1. 160 ml of either water, solutions of 0.1M hydrochloric acid, 0.1M acetic acid, 0.1M nitric acid, 0.1M ammonium nitrate and 0.1M ammonium chloride is added into the 250 ml beaker which a 1/4" tube is vertically placed in the beaker. This vertically placed tube acts as a sampling well.
2. A volume of benzene is added to cover the top surface of the aqueous phase completely. Additional amount of benzene is added if necessary to make sure that liquid benzene always completely covers the top surface of the aqueous during the experimental period.
3. At a specified interval, the stirring is stopped and a rubber bulb is used to purge the water inside the tube 3-4 time in order to make sure that the water inside the tube and the water outside the tube have the same concentration. Then, a small volume of the aqueous phase is sampled from the vertically placed tube to measure the concentration of dissolve benzene in the aqueous phase.
4. The collected samples are analyzed by a gas chromatograph which isothermal program and operating condition is summarized in table 3.4. The trials are carried out until the solubility constant. The experimental setup for the study of the solubility of benzene is shown in Figure 3.2.

Table 3.4 The gas chromatography condition for benzene analysis.

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N ₂ (99.999%)
Carrier gas flow rate (ml/min)	60
Injector temperature (°C)	250
Detector temperature (°C)	250
Column temperature (°C)	80
Analyzed chemical	Benzene

Under the GC conditions above, the retention time of benzene is 2.7 minutes. The preparation of standard sample and the calibration curve for benzene analysis is described in Appendix A.

**Figure 3.2** The experimental setup for the study of the solubility of benzene.

3.3.3 The hydroxylation of benzene

The reaction experiment is carried out in the stainless steel reactor at 110°C reaction temperature and 2 barg using N₂ to pressurize the system. The reaction is carried out for 2 hours which 10:1 of benzene per hydrogen peroxide molar ratio.

The effect of ion type (H⁺, NH₄⁺, CH₃⁺, Cl⁻, NO₃⁻ and CH₃COO⁻) and the amount of ion in solution by carry out the reaction without and with varied ionic solutions (hydrochloric acid, nitric acid, acetic acid, ammonium nitrate and ammonium chloride) at different concentration in the aqueous hydrogen peroxide phase.

Procedures

1. A 150 ml stainless steel SS304 reactor is loaded with 1 g of catalyst. Then, the reactor is slowly filled with 120 ml of either de-ionized water, solutions of hydrochloric acid, nitric acid, acetic acid, ammonium nitrate or ammonium chloride (0.1M or 0.017M). After that 8.9 ml of benzene is filled into the reactor.
2. The reactor is sealed and pressurized to 2 barg with nitrogen gas and placed in an oil bath for heating up to 70°C. The system is kept at this temperature for 1 hour to remove gas from the pore of the catalyst and saturated the aqueous with benzene.
3. After that the reactor temperature is raised to the reaction temperature. Then, 1 ml of aqueous H₂O₂ (30 wt% H₂O₂ in water) is injected via an injection port using a 1 ml syringe. The reaction is carried out for 2 hours.

4. To stop the reaction, the reactor is cooled down by removing the reactor from the oil bath and placed into an ice bath. Then, 100 ml of ethanol is added into the reactor to homogenize the aqueous and the organic phase. The catalyst particle is separated after the reaction by using mini-centrifuge equipped with six tube rotors (1.5 ml tube size).
5. The organic compounds present in the liquid phase are analyzed by a gas chromatograph which operating condition is summarized in table 3.5. The schematic diagram of the reaction system is shown in figure 3.3 and the experimental setup for autoclave reactor is shown in Figure 3.4.

Table 3.5 The gas chromatography condition for product analysis.

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N ₂ (99.999%)
Carrier gas flow rate (ml/min)	60
Injector temperature (°C)	250
Detector temperature (°C)	250
Initial column temperature (°C)	70
Initial hold time (min)	5
Program rate (°C/min)	6
Final column temperature (°C)	230
Final hold time (min)	15
Analyzed chemical	Phenol, undesired product

Any organic products formed which can dissolve in the homogenized liquid phase are analyzed by gas chromatograph. The only organic product observed is phenol. Under the GC conditions above, the retention time of phenol is 12 minutes. The preparation of standard sample and the calibration curve for phenol analysis is described in Appendix A.

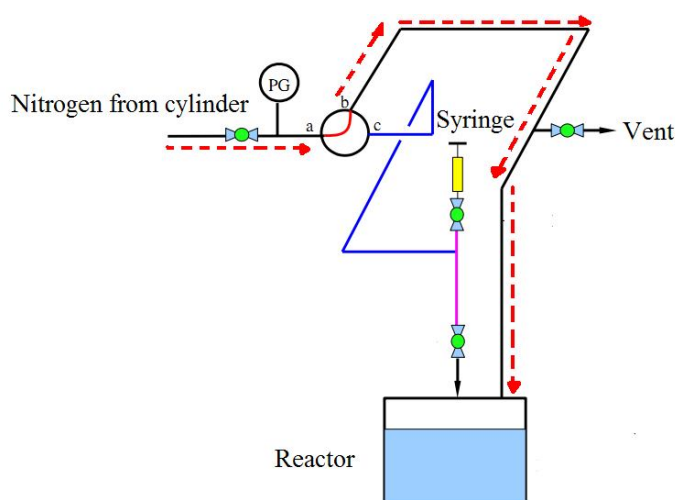


Figure 3.3 Schematic diagram of the reaction system.



Figure 3.4 The experimental setup for autoclave reactor.

CHAPTER IV

RESULTS AND DISCUSSION

The results and discussion of this research consists of three sections. Section 4.1 shows the results of characterization of TS-1 catalyst using XRF, XRD, FT-IR and N₂ adsorption-desorption isotherm. Section 4.2 explains the effect of ions on the solubility of benzene in solution. Finally, section 4.3 illustrates the effect of ions on the hydroxylation of benzene to phenol.

4.1 Catalyst characterization

4.1.1 Catalyst composition and surface area

The composition of TS-1 catalyst is obtained from wavelength dispersive X-ray fluorescence Spectrometer (WDXRF) BRUKER AXS, Germany : Model S4 PIONEER analysis and the catalyst surface area is measured by N₂ adsorption-desorption isotherm using BET equation are shown in Table 4.1

Table 4.1 Chemical compositions and surface area of TS-1.

Catalyst sample	%Si	%Ti	Si/Ti	Surface area (m ² /g)
TS-1	97.03	1.62	59.89	362.5

4.1.2 Catalyst crystal structure

The x-ray diffraction (XRD) pattern of the catalyst showed in Figure 4.1 shows the typical diffraction pattern of the MFI structure (2-Theta = 7.9°, 8.8°, 14.8°, 23.9° and 24.4°)

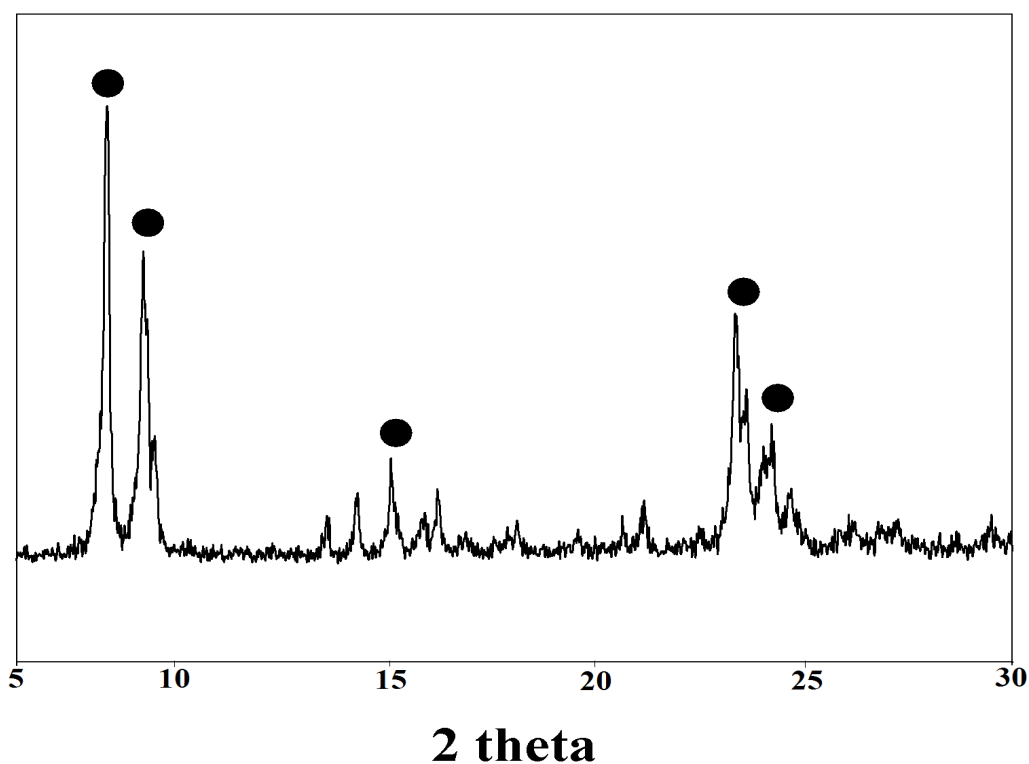


Figure 4.1 The XRD pattern of TS-1 catalyst.

4.1.3 Functional group of catalyst

The FT-IR spectrum illustrated in Figure 4.2 shows a band around 960 cm^{-1} which is normally used as an indicator of the relative abundance of single Ti atom surrounded by Si atoms, indicates that a number of Ti atoms incorporated into framework of TS-1 catalyst.

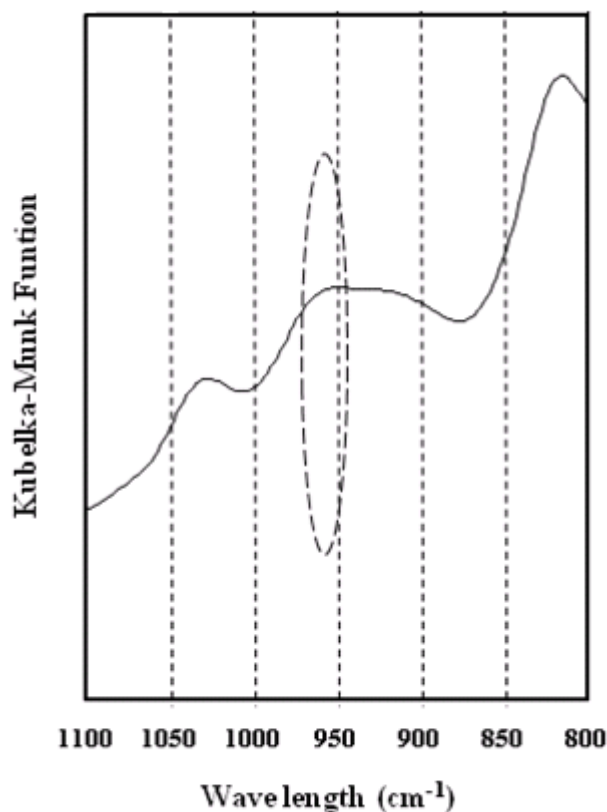


Figure 4.2 The FT-IR spectra of TS-1 catalyst.

4.2 The effect of ions on the solubility of benzene in solution phase

Before discussing the experimental results, please be reminded again that the characteristics of the reaction system in this research are following;

- (i) The reaction is performed in a three phase system which benzene (non polar phase) is on the top surface of the hydrogen peroxide phase (aqueous polar phase) while the solid catalyst stays at the bottom of the reactor as shown in Figure 4.3.
- (ii) Benzene which really involves in the hydroxylation reaction is the benzene already dissolved into the aqueous phase, not the liquid benzene on the top surface of the water layer.

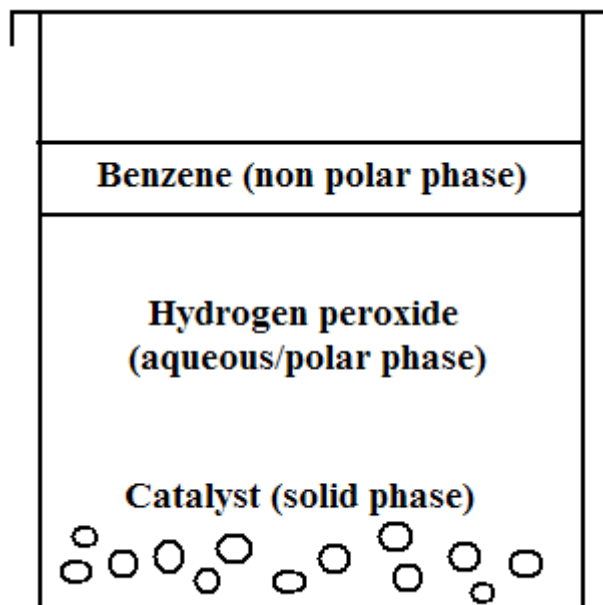


Figure 4.3 Three phase system of the hydroxylation reaction.

- (iii) The amount of benzene in the aqueous phase can affect the extent of the reaction because for the reaction to occur both benzene and hydrogen peroxide must exist on the catalyst surface.
- (iv) The catalyst surface is hydrophobic in nature which prefers to adsorb a non-polar molecule more than a polar molecule. Thus, the solvent in the reaction should not be an organic solvent which has polar part and non-polar part in the same molecule because the solvent and benzene will cover most of the catalyst surface area. This leads to too low amount of hydrogen peroxide molecules on the catalyst surface.

- (v) In order to solve the problem mentioned in the above paragraph (iv), pure water, a solvent miscible with a solution of hydrogen peroxide is used. This technique, however, leads to too low amount of benzene molecule on the catalyst surface instead.
- (vi) The way to solve the lack of benzene on the catalyst surface is easier to solve than the lack of hydrogen peroxide because the catalyst surface can adsorb benzene more than hydrogen peroxide.
- (vii) In our previous researches (Mitpapan, 2011), the increase of reaction temperature and volume of solvent by using pure water as a solvent are methods which can increase the amount of benzene (amount = volume \times concentration) in aqueous phase.
- (viii) However due to the size of the reactor used in our experiment, the maximum volume of solvent is already use in this research. Therefore, if other technique which can increase the solubility of benzene in aqueous phase exist, the chance for the catalyst to contact with benzene molecule should increase this will lead to the increase in the conversion of hydroxyl peroxide should increase.
- (ix) During our preliminary study, we have found that the presence of some ions such as H^+ improved the saturated concentration of benzene in water. Therefore, in this research, we extend our study to cover other ions by dissolving several acids and salts in the aqueous phase.

From the seasons mentioned above, the amount of benzene dissolved in aqueous phase is firstly measured in order to evaluate the equilibrium concentration of benzene and the solubility rate in this study. The experimental results obtained from using acidic solutions and salts solution are shown in Figures 4.4 and 4.5, respectively.

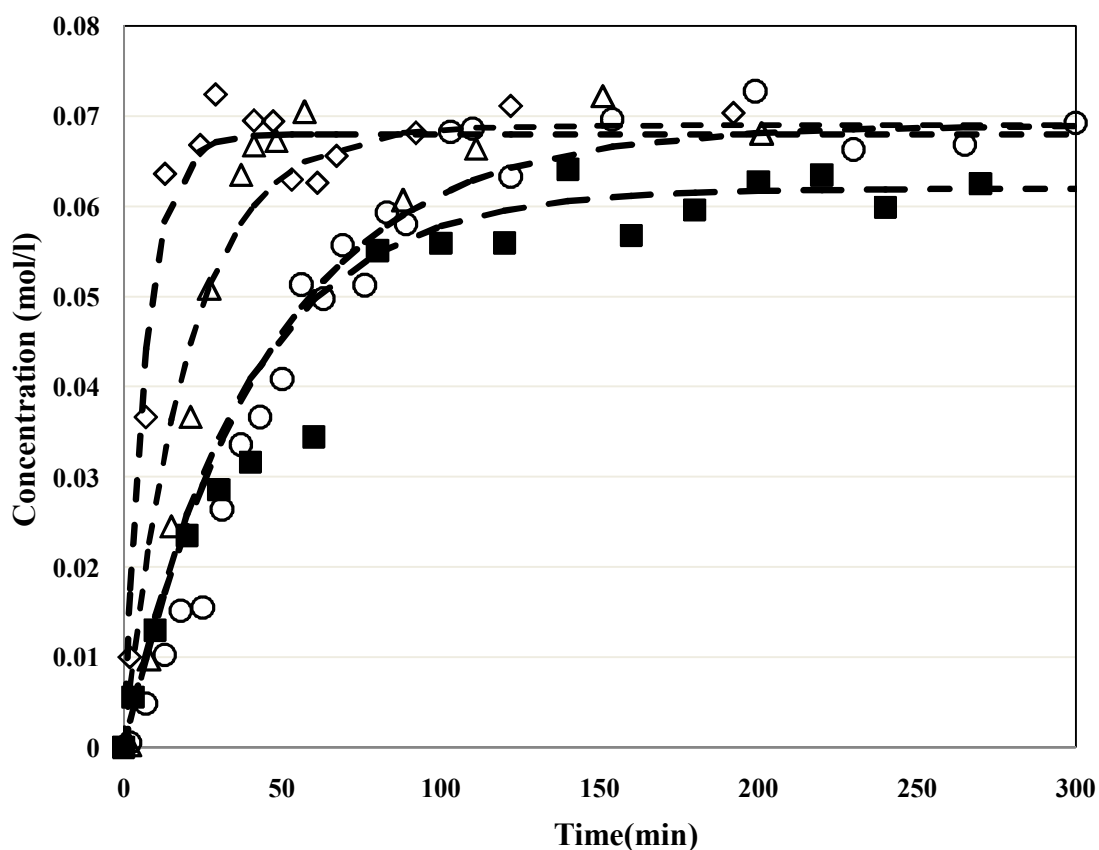


Figure 4.4 The concentration profile of benzene in aqueous phase versus time. Symbols: (\diamond) HNO₃; (Δ) CH₃COOH; (\circ) HCl and (\blacksquare) water. Experimental condition: Room temperature, 160 ml of 0.1M of acid solution.

Figure 4.4 illustrates the concentration of benzene in the aqueous phase versus time in 0.1 M of hydrochloric acid, nitric acid or acetic acid solution. It is found that the concentration of benzene in the nitric acid solution increases faster than in any acidic solution. The solubility rate of benzene concentration in the hydrochloric solution is about the same as of in water. While the solubility rate of

benzene concentration in the acetic solution is between the rate of nitric acid and hydrochloric acid solutions. The equilibrium concentration of benzene in any acid solutions, however, is about the same and slightly higher than the equilibrium concentration of benzene in the de-ionized water.

Three types of acid (nitric acid, hydrochloric acid and acetic acid) dissociate in water solution yielding hydrogen ions and different anions (NO_3^- , Cl^- and CH_3COO^- , respectively). The same ions from the three acids is hydrogen ions which may be the prime factor of the same equilibrium concentration of benzene in aqueous phase. Different anions, however, are deemed to affect the solubility rate whereas NO_3^- ions can give the highest solubility rate of benzene. In order to investigate the hypothesis that hydrogen ions gives the same equilibrium concentration of benzene and different anions give the different solubility rate, the solubility of benzene is tested in ammonium nitrate and ammonium chloride which dissociate in water solution yielding ammonium ions and two anions (NO_3^- and Cl^-). The results are shown in Figure 4.5

The results show that the equilibrium concentration of benzene in ammonium nitrate and ammonium chloride solutions is about the same as in the water. With respect to the solubility rate, the concentration of benzene in the ammonium nitrate solution increases faster than in ammonium chloride solution. From the observed result, the same ions from two solutions is ammonium ions which gives the same equilibrium concentration of benzene and NO_3^- ions can give the solubility rate of benzene concentration faster than Cl^- ions. Compared with the solubility test in three acid (nitric acid, hydrochloric acid and acetic acid), the result is in accord with the result in ammonium nitrate and ammonium chloride solution that NO_3^- and Cl^- affects the solubility rate and NH_4^+ does not affect the equilibrium concentration of benzene in aqueous phase.

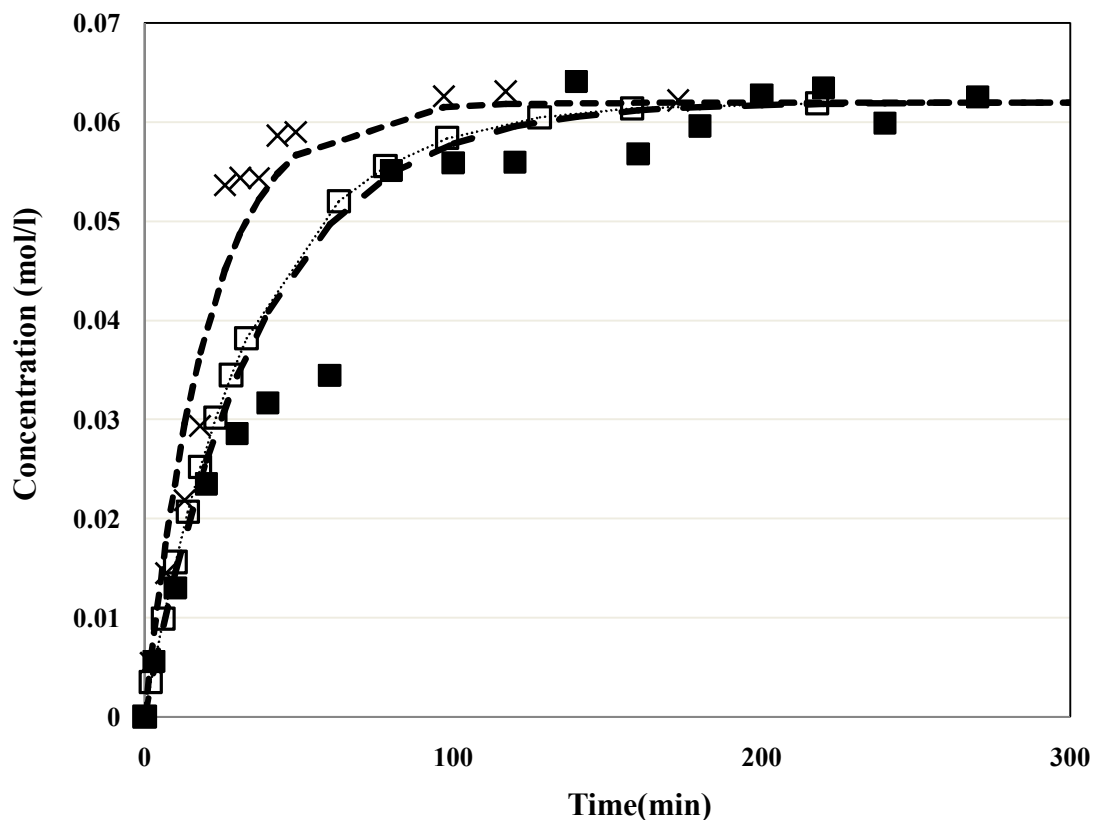


Figure 4.5 The concentration profile of benzene in aqueous phase versus time. Symbols: (x) NH₄NO₃; (□) NH₄Cl and (■) water. Experimental condition: Room temperature, 160 ml of 0.1M of acid solution.

The explanation of the effect of ions on the solubility of benzene in aqueous phase is some type of ions will change the extent and strength of hydrogen bonding which is a network structuring of water. By the principle of solubility, substrate A to be soluble, their molecules must be passed into molecules of substrate B whereas the interaction force in substrate B must be weaker than the interaction force between substrate A and B. On the contrary, if the interaction force in substrate B is stronger than the interaction force between substrate A and B, substrate A can not solute in substrate B. For example, saturated hydrocarbon molecule which is held together by Van der waals forces and water molecule which is held together by hydrogen bonds (H-bonds is stronger than Van der waals forces) therefore hydrocarbon molecules can not solute in water or have little water solubility. At high temperature, the strength of

hydrogen bonds in water molecule decreases, therefore, more hydrocarbon molecules can dissolve.

In this way, hydrogen bonds of water molecule must be broken to dissolve appreciable quantities of non-polar substances in water. Small or multiply-charged ions, with high charge density, called “kosmotropes”, have stronger interactions with water molecules than water with itself. Therefore, the breaking water-water hydrogen bonds leads to more benzene can dissolve in aqueous phase. Large singly charged ions, with low charge density, called “chaotropes”, have weaker interactions with water than water with itself. It has little interfering in the hydrogen bonding of the surrounding water so it does not affect the benzene solubility in water. More information is given in appendix F.

With respect to the solubility test in three acids (HNO_3 , HCl and CH_3COOH), the same equilibrium concentration of benzene in aqueous phase which is higher than in the de-ionized water because three types of acid dissociate in water solution yielding H^+ this is kosmotropes. In case of the solubility test in NH_4NO_3 and NH_4Cl solution, the equilibrium concentration of benzene in aqueous phase is about the same as in the water due to NH_4^+ is chaotropes ions. In addition, NO_3^- and Cl^- are also chaotropes ions.

Moreover, it has been reported that anions and cations seem to change the surface tension (Collins and Washabaugh, 1985). In agreement with surface tension, softer and more polarisable ions go closer to the interface. As a consequence, the surface tension increment is smaller for such ions. With respect to Jones–Dole viscosity B coefficient, negative values can be related to soft ions with low surface density. Positive values signify hard ion.

The first evidence of specific ion effects in aqueous solutions was discovered by Poiseuille in 1847, when he studied systematically their viscosities. In 1929, Jones and Dole proposed a description of the salt concentration dependence with the following equation (Jenkins and Marcus, 1995):

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (\text{eq. 4.2.1})$$

Where η and η_0 are the viscosities of the aqueous solution and pure water, respectively; A is an electrostatic term that is close to one, as long as the salt concentrations are not significantly higher than 0.1M; c is the molarity and B is the so-called Jones–Dole viscosity coefficient. For equally charged ions, the specificity is thus expressed with this B coefficient. The viscosity of neutral solutes would best be described with A = 0.

In the review paper by Jenkins and Marcus in 1995, a comprehensive collection of viscosity data and B coefficients can be found. Table 4.2 shows a few of these Jones–Dole coefficients.

Table 4.2 Jones–Dole viscosity B coefficients.

Cations	B	Anions	B
Mg ²⁺	0.385	PO ₄ ³⁻	0.590
Ca ²⁺	0.285	CH ₃ COO ⁻	0.250
Ba ²⁺	0.220	SO ₄ ²⁻	0.208
Li ⁺	0.150	F ⁻	0.100
Na ⁺	0.086	HCOO ⁻	0.052
H ⁺	0.068	Cl ⁻	-0.007
K ⁺	-0.007	Br ⁻	-0.032
NH ₄ ⁺	-0.007	NO ₃ ⁻	-0.046
Rb ⁺	-0.030	ClO ₄ ⁻	-0.061
Cs ⁺	-0.045	I ⁻	-0.068
		SCN ⁻	-0.103

From Table 4.2, nitrate ion shows more negative value of Jones–Dole coefficients than chloride ions. Therefore, nitrate ions is a softer ion than chloride ion lead to smaller surface tension of the solution (-0.046 for NO_3^- versus -0.007 for Cl). A small negative value of ammonium ions shows that it can decrease the surface tension of solution too. Although, proton and acetate ions have positive value of Jones–Dole coefficients which inhibits the solubility but the results show that proton and acetate ions can simulate the solubility. With respect to proton, the effect of proton on the breaking down of hydrogen bond is more dominant than the increase of viscosity of solution result in more amount of benzene can dissolve to aqueous phase. In case of acetate ions, this is due to the molecule of acetate ions has a non-polar part which can enhance the solubility of benzene. Moreover, giving $A = 0$ equation 4.2.1 will become.

$$\eta/\eta_0 = 1 + Bc \quad (\text{eq. 4.2.2})$$

If we substitute the value of nitrate ion and chloride ion from Table 4.2 in equations 4.2.2 with constant η_0 and c . When B is a negative value, η/η_0 will be less than 1. ie. lower viscosity. The more the negative value of B , the lower the viscosity of the aqueous solution.

From the Jones–Dole coefficients of chloride ions which close to zero, the value of η/η_0 is nearly equal to 1 that means small effect on water molecule which is the reason why the solubility rate in chloride ions solution is approximately the same as in water. In the same way of chloride ions, the equilibrium concentration of benzene in ammonium ions is the same as in water due to the Jones–Dole coefficients of ammonium ions close to zero.

Furthermore, the relationship between viscosity and surface tension of solution is shown in equation 4.2.3. According to Pelofsky in 1966, this empirical relation can be applied for both organic and inorganic phases of pure and mixed components. Several fluids were shown to follow these relations.

$$\ln \sigma = \ln A + \frac{B}{\eta} \quad (\text{eq. 4.2.3})$$

Where A and B are constants, σ is the surface tension, and η is the viscosity. The value of A and B are depended on type of fluid used. However, the value of $\ln A$ is always positive and the value of B is always negative. Hence, the lower the value of η leads to the lower the surface tension of the aqueous solution.

From the solubility test, the result shows that the solubility rate of benzene in nitrate ion solution is higher than in chloride ion solution. This can be explained that because of the lower surface tension and viscosity in nitrate ion solution than chloride ion solution lead to benzene can dissolve faster in nitrate ion solution.

In order to confirm the reasons mentioned above, an additional experiment was carried in 0.1 mol/l of sodium nitrate and sodium chloride solution. With 0.086 of Jones–Dole coefficients value for sodium ions, the surface tension in sodium nitrate and sodium chloride solution is higher than in pure water. Thus, the solubility rate and the equilibrium concentration of benzene in sodium nitrate and sodium chloride solution should lower than in pure water. The obtained results are compared in Figure 4.6.

The results show that the solubility rate and the equilibrium concentration of benzene in sodium nitrate and sodium chloride solutions are lower than pure water. In addition, the solubility rate and the equilibrium concentration of benzene in sodium nitrate solution is the same as in sodium chloride solution.

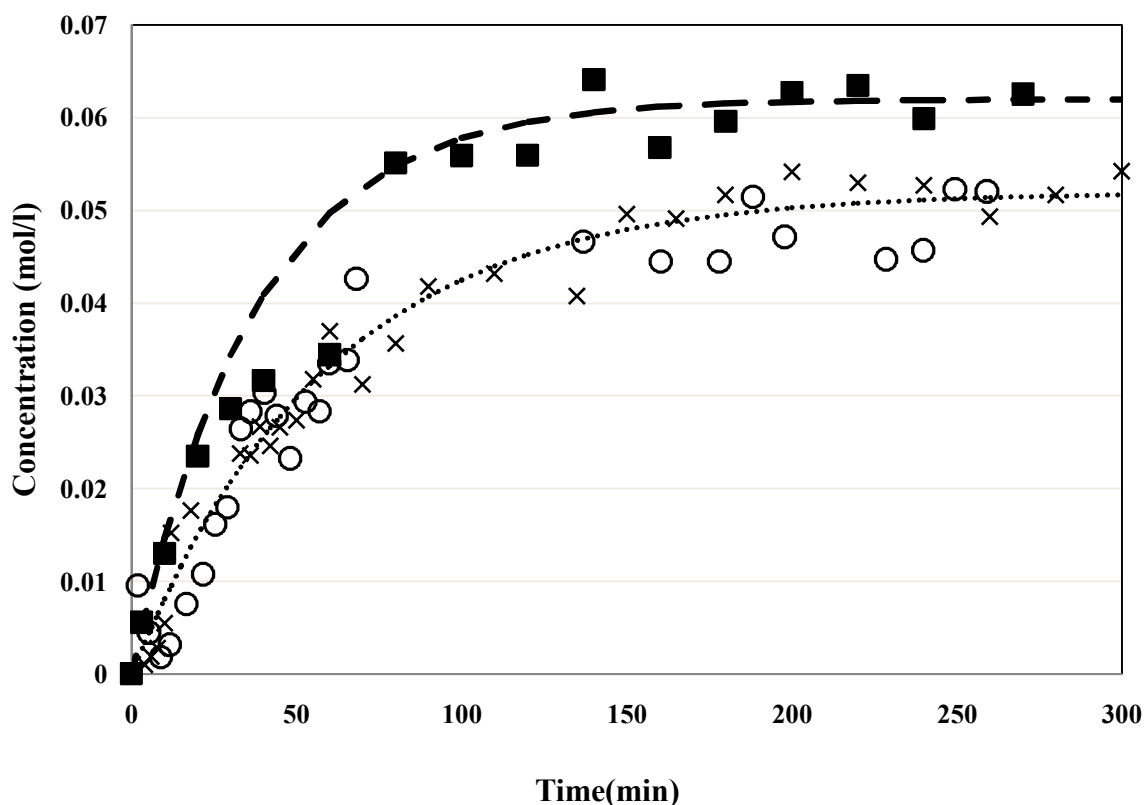


Figure 4.6 The concentration profile of benzene in aqueous phase versus time. Symbols: (x) NaNO₃; (o) NaCl and (■) water. Experimental condition: Room temperature, 160 ml of 0.1M of acid solution.

This is due to high positive value of Jones–Dole coefficients for sodium ions compared with nitrate ions and chloride ions (0.086 for Na⁺ versus -0.046 for NO₃⁻ and -0.007 for Cl⁻). Therefore, sodium ions dominates over nitrate ions and chloride ions.

From all observed results, the addition of ions (H⁺, NH₄⁺, NO₃⁻, Cl⁻, Na and CH₃COO⁻) can affect the solubility rate and equilibrium concentration of benzene in aqueous phase. The equilibrium concentration of benzene is increased by H⁺ breaks down hydrogen bond of water molecule and CH₃COO⁻ has a non-polar part which helps the solubility of benzene. In case of NH₄⁺, NO₃⁻, and Cl⁻, the faster solubility rate of benzene than pure water is exhibited owing to the decrease of surface tension

and viscosity of solution. Nevertheless, Na^+ increases surface tension and viscosity of solution lead to low solubility rate and amount of benzene in aqueous phase.

4.3 The effect of ions on the hydroxylation of benzene

4.3.1 The effect of reaction temperature on the hydroxylation of benzene with variation of ions

From the solubility test of benzene in aqueous phase, more benzene can dissolve in aqueous phase when using some acid as solvent. In this consequence, one may expect that if we increase the amount of benzene in aqueous phase, the conversion of hydrogen peroxide should increase. Four aqueous solutions containing nitric acid, acetic acid, ammonium nitrate and ammonium chloride are used in this study. The aqueous solutions containing nitric acid and acetic acid represent aqueous phase solutions having higher solubility rate and equilibrium concentration of benzene than pure water. The aqueous solutions containing ammonium nitrate represents aqueous phase solutions having higher solubility rate of benzene than pure water but with approximate the same equilibrium concentration. Finally, ammonium chloride solution represents the solution having the same rate and equilibrium concentration of benzene as pure water. The reaction was carried out at 70°C and 110°C. The experimental results are graphically illustrated in Figure 4.7.

As a results of the large amount of benzene used in this system in order to completely cover the surface of the solution; hence, hydrogen peroxide is a limited reactant. Therefore, the interpretation of all results in this research is depended on the conversion of hydrogen peroxide. Due to the fact that phenol is the only product, the calculation of the hydrogen peroxide conversion is shown in equation 4.3.1.1 below.

$$\text{Hydrogen peroxide conversion} = \frac{\text{mole}_{phenol}}{\text{mole}_{H_2O_2}} \times 100 \quad (\text{eq. 4.3.1.1})$$

At 70°C, when acidized by acetic acid and nitric acid at concentration 0.1 mol/l, the reaction exhibits higher phenol formed than in the pure water. The result obtained from the 0.1 mol/l ammonium chloride solution, the phenol formed shows about the same as in the water. With respect to acidification by ammonium nitrate, the phenol formed in 0.1 mol/l ammonium nitrate solutions is higher than in the pure water.

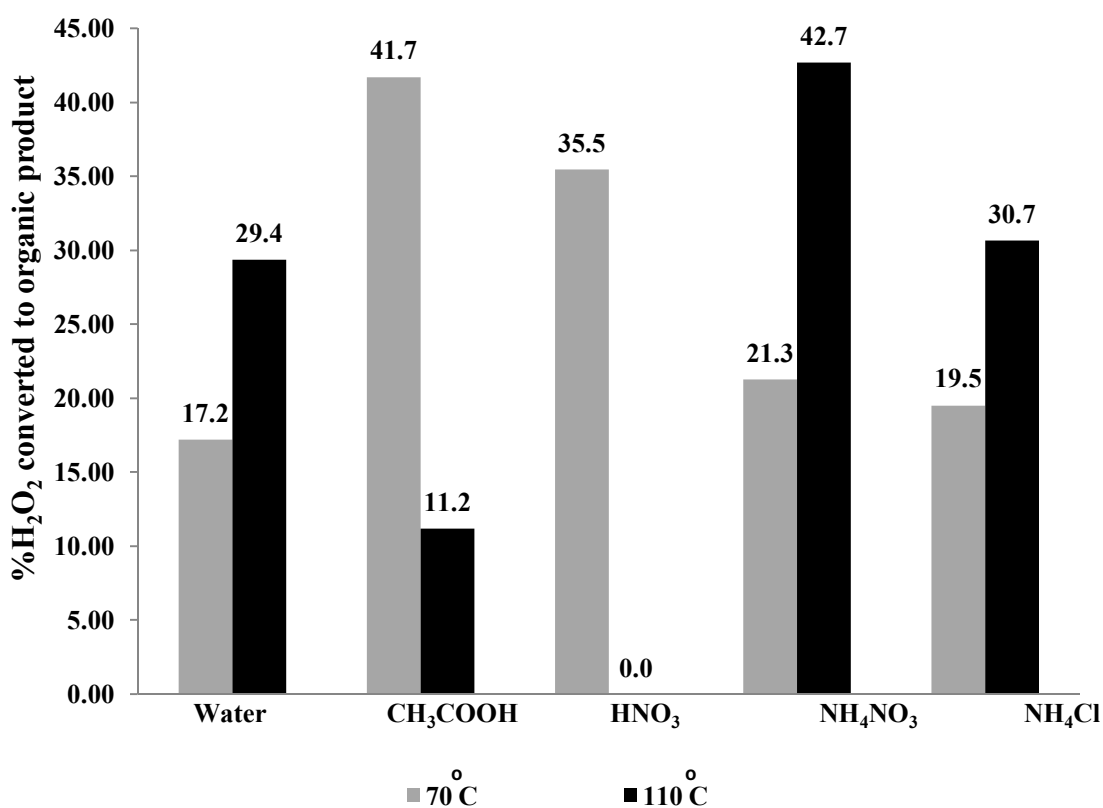


Figure 4.7 Percentage of hydrogen peroxide converts to phenol at reaction temperature 70°C and 110°C in solutions of HNO₃, CH₃COOH, NH₄NO₃ and NH₄Cl. Reaction condition: 0.1 mol of benzene and 0.01 mol of hydrogen peroxide, 1 g of TS-1 catalyst, 120 ml of solution, reaction time 2 hour and reaction temperature 70°C and 110°C.

It is found that the obtained result was as expected that the higher amount of benzene can dissolve in aqueous phase lead to the higher chance for the catalyst to contact with benzene. Thus, the conversion of hydroxyl peroxide should increase.

Please be reminded again that the solubility test is performed at room temperatures. Thus, the solubility rate and the equilibrium concentration of benzene at high temperature of reaction should increase from room temperature.

At 110°C, different results were observed. As the reaction temperature increase, the formation of phenol in pure water, ammonium nitrate and ammonium chloride solution keeps increasing. On the contrary, the percentage of conversion of hydrogen peroxide converted to organic products in acetic acid solution sharply drops and in case of nitric acid solution drops to zero.

In case of pure water, ammonium nitrate and ammonium chloride solution it is expected that before injecting hydrogen peroxide in to the reactor. All three systems have the same equilibrium concentration of benzene in water. As soon as hydrogen peroxide was injected into the aqueous phase, the concentration of benzene in the aqueous phase drops due to the hydroxylation reaction until reaching a new equilibrium concentration. The level of new equilibrium concentration depends on the solubility rate of benzene. Since ammonium nitrate solution has higher solubility rate of benzene than pure water and ammonium chloride solution, the new equilibrium concentration of benzene is higher, see Figure 4.7. Therefore, higher amount of benzene exists on the catalyst surface submersed in ammonium nitrate solution. This leads to higher percentage of conversion of hydrogen peroxide converted to organic product than using pure water or ammonium chloride solution which give approximately the same value.

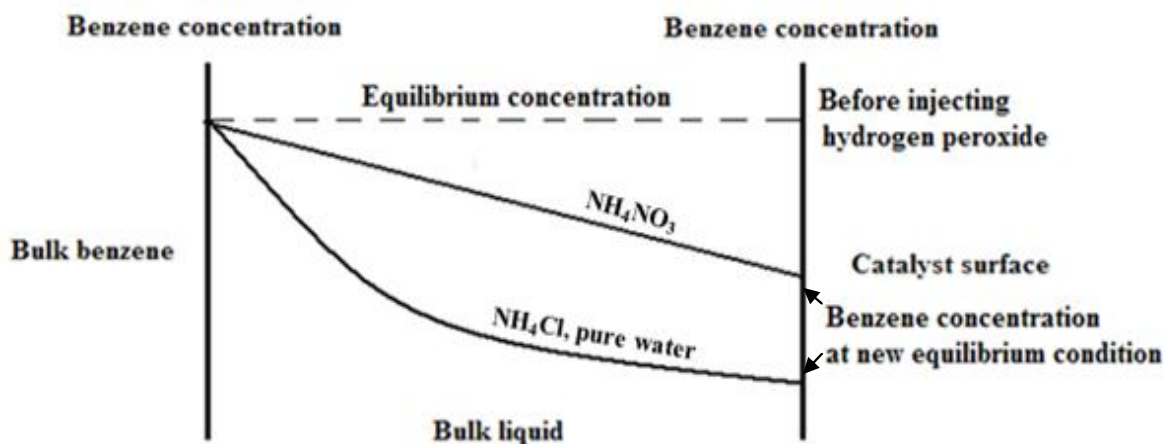


Figure 4.8 The profile of benzene concentration from bulk benzene to catalyst surface.

In order to confirm the reasons mentioned above, an additional experiment was carried in 0.1 mol/l of sodium nitrate and sodium chloride solution which has lower solubility rate and equilibrium concentration of benzene than pure water. If the solubility rate affects the reaction, the hydrogen peroxide conversion in sodium nitrate and sodium chloride solution should lower than in pure water. The obtained results are compared graphically in Figure 4.9.

From Figure 4.9, the obtained results comply with the expectation that the hydrogen peroxide conversion in sodium nitrate and sodium chloride solution should lower than in pure water due to the lower solubility rate and the equilibrium concentration of benzene in sodium nitrate solution than pure water.

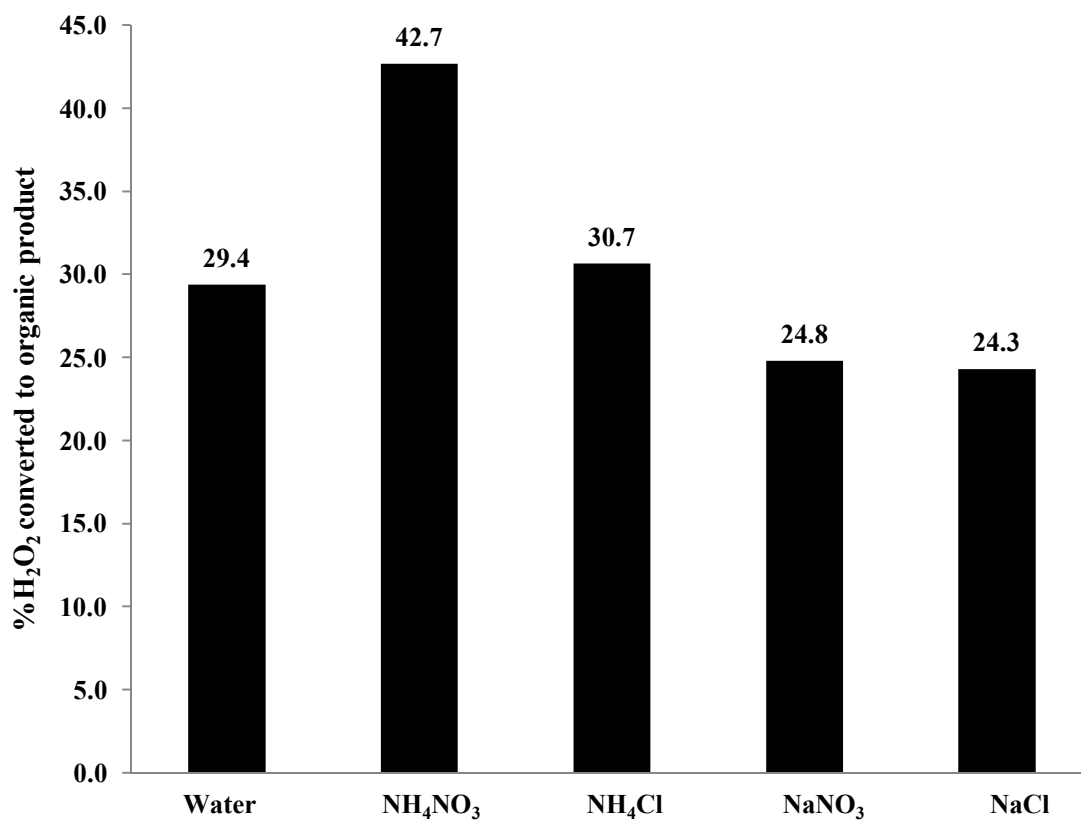


Figure 4.9 Percentage of hydrogen peroxide converts to phenol at reaction temperature 110°C in solutions of 0.1M NH₄NO₃, NH₄Cl, NaNO₃ or NaCl. Reaction condition: 0.1 mol of benzene and 0.01 mol of hydrogen peroxide, 1 g of TS-1 catalyst, 120 ml of solution, reaction time 2 hour and reaction temperature 110°C

The results obtained from using acid solutions can be explained by using Langmuir-Hinshelwood kinetic model. In this case, two substrates (A and B) will adsorb on the catalyst surface and react to produce product. As a result of the surface coverage, the catalyst surface is covered by substrate B at low concentration of A which leads to low reaction rate because of few amount of reacted substrate A. Thus, if we continue to increase the concentration of A, the increase amount of A on the catalyst surface will increase the reaction rate. At highest reaction rate, the amount of substrate A adsorbed on catalyst surface is the same as amount of substrate B. After that if we continue to increase the concentration of A, the increasing of substrate A will cause an adsorption hindrance of B which leads to low reaction rate again.

Although the molar ratio of substrates A and B necessary on the catalyst surface to produce highest reaction rate is 1:1, it does not mean we must have the same concentration of A and B in bulk liquid. As a result of the ability of adsorption between catalyst surface and substrate, if the catalyst surface can adsorb the same amount of two substrates, the concentration of two substrates in bulk liquid should be equal in order to make the same amount of two substrates on catalyst surface. In this way, if substrate A can adsorb on the catalyst surface more than B, the higher amount of substrate B than A in bulk liquid should be required.

In case of pure water, ammonium chloride or ammonium nitrate solution, the concentration of benzene on catalyst surface at 70°C is lower than the maximum conversion point. On the contrary, the concentration of benzene on catalyst surface at 70°C in nitric acid and acetic acid solution is likely more than the maximum conversion point.

When the temperature is increased, more amount of benzene can dissolve into the aqueous phase. The hydrogen peroxide conversion increases when pure water, ammonium chloride or ammonium nitrate solution is used. For example, the situation in ammonium nitrate solution is shown in Figure 4.10 by going from point A to point B. This is due to more amount of benzene on the catalyst surface react with hydrogen peroxide. The decreasing of hydrogen peroxide conversion in nitric acid and acetic acid solution (e.g. point C to point D as shown in Figure 4.10) is exhibited because the excessive of benzene on catalyst surface caused a diffusion hindrance of hydrogen peroxide to catalyst surface. The relationship between the change in surface concentration of benzene and reaction rate when using different aqueous media and reaction temperatures are shown in Figure 4.10.

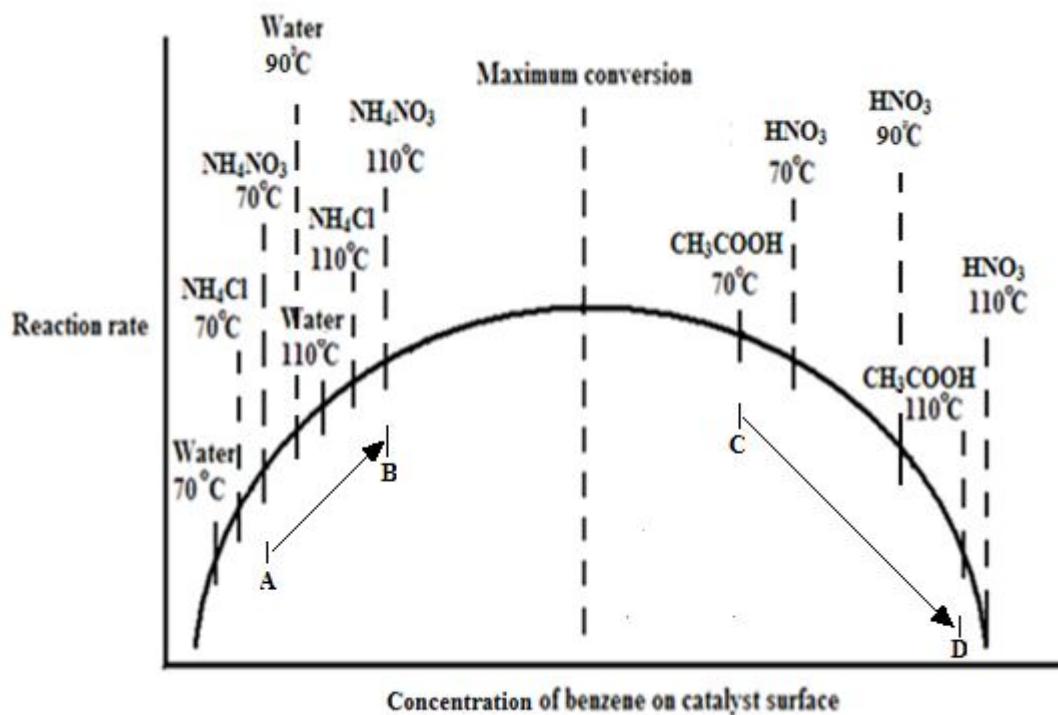


Figure 4.10 The relationship between the concentration of benzene on catalyst surface at different reaction temperature and aqueous media and reaction rate (Langmuir-Hinshelwood model).

In order to confirm the reasons mentioned above, an additional experiment was carried at 90°C using water and HNO₃ solution as reaction media. The obtained results are compared graphically with the results obtained 70°C and 110°C in Figure 4.11.

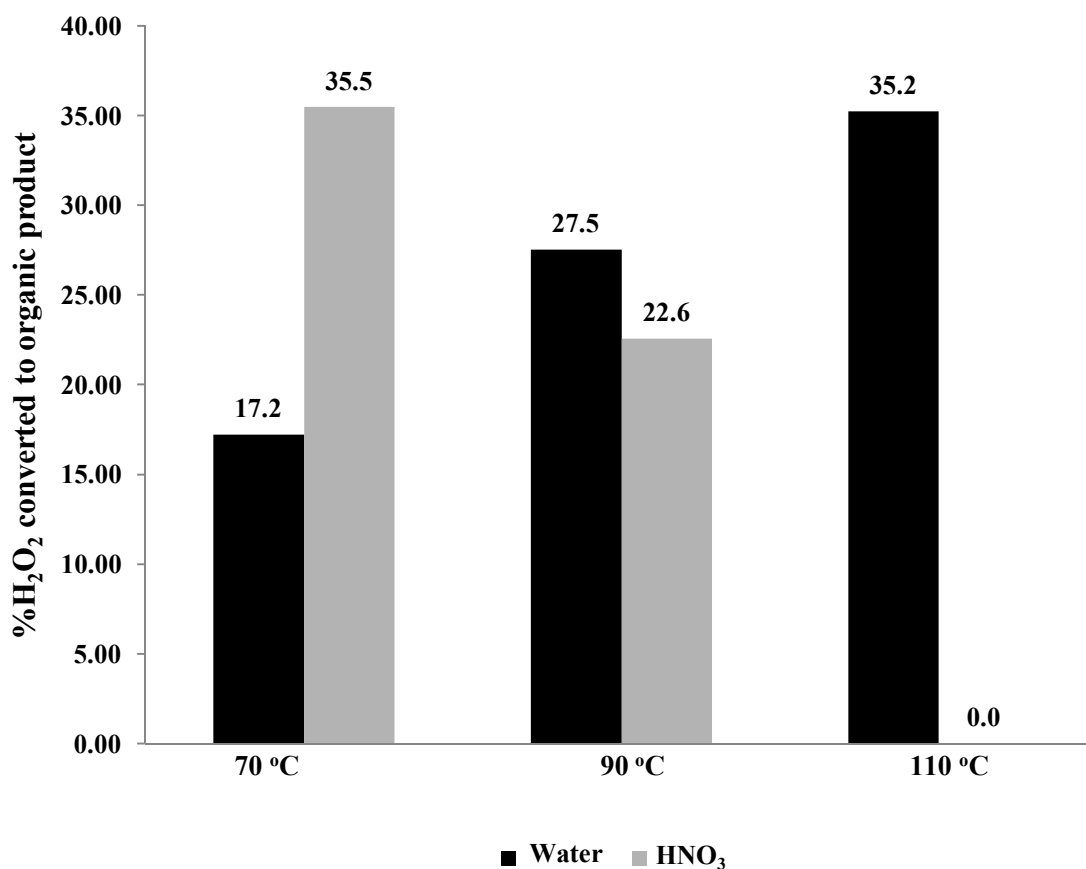


Figure 4.11 Percentage of hydrogen peroxide converts to phenol at reaction temperature 70°C, 90°C and 110°C in solution of 0.1M HNO₃ and water. Reaction condition: 0.1 mol of benzene and 0.01 mol of hydrogen peroxide, 1 g of TS-1 catalyst, 120 ml of solution, reaction time 2 hour and reaction temperature 70°C, 90°C and 110°C.

Figure 4.11 illustrates the effect of ions on the percentage of hydrogen peroxide converted to phenol obtained with different temperatures (70°C, 90°C and 110°C) in 0.1 mol/l of concentration of nitric acid and water. When the reaction temperature is increased, phenol formed is nearly twice increased when the reaction is performed in pure water which has low solubility rate of benzene. On the contrary, it is found that the phenol forms in nitric acid solution when the reaction temperature increase from 70 °C to 110 °C decreases significantly.

The increasing of reaction temperature, which results in increasing the solubility rate and equilibrium concentration of benzene in aqueous phase, causes the excessive amount of benzene dissolve in nitric acid solution. In spite of the increasing of temperature, this phenomenon does not occur in pure water due to the low solubility rate of benzene.

With respect to the amount of benzene in aqueous phase, from preliminary calculation by using the solubility data at room temperature, it shows that 0.006-0.007 mol of benzene and 0.01 mol of hydrogen peroxide exists in the aqueous phase which is closely approximate. When the reaction temperature is increased, the more amount of benzene in aqueous phase results in increasing a chance of the excessive of benzene absorbed on the catalyst surface and diffusion hindrance of hydrogen peroxide to catalyst surface. Hence, the excessive amount of benzene (in case of the addition of acid with increasing reaction temperature) causes low conversion.

Although benzene and hydrogen peroxide necessary to react with molar ratio 1:1, it does not mean using the same concentration of benzene and hydrogen peroxide in bulk liquid. As a result of the hydrophobic in nature of catalyst surface, the higher amount of hydrogen peroxide than benzene in bulk liquid should be required in order to avoid the excessive of benzene absorbed on the catalyst surface.

It is found that the obtained result was as expected that this reaction can be described by Langmuir-Hinshelwood model which optimal amount of two substrates adsorb on catalyst surface is necessary to reach the maximum conversion.

4.3.2 The effect of amount of ions on the hydroxylation of benzene

In order to further confirm the hypothesis that the solubility rate and equilibrium concentration of benzene can affect the reaction, the reaction is additionally performed at different amount of ions in solution (0.017 mol/l of each acid). At low amount of ions in solution, the solubility rate and equilibrium concentration of benzene will decrease. The observed conversion of hydrogen

peroxide should increase with using solvent (nitric acid, hydrochloric acid and acetic acid) which has too high solubility rate and equilibrium concentration. This is due to the excessive amount of benzene in aqueous phase when 0.1 mol/l of solution is used at 110 °C. If the substitution rate of benzene to reacted benzene in aqueous phase affects the reaction, the observed conversion of hydrogen peroxide should decrease with using solvent (ammonium nitrate) which has not high solubility rate and equilibrium concentration of benzene. Moreover, the conversion of hydrogen peroxide obtained from ammonium chloride should be the same as in water and the previous concentration (0.1 mol/l) due to ammonium chloride does not affect the solubility rate and equilibrium concentration of benzene. The results obtained are shown in Figure 4.12.

Figure 4.12 shows the effect of ions on the percentage of hydrogen peroxide converted to phenol obtained at 110 °C of reaction temperature with different amount of ions in solution (0.1 mol/l and 0.017 mol/l). When the concentration of the acid solutions is decreased to 0.017 mol/l, different results are observed. More phenol formed is found for nitric acid solution but still lower than in the de-ionized water. For the hydrochloric acid solution, decrease the concentration of hydrochloric acid from 0.1 mol/l to 0.017 mol/l results in a slight increase in the amount of phenol forms. The result obtained from the acetic acid solution shows an interesting phenomenon. It is found that the phenol forms when the concentration of acetic acid is decreased from 0.1 mol/l to 0.017 mol/l increase nearly four times and higher than in the de-ionized water. For the decreasing of the concentration of ammonium nitrates solution from 0.1 mol/l to 0.017 mol/l, the amount of phenol formed decrease. Although the concentration of ammonium chloride is decreased from 0.1 mol/l to 0.017 mol/l, the phenol formed is the same as in using water.

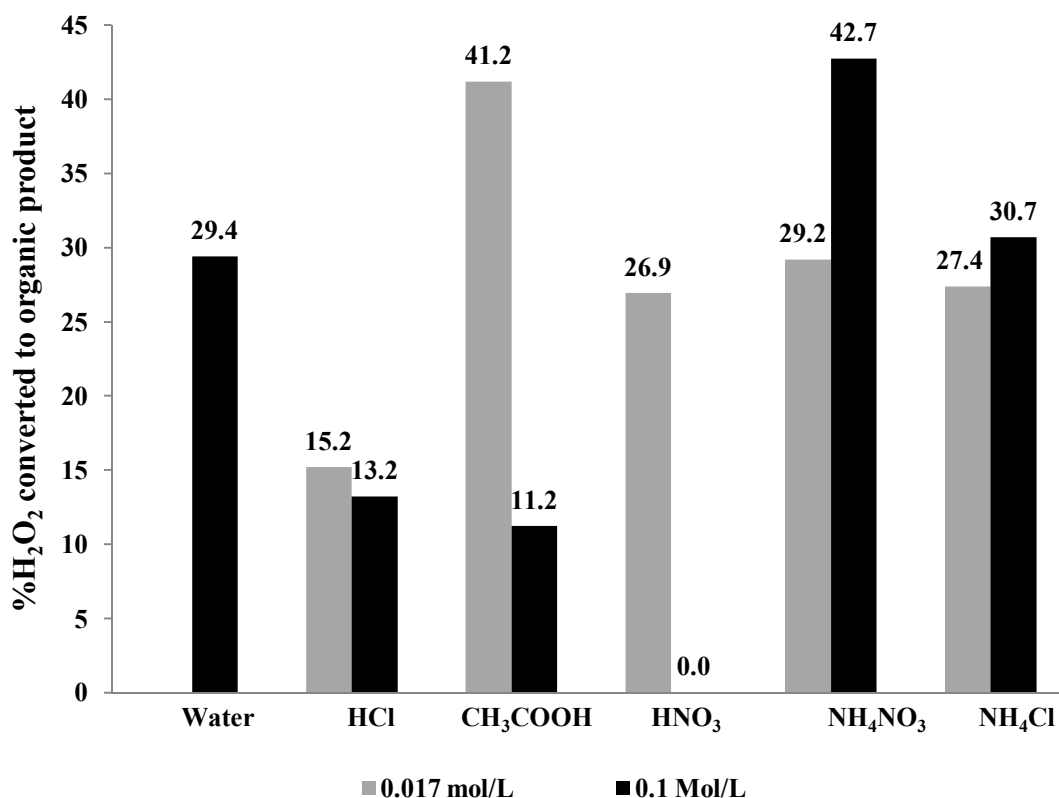


Figure 4.12 Percentage of hydrogen peroxide converts to phenol at reaction temperature 110°C in solutions of 0.1M and 0.017M of HNO₃, HCl, CH₃COOH, NH₄NO₃ and NH₄Cl. Reaction condition: 0.1 mol of benzene and 0.01 mol of hydrogen peroxide, 1 g of TS-1 catalyst, 120 ml of solution, reaction time 2 hour and Temperature 110°C.

The obtained results can be graphically illustrated using Langmuir-Hinshelwood model as shown in Figure 4.13. In case of pure water, 0.1 mol/L of ammonium chloride or ammonium nitrate solution, the concentration of benzene on catalyst surface is lower than the maximum conversion point. When the concentration of ammonium chloride or ammonium nitrate solution is decreased to 0.017M, the hydrogen peroxide conversion slightly increases due to more amount of benzene on the catalyst surface. For example, the phenomenon in ammonium nitrate solution is shown in Figure 4.13 by going from point A to point B.

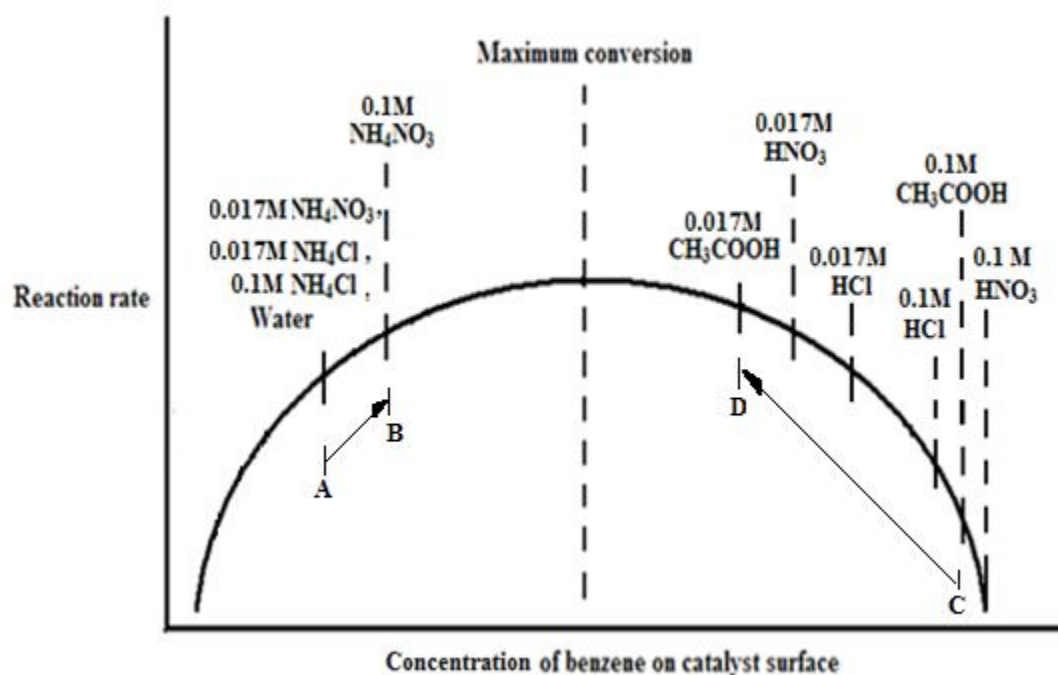


Figure 4.13 The relation between the concentration of benzene on catalyst surface at different concentration of a variety of aqueous media and reaction rate (Langmuir-Hinshelwood model).

On the contrary, the concentration of benzene on catalyst surface in 0.1M nitric acid and acetic acid solution is likely more than the maximum conversion point. For the decreasing of the concentration of nitric acid and acetic acid solution (e.g. point C to point D as shown in Figure 4.13) from 0.1mol/l to 0.017 mol/l, the increasing of hydrogen peroxide conversion is exhibited due to the decreasing of the excessive of benzene which intercepts the diffusion of hydrogen peroxide to catalyst surface.

It is found that the obtained results comply with the hypothesis that the solubility rate and equilibrium concentration of benzene can affect the reaction. These results suggested that the optimization of solubility rate of benzene to replace in reacted benzene on the catalyst surface is required for this reaction. This is due to the changing of solubility rate of benzene can change the mass transfer resistance of this reaction. Furthermore, the optimum amount of benzene adsorbed on the catalyst surface will simulate the reaction.

Furthermore, an additional experiment is performed at 70°C using 0.017 mol/l of acetic acid solution in order to confirm the expectation. The observed conversion of hydrogen peroxide obtained from 0.017 mol/l of acetic acid at 70°C should be lower than the result obtained from 0.1 mol/l because the solubility rate at 0.01 mol/l is lower than at 0.1 mol/l. From the experimental results reported in Sections 4.3.1, the conversion of hydrogen peroxide obtained from 0.017 mol/l of acetic acid at 110°C is higher than the conversion at 0.1 mol/l because of the excessive solubility rate of benzene at high temperature. The results are shown in Figure 4.14.

Figure 4.14 shows the effect of ions on the percentage of hydrogen peroxide converted to phenol obtained with different temperature (70°C and 110°C) at 0.1 mol/l and 0.017 mol/l of concentration of acetic acid. At low reaction temperature, the high concentration of acetic acid gives more hydrogen peroxide conversion than using low concentration. On the other hand, the low concentration of acetic acid gives more hydrogen peroxide conversion than using high concentration at high reaction temperature. It is found that the concentration of acid or reaction temperature should not too high or too low but should be at an optimum to compromise between the solubility rate and the equilibrium concentration of benzene.

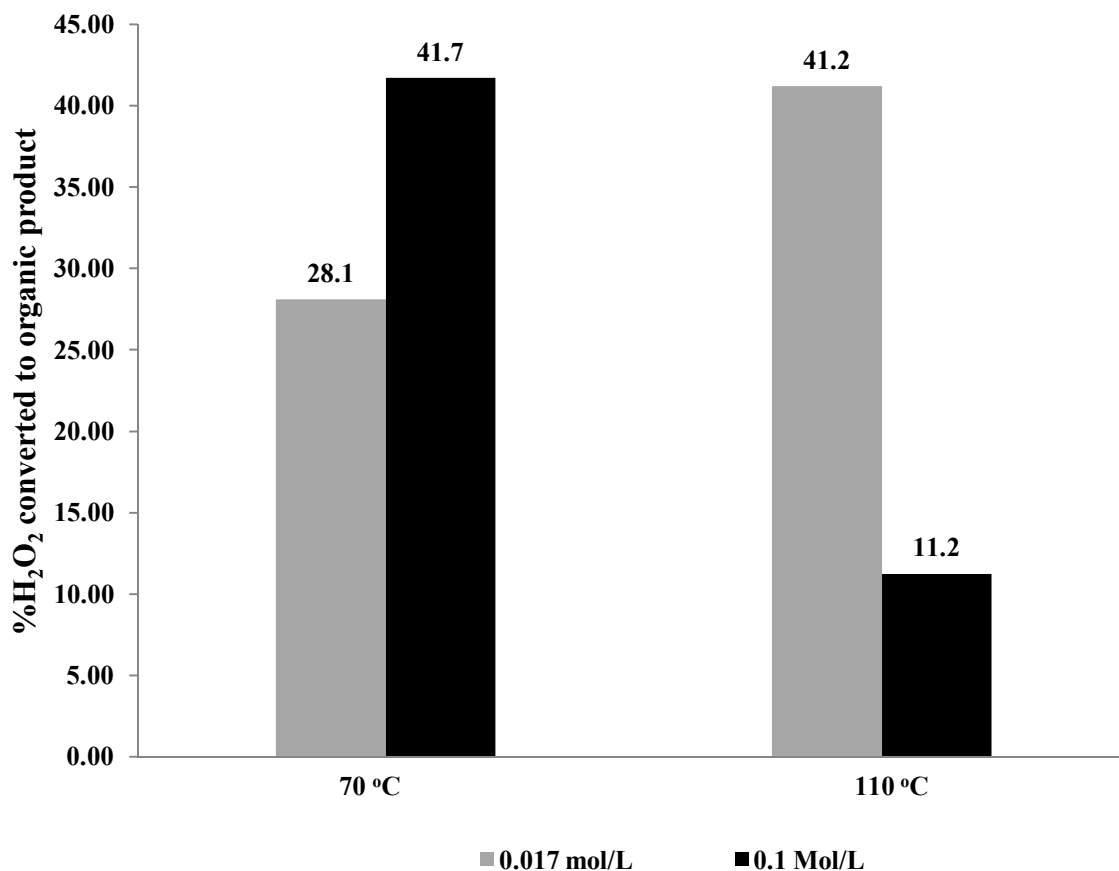


Figure 4.14 Percentage of hydrogen peroxide converts to phenol at reaction temperature 70°C and 110°C in solutions of 0.1M and 0.017M CH₃COOH. Reaction condition: 0.1 mol of benzene and 0.01 mol of hydrogen peroxide, 1 g of TS-1 catalyst, 120 ml of solution, reaction time 2 hour, pressure 2 barg and reaction temperature 70°C and 110°C.

From all of observed results, these are in line with the expectation that the addition of ions affect the solubility rate and equilibrium concentration of benzene. Furthermore, it is proved that the conversion of hydrogen peroxide increases significantly if the solubility rate and equilibrium concentration of benzene is at the optimum point.

4.3.3 The effect of hydrochloric acid on the hydroxylation of benzene

Although, the same equilibrium concentration of benzene in aqueous phase is higher in all acid solution but different reaction result is obtained from aqueous phase acidified by hydrochloric acid. When the reaction temperature is increased, the hydrogen peroxide conversion in 0.1 mol/l of acetic acid solution sharply drops and in case of nitric acid solution drops to zero. On the contrary, it is found that the phenol forms when the reaction temperature of hydrochloric acid solution is increase from 70 °C to 110°C increase from 5.5% to 13.2%. The observed results are shown in Figure 4.15.

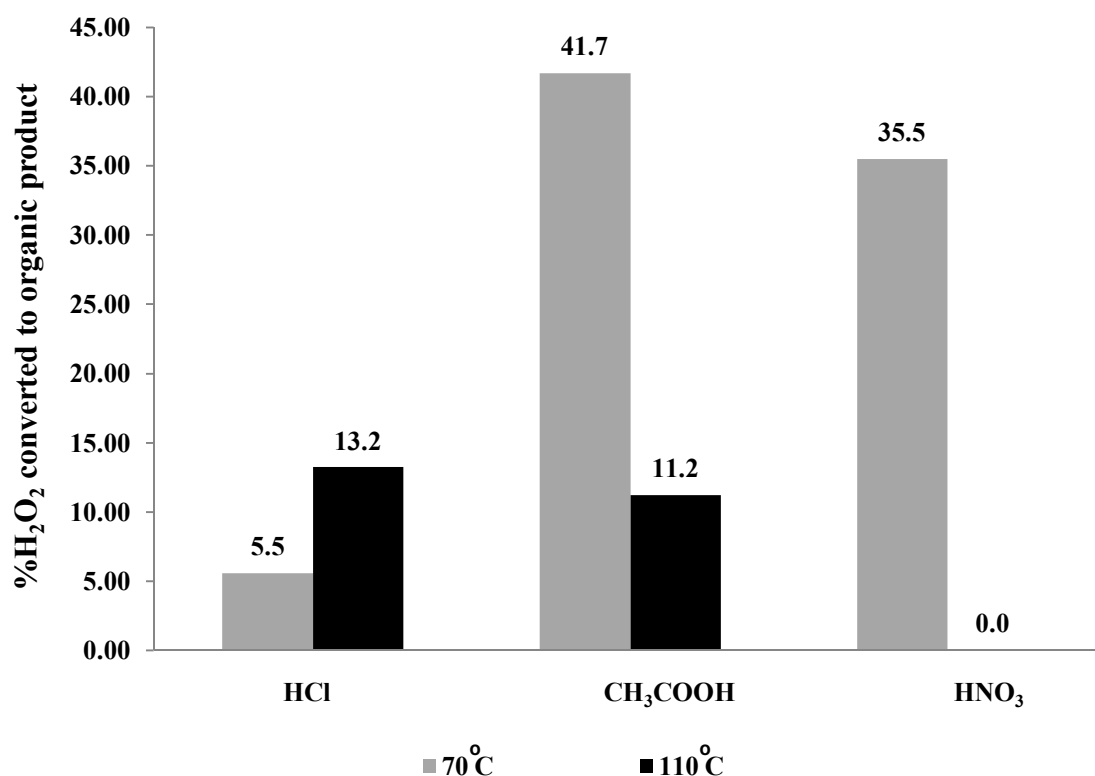


Figure 4.15 Percentage of hydrogen peroxide converts to phenol at reaction temperature 70°C and 110°C in solutions of 0.1M HCl, CH₃COOH and HNO₃. Reaction condition: 0.1 mol of benzene and 0.01 mol of hydrogen peroxide, 1 g of TS-1 catalyst, 120 ml of solution, reaction time 2 hour, pressure 2 barg and reaction temperature 70°C and 110°C.

This is possibly due to the formation of HOCl which formed when chloride ions react with hydroxyl radical (OH·). HOCl is an oxidizer. With the different property of oxidize and adsorption ability on the catalyst surface between H₂O₂ and HOCl, the different results in hydrochloric acid are observed.

This phenomenon is disclosed from another parallel research in the oxidation of toluene in the same reaction system (Kaenthong, 2012). That research reports that the different selectivity of product (benzaldehyde, ortho-cresol and para-cresol) is obtained by the changing of solvent (hydrochloric acid and nitric acid). Para-cresol is formed when hydrochloric acid is used whereas only benzaldehyde is only detected when using nitric acid. As a result of the different selectivity of product, it can imply that new oxidizer is formed beside hydrogen peroxide.

Conclusions

From the experimental results discussed in this chapter, the following conclusions can be drawn.

- (i) The amount of benzene adsorbed on the catalyst surface is the important factor for the progress of the reaction.
- (ii) The factors which affect the amount of benzene adsorbed on the catalyst surface are;
 - (a) the equilibrium concentration of benzene in aqueous phase, and
 - (b) the solubility rate of benzene from surface layer to aqueous phase.

- (iii) The equilibrium concentration of benzene in the aqueous phase affects the starting of the reaction. In this research, we enhance the amount of benzene in aqueous phase before the occurring of the reaction. Thus, the excessive amount of benzene adsorbed on the catalyst surface causes the diffusion hindered of hydrogen peroxide to catalyst surface lead to low conversion.

- (iv) From preliminary calculation of the amount of benzene in aqueous phase by using the solubility data at room temperature, it shows that 0.006-0.007 mol of benzene and 0.01 mol of hydrogen peroxide exists in the aqueous phase which is closely approximate. Therefore, if more amount of benzene dissolve to aqueous phase before the starting of the reaction, the reaction will undergo the excessive of benzene absorbed on the catalyst surface. Hence, the excessive amount of benzene (in case of the addition of acid with increasing reaction temperature) causes low conversion.

- (v) Nevertheless, the solubility rate of benzene from surface layer to aqueous phase is the important factor to stipulate the reaction. From the observed result, it shows that using salt (ammonium nitrate) which gives fast solubility rate but not high equilibrium concentration of benzene leads to more phenol formed.

- (vi) Finally, either the increasing of reaction temperature or the addition of some ions, the optimization of solubility rate and equilibrium concentration of is required for this reaction to reach high conversion.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

In the present work, the effects of ions (H^+ , NH_4^+ , NO_3^- , Na^+ , Cl^- and CH_3COO^-) on the solubility of benzene in aqueous phase and hydroxylation of benzene to phenol is studied. The conclusions obtained from all experiments results are summarized in section 5.1. In addition, recommendations are given in section 5.2.

5.1 Conclusions

- The addition of ions in solution can affect the equilibrium concentration of benzene in aqueous phase. The equilibrium concentration of benzene increased by the addition of H^+ while NH_4^+ does not affect. This is due to the additions of ions will break down the extent and strength of hydrogen bonding which is a network structuring of water.

- The addition of ions in solution can affect the solubility rate of benzene in aqueous phase. The solubility rate is in following order $NO_3^- > CH_3COO^- > Cl^- > Na^+$. As a result of the changing of surface tension, the solubility rate in NO_3^- solution is faster than in Cl^- solution. In case of CH_3COO^- , the molecule has a part of non-polar which can help benzene to dissolve. Nevertheless, Na^+ increases surface tension and viscosity of solution lead to low solubility rate and amount of benzene in aqueous phase.

- The addition of ions should not adsorb on the catalyst surface because of the hydrophobic of the catalyst surface.

- The solubility rate and equilibrium concentration of benzene can affect the hydroxylation of benzene to phenol. Hence, the optimal rate of benzene dissolved from the top surface of the reactor to aqueous phase is required to this reaction in order to replace in reacted benzene. In this way, using solvent which helps the

optimization of solubility rate and equilibrium concentration of benzene in aqueous phase can help the reaction reach high conversion. The maximum hydrogen peroxide conversion in this research is obtained from 0.1 M of ammonium nitrate solution at 110 °C of reaction temperature.

- The excessive solubility rate and equilibrium concentration of benzene in aqueous phase lead to inhibit the reaction. This is owing to the excess amount of benzene in aqueous phase will cover the catalyst surface cause a diffusion hindrance of benzene molecule into catalyst's channel and the competitive absorption of solvent with hydrogen peroxide to adsorb on TS-1 catalyst.

- The hydroxylation of benzene to phenol by hydrogen peroxide over TS-1 catalyst is explained by Langmuir-Hinshelwood model which the adsorption of two reactants on catalyst's surface is necessary for the reaction to occur but between two substances may have only one of them adsorbed on the catalyst surface lead to the decreasing of reaction rate.

5.2 Recommendations

The maximum conversion of hydrogen peroxide should be found in this reaction system by compromise between the concentration of solution and the reaction temperature. However, solubility test should be performed at the same condition as the reaction condition (110°C and 2 barg) to ensure the change in conversion of hydrogen peroxide.

For future work, due to the hydrophobic in nature of catalyst surface which prefers to adsorb a non-polar molecule more than a polar molecule, the changing of catalyst surface to hydrophilic should be tested in order to avoid the excessive of benzene cover the catalyst surface.

REFERENCES

- Balducci, L., and others. Direct oxidation of benzene to phenol with hydrogen peroxide over a modified titanium silicalite. Angewandte Chemie-International 42 (2003): 4937-4940.
- Bengoa, J. F., Gallegos, N. G., Marchetti, S. G., Alvarez, A. M., Cagnoli, M. V. and Yeramian, A. Influence of TS-1 structural properties and operation conditions on benzene catalytic oxidation with H₂O₂. Microporous and Mesoporous Materials 24 (1998): 163-172.
- Bhaumik, A., Mukherjee, P. and Kumar, R. Triphase catalysis over titanium-silicate molecular sieves under solvent-free conditions I. Direct hydroxylation of benzene. Journal of Catalysis 178 (1998): 101-107.
- Bianchi, D., and others. Oxidation of benzene to phenol with hydrogen peroxide catalyzed by a modified titanium silicalite (TS-1B). Advanced Synthesis & Catalysis 349 (2007): 979-986.
- Chammingkwan, P., Hoelderich, W. F., Mongkhonsi, T., Kanchanawanichakul P. Hydroxylation of benzene over TS-PQTM catalyst. Applied Catalysis A: General 352 (2009): 1-9.
- Collins, K.D. and Washabaugh, M.W. The Hofmeister effect and the behaviour of water at interfaces. Quart. Rev. Biophys 18(1985): 323-422.
- Gao, X. H. and Xu, J. A new application of clay-supported vanadium oxide catalyst to selective hydroxylation of benzene to phenol. Applied Clay Science 33 (2006): 1-6.
- Grossfield, A., Ren, P. and Ponder J. W. Ion solution thermodynamics from simulation with a polarizable force field. J. Am. Chem. Soc. 125 (2003): 15671-15682.
- Hajdu, F. A model of liquid water Tetragonal clusters: description and determination of parameters, Acta Chim. (Budapest) 93 (1977): 371-394.

- He, J., Xu, W. P., Evans, D. G., Duan, X., Li, C. Y. Role of pore size and surface properties of Ti-MCM-41 catalysts in the hydroxylation of aromatics in the liquid phase. Microporous and Mesoporous Materials 44 (2001): 581-586.
- Hu, X., Zhu, L., Guo, B., Liu, Q., Li, G., Hu, C. Hydroxylation of benzene to phenol via hydrogen peroxide in hydrophilic triethylammonium acetate ionic liquid. CHEM. RES. Chinese university 27 (2011): 503—507.
- Jenkins, H. D. B. and Marcus, Y. Viscosity B-coefficients of ions in solution. Chem. Rev. 95 (1995): 2695–2724.
- Kaenthong, S. effect of ions in electrolyte solution of the oxidation reaction of toluene to benzaldehyde over Al-TS-1 catalyst. Master's thesis, Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University, 2012.
- Kasemsukphaisan, N. Effect of acidity of solution on the reaction between toluene and hydrogen peroxide over TS-1. Master's thesis, Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University, 2009.
- Kumar, R., Mukherjee, P. and Bhaumik, A. Enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/H₂O₂ under solvent-free triphase conditions. Catalysis Today 49 (1999): 185-191.
- Lemke, K., Ehrich, H., Lohse, U., Berndt, H. and Jahnisch, K. Selective hydroxylation of benzene to phenol over supported vanadium oxide catalysts. Applied Catalysis A:General 243 (2003): 41-51.
- Meng, T., Yang, C., Wang, D., Xia, T., Zhang, L. A new process for the direct hydroxylation of benzene to phenol. Journal of Beijing University of Chemical Technology (Natural Science) 38 2011, No. 2.
- Mitpapan, S. Benzene hydroxylation by hydrogen peroxide at elevated temperature over titanium silicalites-1 catalyst. Master's thesis, Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University, 2010.

- Mongkhonsi, T. and Mitpapan, S. (2011) Hydroxylation of benzene to phenol over TS-1 catalyst at elevated temperature. Journal of Pathumwan Institute of technology 2 (2011): 5-10.
- Pelofsky, A.H. Study Surface Tension and Viscosity for mixed alkanes. J. Chem. Eng. Data 11 (1966): 394-397.
- Sales-Curz, M., Gani, R. Product and process design through ICAS. TUTORIAL 3 Course 28420, Department of Chemical Engineering, Technical University of Denmark, 2004.
- Setthapong, N. Effect of acidity on the oxidation of toluene to benzaldehyde by hydrogen peroxide over TS-1. Master's thesis, Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University, 2011.
- Shenchunthichai, K. Catalytic study of iron, aluminium, cobalt and vanadium modified titanium silicalites-1 in the hydroxylation of benzene to phenol by hydrogen peroxide. Master's thesis, Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University, 2006.
- Tanev, P. T., Chibwe, M., Pinnavaia, T. J. Titanium containing mesoporous molecular sieves for catalytic oxidation of aromatic compounds. Nature 368 (1994): 321-323.
- Thangaraj, A., Kumar, R. Ratnasamy, P. Direct catalytic hydroxylation of benzene with hydrogen peroxide over titanium-silicate zeolites. Applied Catalysis 57 (1990): L1-L3.
- Zhang, J., Tang, Y., Li, G. Y. and Hu, C. Room temperature direct oxidation of benzene to phenol using hydrogen peroxide in the presence of vanadium-substituted heteropolymolybdates. Applied Catalysis A:General 278 (2005): 251-261.

APPENDICES

APPENDIX A

GC STANDARD PREPARATION AND CALIBRATION CURVES

This part illustrates the preparation of standard sample and calibration curves in order to calculate the concentration of benzene in aqueous phase in the solubility test and phenol formed in the hydroxylation of benzene to phenol test. Gas chromatograph Shimadzu model 9A equipped with flame ionization detector is used to analyze the concentration of benzene and phenol by using a 1.8-m glass column packed with GP10% SP2100.

With respect to the standard of benzene, liquid benzene is weighted into a 10 ml volumetric flask with a 4 decimals digital balance and added toluene into the volumetric flask until the level of solution reached 10 ml mark line. In case of the standard of phenol, solid phenol is dried in an oven in order to make sure the purification of phenol crystals and weighted into a 10 ml volumetric flask with a 4 decimals digital balance. Then, water is filled into the volumetric flask until the level of solution reached mark line.

The concentration of standard samples is calculated based on weight percent basis using the equations below;

$$\text{Concentration of standard } i = \left(\frac{g_i}{MW_i \times V} \times 1000 \right) \quad (\text{eq. A1})$$

Where;

- g_i is weight of standard i in the sample in gram
- MW_i is the molecular weight of standard i in gram per mole
- V is the volume of sample in milliliter (in this case equal to 10 ml)

This is due to the calibration curve of standard samples has to plot the relation between amount of mole of standard sample and peak area from integrator. Thus, different amount of volume of standard samples is injected to GC in order to measure the peak area with vary in amount of mole of standard samples. Mole of standard calculation is shown in equation below;

$$mole_i = M_i \times V_{inject} \quad (\text{eq. A2})$$

Where;

$mole_i$ is mole of standard i

M_i is the molar concentration of standard i

V_{inject} is the injection volume of sample to gas chromatography

Mole of standard sample is plotted in y-axis and area reported by gas chromatography is plotted in x-axis. The calibration curves of benzene and phenol are shown in the Figures 1A and 2A respectively.

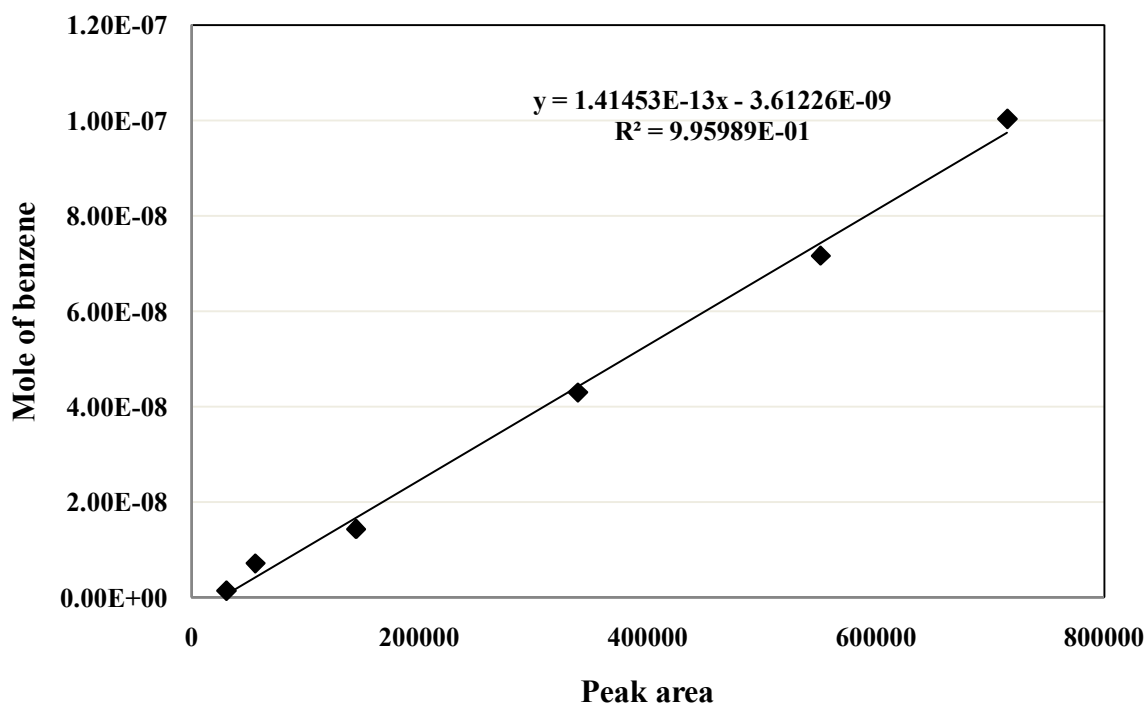


Figure A1 The calibration curve of benzene

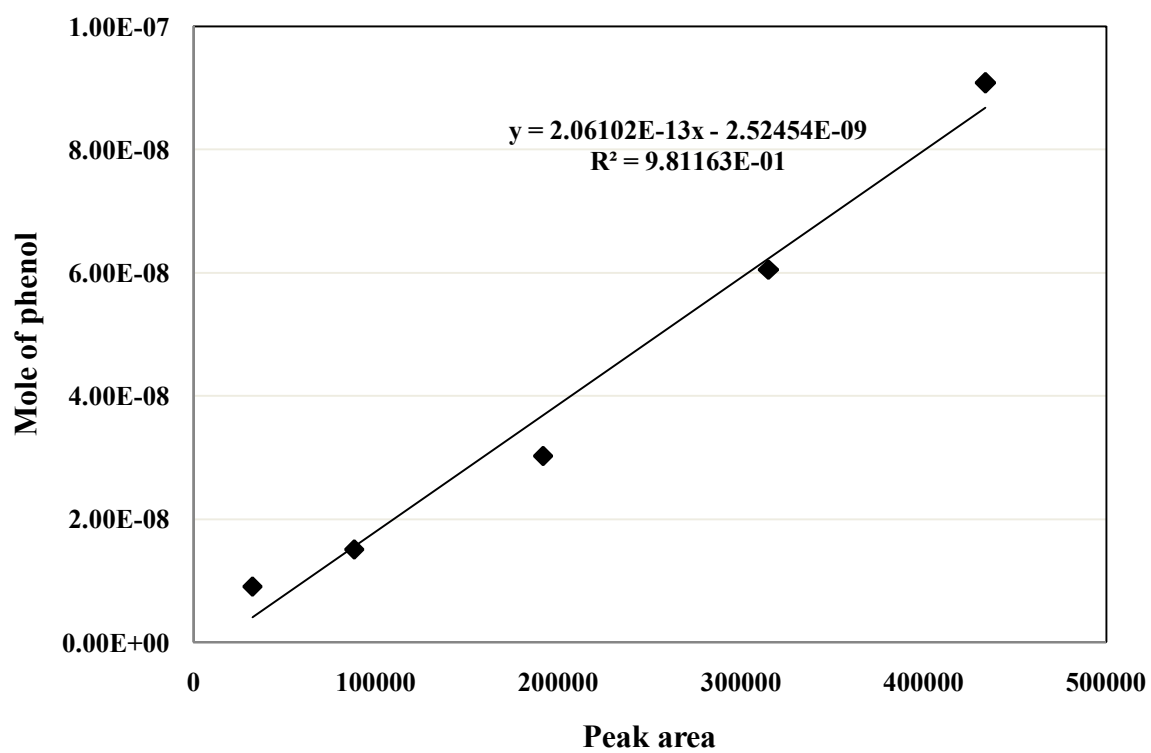


Figure A2 The calibration curve of phenol

APPENDIX B

CALCULATION FOR THE CONCENTRATION OF BENZENE IN AQUEOUS PHASE

This part describes the calculation of the concentration of benzene in aqueous phase. In the solubility test, 1 μL of sample is sampled from 120 ml of solvent covered by benzene layer and injected to GC. The obtained peak area is calculated to the amount of mole of benzene in 1 μL by using slope equation from the correlated calibration curve as shown in equation below;

$$n_i = A_i \times Slope_i \quad (\text{eq. B1})$$

Where;

- n_i is the amount of mole of benzene in the 1 μL of sample
 A_i is the peak area of product i
 $Slope_i$ is the slope from the correlated calibration curve

The result from equation B1 is the amount of mole of benzene in 1 μL . Thus, the concentration of benzene in mol/L is obtained by using equation below;

$$N_i = \left(\frac{n_i \text{ mol}}{V_{\text{inject}}} \times \left[\frac{1 \mu\text{L}}{10^{-6} \text{ L}} \right] \right) \quad (\text{eq. B2})$$

Where;

- N_i is the overall mole of benzene in 1 liter
 n_i is the amount of mole of benzene in the 1 μL of sample
 V_{inject} is the injection volume of sample to gas chromatography
(in this case equal to 1 μl)

For example, the peak area obtained from GC is 523520 A.U. using equation B1, B2 and slope equation ($1.41453 \times 10^{-13} X - 3.61226 \times 10^{-19}$) to get the concentration of benzene in aqueous phase.

From equation B1

$$n_i = 1.41453 \times 10^{-13} \times 523520 - 3.61226 \times 10^{-9}$$

$$n_i = 7.04033 \times 10^{-8} \text{ mol}$$

Substitutes the value of $n_i = 7.04033 \times 10^{-8} \text{ mol}$ into equation B2

$$N_i = \left(\frac{7.04033 \times 10^{-8} \text{ mole}}{1 \mu L} \times \left[\frac{1 \mu L}{10^{-6} L} \right] \right)$$

$$N_i = 0.07040328 \text{ mol/L}$$

APPENDIX C

CALCULATION FOR THE HYDROGEN PEROXIDE CONVERSION TO PHENOL

Appendix C illustrates the example of hydrogen peroxide conversion calculation. After the reaction, 100 ml of ethanol is added to the reaction solution in order to homogenize the mixture. Then, 5 μL of sample is injected to GC to investigate the product of this reaction. However, only phenol product is observed.

The mole of phenol product in 5 μL is obtained from using the slope from the correlated calibration curve ($2.06102 \times 10^{-13} X - 2.52454 \times 10^{-9}$) as shown in equation C1.

$$n_i = A_i \times Slope_i \quad (\text{eq. C1})$$

Where;

- n_i is the overall mole of phenol in the 5 μL of sample
- A_i is the peak area of product i
- $Slope_i$ is the slope from the correlated calibration curve

The overall mole of phenol in the reaction mixture (8.9 ml of benzene + 120 ml of solvent + 1 ml of hydrogen peroxide + 1 ml of water + 100 of ethanol = 230.9 ml of the reaction mixture) is calculated following equation (C2) below;

$$N_i = \left(n_i \times \left[\frac{230.8 \text{ ml}}{V_{\text{inject}}} \right] \left[\frac{1000 \mu\text{L}}{1 \text{ ml}} \right] \right) \quad (\text{eq. C2})$$

Where;

- N_i is the overall mole of phenol in the reaction mixture
 n_i is the overall mole of phenol in the 5 μ L of sample
 V_{inj} is the injection volume of sample to gas chromatography
 (in this case equal to 5 μ l)

The hydrogen peroxide conversion is obtained from using equation C3. However, 0.00979 mole of hydrogen peroxide is used in all the reaction trial.

$$X_i = \left(\frac{N_i \times 100}{0.00979 \text{ mol}_{\text{hydrogenperoxide}}} \right) \quad (\text{eq. C3})$$

For example, the peak area detected is 441096 A.U. in the reaction which is performed at 70 °C using 0.1M of acetic acid as solvent. The hydrogen peroxide conversion is calculated following equations C1 to C3 below;

From equation C1

$$n_i = 441096 \times 2.06102 \times 10^{-13} - 2.52454 \times 10^{-9}$$

$$n_i = 8.83862 \times 10^{-8} \text{ mol}$$

Substitutes the value of $n_i = 8.83862 \times 10^{-8}$ mol into equation C2

$$N_i = \left(8.83862 \times 10^{-8} \times \left[\frac{230.8 \text{ ml}}{5 \mu\text{L}} \right] \left[\frac{1000 \mu\text{L}}{1 \text{ ml}} \right] \right)$$

$$N_i = 0.004081674 \text{ mol}$$

Substitutes the value of $N_i = 0.004081674 \text{ mol}$ into equation C3

$$X_i = \left(\frac{0.004081674 \text{ mol}_{phenol} \times 100}{0.00979 \text{ mol}_{hydrogenperoxide}} \right)$$

$$X_i = 41.69$$

APPENDIX D

CALCULATION OF THE REQUIRED AMOUNT OF ETHANOL FOR HOMOGENIZING THE REACTION MIXTURE

In this present work, ethanol is used to homogenize the mixture before GC analysis. The required amount of ethanol to homogenize the reaction mixture is necessary before GC analysis because the multi phase of reaction mixture in GC analysis step causes the inexact analysis results. Hence, the deficient of ethanol can lead to analysis incorrect. Thus, the triangular phase diagram of ethanol-benzene-water system as shown in Figure D1 is used to calculate the required amount of ethanol.

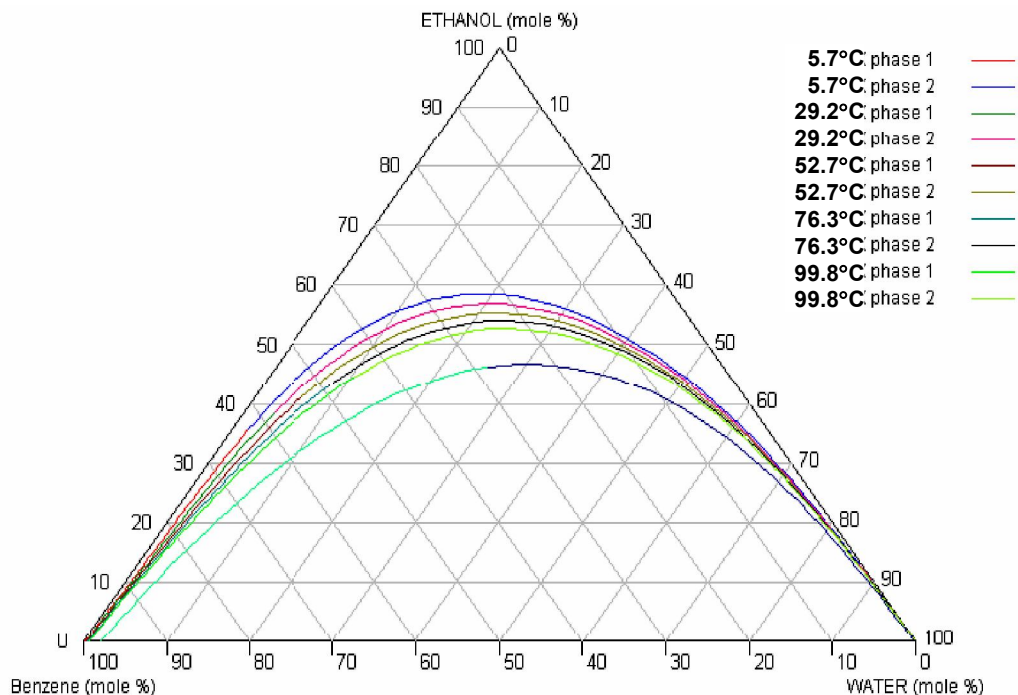


Figure D1 Triangular phase diagram for ethanol-benzene-water system (Sales-Curz, 2004).

From the triangular phase diagram, the corner of the triangle represents 100 % of the corresponding component which pure benzene, ethanol and water exist at the top corner. The mixture containing two components lie on an edge of the triangle. The region below the curve shows two phase mixture. All fractions above the curve, the mixture exhibits homogeneous phase. For example to plot in the triangular phase diagram, if the fraction of three substrate is 60% of benzene, 20% of water and 20% of ethanol so the point is shown below;

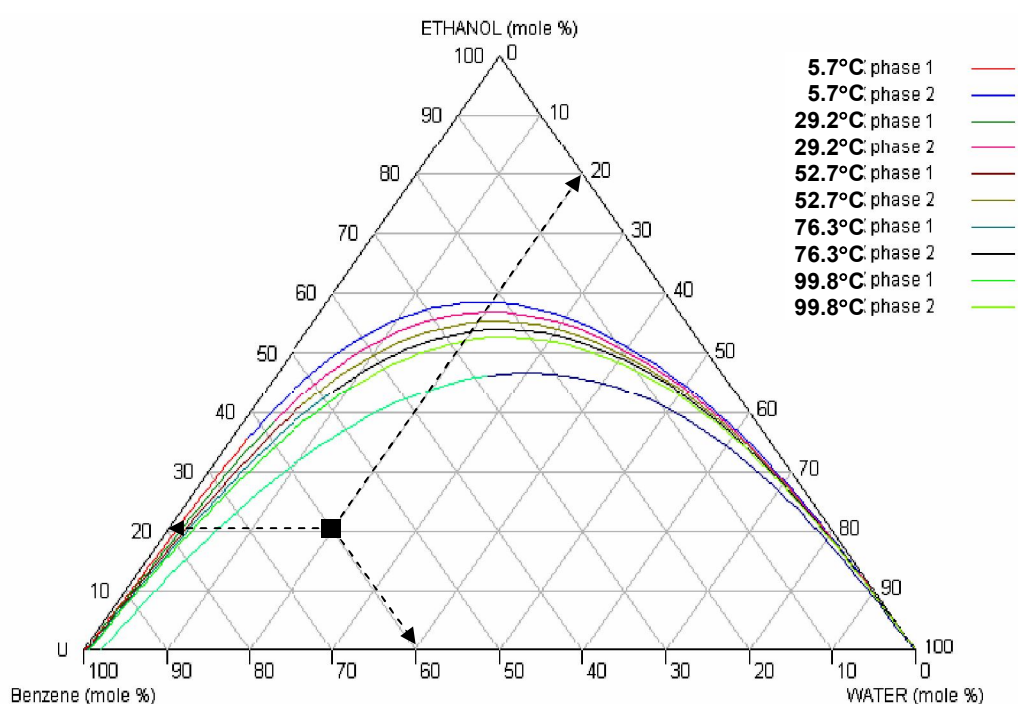


Figure D2 Example of triangular phase diagram for ethanol-benzene-water system plotting.

As a result of the two phase mixture below the curve, the minimum required amount of ethanol is obtained from the calculation based on the curve. However, any point above the curve can be used as the required amount of ethanol to homogenize the mixture. The calculation example for the following reaction conditions is shown below;

The reaction mixture consists of benzene 8.9 ml (0.09987 mol), H₂O₂ (30 wt. %) 1 ml (0.00978 mole H₂O₂), solvent 120 ml and additional water 1 ml. The solvent is water which addition of ion (H⁺, NH₄⁺, NO₃⁻, Cl⁻ and CH₂COO⁻) and hydrogen peroxide solution contents in water. Thus, the water in this system is around 122 ml which is equal to 6.76 mol. As a result of the reaction which is performed in a closed system, the amount of water has to remain. Assume the hydrogen peroxide conversion is around 10%, benzene left after reaction is around 0.0898 mol. After reaction, the overall content of water and benzene in the mixture are in following;

The fraction of water in the reaction mixture = 98.7 mol%

The fraction of benzene in the reaction mixture = 2.3 mol%

Using the triangular phase diagram to find the required amount of ethanol by drawing the straight line from the estimation point (98.7 mol% water and 2.3 mol% benzene) to the corner of ethanol is shown in Figure D3.

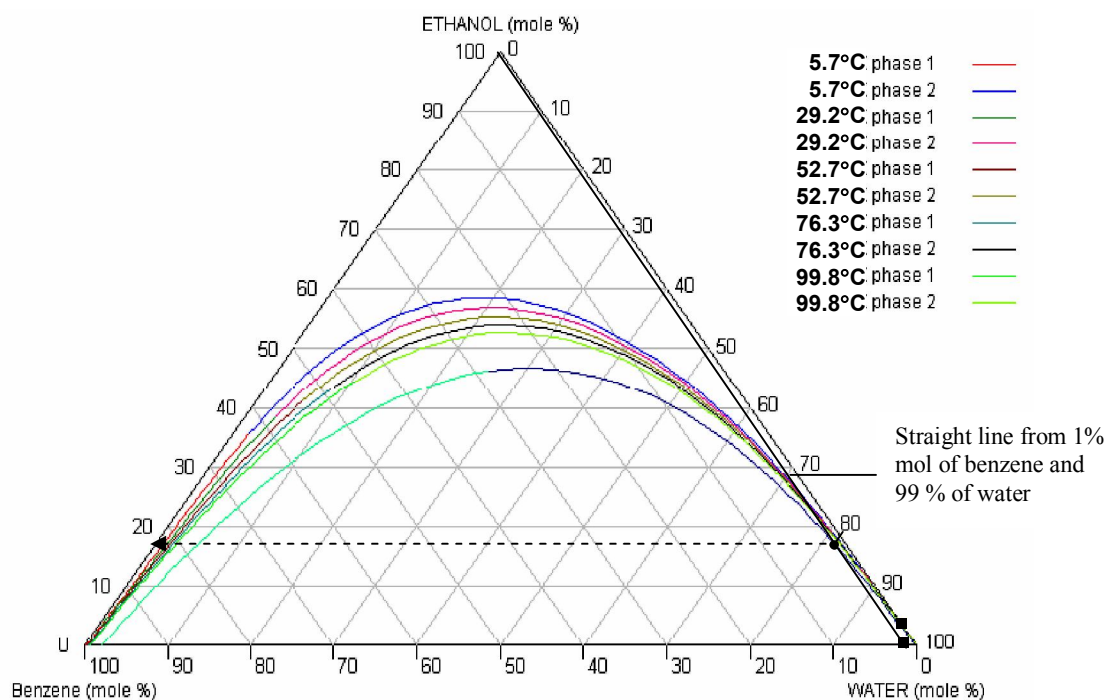


Figure D3 Estimation the required amount of ethanol.

From Figure D2, the straight line from the estimation point (98.7 mol% water and 2.3 mol% benzene) crosses the equilibrium curve at 19% of ethanol, 80% of water and 1% of benzene. At this point, the minimum required amount of ethanol is calculated as shown below;

$$\frac{6.76 \text{ mole H}_2\text{O} \times 19\% \text{ EtOH}}{80\% \text{ H}_2\text{O}} = 1.61 \text{ mole EtOH}$$

The minimum required amount of ethanol is 1.610mol which is calculated to amount of volume as shown below;

$$V_{\text{Ethanol}} = 1.61 \text{ mole EtOH} \left[\frac{46.07 \text{ g}}{1 \text{ mole EtOH}} \right] \left[\frac{1 \text{ ml}}{0.789 \text{ g}} \right]$$

$$V_{\text{Ethanol}} = 94 \text{ ml}$$

Therefore, 100 ml of ethanol is added to homogenize the reaction mixture in this research.

APPENDIX E

DATA OF EXPERIMENTS

Table E1 Data of Figure 4.4

Solvent	Time(min)	Benzene concentration (mol/L)
water	0	0.000
	3	0.006
	10	0.013
	20	0.023
	30	0.029
	40	0.032
	60	0.034
	80	0.055
	100	0.056
	120	0.056
	140	0.064
	160	0.057
	180	0.060
	200	0.063
	220	0.063
	240	0.060
270	0.063	
HNO₃	0	0.000
	2	0.010
	7	0.037
	13	0.064
	24	0.067
	29	0.072
	41	0.069
	47	0.069
	53	0.063
	61	0.063
	67	0.066
	92	0.068
	122	0.071
	192	0.070

Solvent	Time(min)	Benzene concentration (mol/L)
CH₃COOH	0	0.000
	2	0.000
	8	0.010
	15	0.025
	21	0.037
	27	0.051
	37	0.064
	41	0.067
	48	0.067
	57	0.071
	88	0.061
	111	0.066
	151	0.072
	201	0.068
HCl	0	0.000
	2	0.001
	7	0.005
	13	0.010
	18	0.015
	25	0.016
	31	0.026
	37	0.034
	43	0.037
	50	0.041
	56	0.051
	63	0.050
	69	0.056
	76	0.051
	83	0.059
	89	0.058
	103	0.068
	110	0.069
	122	0.063
	154	0.070
199	0.073	
230	0.066	
265	0.067	

Table E2 Data of Figure 4.5

Solvent	Time(min)	Benzene concentration (mol/L)
NH₄NO₃	0	0.000
	2	0.005
	7	0.014
	13	0.022
	18	0.029
	26	0.054
	31	0.054
	37	0.054
	43	0.059
	49	0.059
	97	0.063
	117	0.063
	173	0.062
	NH₄Cl	0
2		0.000
6		0.004
10		0.011
14		0.021
18		0.025
23		0.037
28		0.035
33		0.043
63		0.050
78		0.059
98		0.055
128		0.064
158		0.057
218		0.061

Table E3 Data of Figure 4.6

Solvent	Time(min)	Benzene concentration (mol/L)
NaNO₃	0	0.000
	2	0.000
	4	0.001
	6	0.002
	8	0.003
	10	0.005
	12	0.015
	18	0.018
	30	0.028
	33	0.024
	36	0.024
	39	0.027
	42	0.025
	45	0.027
	50	0.027
	55	0.032
	60	0.037
	70	0.031
	80	0.036
	90	0.042
	110	0.043
	135	0.041
	150	0.050
	165	0.049
	180	0.052
	200	0.054
	220	0.053
240	0.053	
260	0.049	
280	0.052	
300	0.054	

Solvent	Time(min)	Benzene concentration (mol/L)
NaCl	0	0.000
	2	0.010
	5	0.004
	9	0.002
	12	0.003
	17	0.008
	22	0.011
	25	0.016
	29	0.018
	33	0.026
	36	0.028
	40	0.030
	44	0.028
	48	0.023
	53	0.029
	57	0.028
	60	0.033
	65	0.034
	68	0.043
	137	0.047
	160	0.044
	178	0.044
	188	0.051
	198	0.047
228	0.045	
240	0.046	
249	0.052	
259	0.052	

APPENDIX F

THE EFFECT OF IONS ON WATER MOLECULES

This part illustrates how to ions can break down the hydrogen bond and change the viscosity of water. After the addition of kosmotropes ions in pure water, the strength of hydrogen bonded is decreased which having effects similar to increased temperature. Moreover, the addition of chaotropes ions is also able to change the viscosity of water.

With the structure of water (Hajdu, 1977), the tetrahedral water cluster is consisted of 14 water molecules. Regular arrangement of twenty of these 14-molecule structures may form an icosahedral network. The icosahedral water cluster shows the equilibrium of two structure between expanded structure and collapsed structure.

The breaking down of hydrogen bond can be explained (Grossfield et. al., 2003) that kosmotropes ions considerably increase the difference between the hydrogen bond donating and accepting capacity of the linked water molecules resulting in the breakdown of the tetrahedral network (as shown in Figure F1).

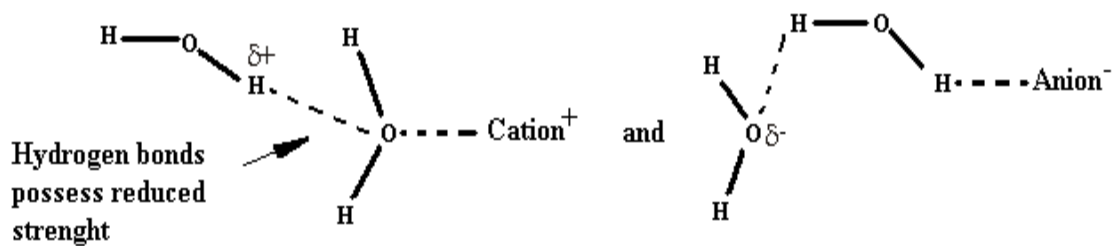


Figure F1 The effect of ions on the strength of hydrogen bonds.

The decrease of viscosity is due to large chaotropes ions possess low surface charge density can fit into the icosahedral water network without affecting its hydrogen bonding. Pressure shifts the expand structure of water \rightleftharpoons collapsed structure equilibrium towards collapsed structure formation. On the other hand, small chaotropes ions possess high surface charge density is tightly bonds with water molecules. Hence, there is less localized water molecule mobility (Collins and Washabaugh, 1985).

APPENDIX G

MATERIAL SAFETY DATA SHEET

This part presents material safety data sheet of benzene, hydrogen peroxide, phenol and the variety of ionic solution used. This data are obtained from Science Lab.com, Inc.

Safety data for benzene

General

Synonyms	: benzol, phenyl hydride, coal naphtha
Molecular formula	: C ₆ H ₆

Physical data

Appearance	: colourless liquid
Melting point	: 5.5°C
Boiling poin	: 80°C
Specific gravity	: 0.87
Vapour pressure	: 74.6 mm Hg at 20 °C
Flash point	: -11 °C
Explosion limits	: 1.3 % - 8 %
Autoignition temperature	: 561 °C

Stability

Stable. Substances to be avoided include strong oxidizing agents, sulfuric acid, nitric acid. Highly flammable.

Toxicology

This material is a known carcinogen. The risks of using it in the laboratory must be fully assessed before work begins. TLV 10 ppm. Short-term exposure may cause a variety of effects, including nausea, vomiting, dizziness, narcosis, reduction in blood pressure, CNS depression. Skin contact may lead to dermatitis. Long-term exposure may lead to irreversible effects. Severe eye irritant. Skin and respiratory irritant.

Personal protection

Safety glasses, gloves, good ventilation. Thought should be given to using an alternative, safer product.

Safety data for hydrogen peroxide

General

Synonyms	: Peroxide, 100 volume peroxide, Hydrogen dioxide solution, Hydrogen peroxide, 30%, unstabilized, Hydrogen Peroxide, 30%
Note	: Typical concentrations lie in the range 3%-35%. Solutions of much higher concentration (e.g. 60% and above) present significantly increased risks, and should not be used unless such strength is absolutely essential.
Molecular formula	: H ₂ O ₂

Physical data

Appearance	: colourless liquid
Melting point	: -28 °C
Boiling point	: 114 °C
Specific gravity	: typically near 1.19
Vapour pressure	: 23.3°C at 30 °C

Stability

Unstable - readily decomposes to water and oxygen. Light sensitive. May develop pressure in the bottle - take care when opening. Forms potentially explosive compounds with ketones, ethers, alcohols, hydrazine, glycerine, aniline, sodium borate, urea, sodium carbonate, triethylamine, sodium fluoride, sodium pyrophosphate and carboxylic acid anhydrides. Materials to avoid include combustibles, strong reducing agents, most common metals, organic materials, metallic salts, alkali, porous materials, especially wood, asbestos, soil, rust, strong oxidizing agents.

Toxicology

Toxic. Corrosive - can causes serious burns. Eye contact can cause serious injury, possibly blindness. Harmful by inhalation, ingestion and skin contact. Typical OEL 1 ppm.

Hazards Identification

Strong oxidizer. Contact with other material may cause a fire. Harmful if inhaled. Corrosive. Causes eye and skin burns. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns.

Potential Health Effects

Inhalation : Vapors are corrosive and irritating to the respiratory tract. Inhalation of mist may burn the mucous membrane of the nose and throat. In severe cases, exposures may result in pulmonary edema and death.

Ingestion : Corrosive and irritating to the mouth, throat, and abdomen. Large doses may cause symptoms of abdominal pain, vomiting, and diarrhea as well as blistering or tissue destruction. Stomach distention (due to rapid liberation of oxygen), and risk of stomach perforation, convulsions, pulmonary edema, coma, possible cerebral edema (fluid on the brain), and death are possible.

Skin Contact : Corrosive. Symptoms of redness, pain, and severe burn can occur.

Eye Contact : Vapors are very corrosive and irritating to the eyes. Symptoms include pain, redness and blurred vision. Splashes can cause permanent tissue destruction.

Personal protection

Safety glasses are essential; acid-resistant gloves are suggested. Suitable ventilation.

Safety data for phenol

General

Synonyms : benzenol, carbolic acid, hydroxybenzene, monohydroxybenzene, monophenol, oxybenzene, phenic acid, phenylic acid, phenyl alcohol, phenyl hydrate, phenyl hydroxide, phenylic alcohol

Molecular formula : C₆H₅OH

Physical data

Appearance	: colourless crystals
Melting point	: 40°C -42°C
Boiling point	: 182°C
Specific gravity	: 1.07
Vapour pressure	: 0.35 mm Hg at 20°C
Flash point	: 79°C
Explosion limits	: 1.5 % - 8.6 %
Autoignition temperature	: 715°C

Stability

Substances to be avoided include strong oxidizing agents, strong bases, strong acids, alkalies, calcium hypochlorite. Flammable. May discolour in light.

Toxicity

This material is a systemic poison and constitutes a serious health hazard. The risks of using it in the laboratory must be fully assessed before work begins. Vesicant. Typical MEL 2 ppm; typical OEL 1 ppm. Acute poisoning by ingestion, inhalation or skin contact may lead to death. Phenol is readily absorbed through the skin. Highly toxic by inhalation. Corrosive - causes burns. Severe irritant.

Personal protection

Safety glasses, gloves, good ventilation.

Safety data for hydrochloric acid**General**

Synonyms	: Muriatic acid; hydrogen chloride, aqueous
Chemical Formula	: HCl

Physical data

Physical State	: liquid
Appearance	: clear
Color	: colorless
Odor	: Pungent odor
Molecular Weight	: 36.46
Boiling Point	: 140-221 F (60.0-105 C)
Freezing Point	: -29 to 5 F (-34 to -15 C)
Vapor Pressure	: 14.6-80 mmHg @ 20 C
Vapor Density: (air=1)	: 1.3 @ 20 C
Specific Gravity (water=1)	: 1.05-1.18
Bulk Density	: 8.75-9.83 lbs/gal
Water Solubility	: 100%
PH	: 2 (.02% solution)
Volatility	: 9-36% by volume
Odor Threshold	: 0.3 ppm (causes of factory fatigue)
Evaporation Rate	: <1.00 (butyl acetate=1)

Stability

Stable under normal temperatures and pressures. Containers may burst when heated. Avoid heat, flames, sparks and other sources of ignition. Contact with water may produce a strong exothermic reaction with spattering. Contact with metals may evolve flammable hydrogen gas. Hydrogen chloride may react with cyanide, forming lethal concentrations of hydrocyanic acid.

Toxicity

Poison, danger, corrosive, liquid and mist cause severe burns to all body tissue. May be fatal if swallowed or inhaled. Inhalation may cause lung damage.

Personal protection

Safety glasses, gloves, good ventilation.

Safety data for nitric acid**General**

Synonyms	: Aqua fortis, Azotic acid, Hydrogen nitrate, Nitryl hydroxide, Nitral, Engraver's acid
Chemical Formula	: HNO ₃

Physical data

Physical State	: Liquid
Appearance	: clear to yellow
Odour	: strong odour – acrid odour
pH	: 1.0 (0.1 M solution)
Vapour Pressure	: (2.78-3 mm Hg) at 20°C

Vapour Density	: 2.17 (air = 1) (calculated).
Boiling Point	: 68% (w/w): 120.5°C
Freezing/Melting Point	: 70% (w/w): -41°C
Solubility	: Soluble in all proportions.
Density	: 1.41 g/cm ³
Molecular Formula	: HNO ₃
Molecular Weight	: 63.0119

Stability

Decomposes when in contact with air, light, or organic matter. Avoid High temperatures, incompatible materials, moisture, reducing agents.

Toxicity

During a fire, nitric acid decomposes with the release of corrosive nitrogen oxide gases. Closed containers may develop pressure on prolonged exposure to heat. Contact with combustible and easily oxidizable materials may result in fire and/or explosion. May react violently or explosively and/or ignite spontaneously with many organic and inorganic chemicals. Releases extremely flammable hydrogen gas on contact with many metals, particularly in powdered form. Generates heat when mixed with water. Nitric acid poses a very serious inhalation hazard. Symptoms of exposure include dryness of the nose and throat, cough, chest pain, shortness of breath and difficulty breathing. Causes lung injury-effects may be delayed. Corrosive to the eyes, skin and respiratory tract. Causes severe burns. May cause permanent eye injury or blindness and permanent scarring.

Personal protection

Safety glasses, gloves, good ventilation.

Safety data for acetic acid

General

Synonyms	: Acetic acid; glacial acetic acid
Chemical Formula	: CH ₃ COOH

Physical data

Physical state	: Liquid.
Odor	: Pungent, vinegar-like, sour (Strong.)
Taste	: Vinegar, sour (Strong.)
Molecular Weight	: 60.05 g/mole
Color	: Colorless. Clear (Light.)
pH (1% soln/water)	: 2 (Acidic.)
Boiling Point	: 118.1°C (244.6°F)
Melting Point	: 16.6°C (61.9°F)
Critical Temperature	: 321.67°C (611°F)
Specific Gravity	: 1.049 (Water = 1)
Vapor Pressure	: 1.5 kPa (@ 20°C)
Vapor Density	: 2.07 (Air = 1)
Odor Threshold	: 0.48 ppm
Solubility	: Easily soluble in cold water, hot water. Soluble in diethyl ether, acetone. Miscible with Glycerol, alcohol, Benzene, Carb Tetrachloride. Practically insoluble in Carbon Disulfide.

Stability

The product is stable.

Toxicity

Acute Potential Health Effects: Skin: Extremely irritating and corrosive. Causes skin irritation (reddening and itching, inflammation). May cause blistering, tissue damage and burns. Eyes: Extremely irritating and corrosive. Causes eye irritation, lacrimation, redness, and pain. May cause burns, blurred vision, conjunctivitis, conjunctival and corneal destruction and permanent injury. Chronic exposure via ingestion may cause blackening or erosion of the teeth and jaw necrosis, pharyngitis, and gastritis. It may also behavior (similar to acute ingestion), and metabolism (weight loss). Chronic exposure via inhalation may cause asthma and/or bronchitis with cough, phlegm, and/or shortness of breath. It may also affect the blood (decreased leukocyte count), and urinary system (kidneys). Repeated or prolonged skin contact may cause thickening, blackening, and cracking of the skin.

Personal protection

Safety glasses, gloves, good ventilation.

Safety data for ammonium nitrate**General**

Synonyms	: Ammonium Saltpeter; Nitric acid, ammonium salt
Chemical Formula	: NH_4NO_3

Physical data

Physical state and appearance	: Solid (white granular solid. Deliquescent solid.)
Odor	: Odorless.
Molecular Weight	: 80.05 g/mole
pH (1% soln/water)	: 4.5 - 6.0 @ 25 deg. (Acidic.)
Boiling Point	: Decomposition temperature: 210°C (410°F)
Melting Point	: 169.6°C (337.3°F)
Specific Gravity	: 1.725 (Water = 1)
Dispersion Properties	: See solubility in water, methanol, acetone.
Solubility	: Easily soluble in cold water, hot water. Soluble in acetone. Partially soluble in methanol. Insoluble in diethyl ether.

Stability

The product is stable.

Toxicity

Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation (lung irritant). Slightly hazardous in case of skin contact (permeator). Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation.

Personal protection

Safety glasses, gloves, good ventilation.

Safety data for ammonium chloride

General

Synonyms	: Ammonium Chloratum; Ammonium Chloridum; Ammonium Muriate; Sal Ammonia; Salmiac
Chemical Formula	: NH_4Cl

Physical data

Physical state and appearance	: Solid. (Solid crystalline powder.)
Odor	: Odorless. (Slight.)
Taste	: Cooling, Saline.
Molecular Weight	: 53.49 g/mole
Color	: White.
pH (1% soln/water)	: 5.5 (Acidic.)
Boiling Point	: 520°C (968°F)
Melting Point	: Decomposition temperature: 338°C
Specific Gravity	: 1.53 (Water = 1)
Dispersion Properties	: See solubility in water, methanol.
Solubility	: Soluble in cold water, hot water, methanol. Insoluble in diethyl ether, acetone. Almost insoluble in ethyl acetate. Very slight soluble in Ethanol; Solubility in Ethanol: 0.6 g/100 ml water at 19 deg. C. Solubility in Water: 29.7 g/100ml water at 0 deg. 75.8 g/100 ml water at 100 deg. C 37.8 lbs./100 lbs. water at 70 deg. F 28.3% (w/w) in water at 25 deg. C Soluble in liquid ammonia.

Stability

The product is stable.

Toxicity

It can cause skin irritation which is usually mild. Eyes: Causes moderate eye irritation. It may cause Salt Cataract, increased ocular pressure, and degeneration of the retina Inhalation: It can cause respiratory tract and mucous membrane irritation which is usually mild. Ingestion: May be harmful if swallowed. May cause digestive tract irritation with nausea and vomiting, and thirst. May affect behavior/central nervous system (headache, somnolence, confusion drowsiness, tremor, convulsions, coma), eyes (Mydriasis), cardiovascular system (bradycardia), respiration (respiratory stimulation, apnea, hyperventilation, pulmonary edema).

Personal protection

Safety glasses, gloves, good ventilation.

APPENDIX H

LIST OF PUBLICATION

Rudemas Manosak and Tharathon Mongkhonsi, “Effect of acidity on the hydroxylation of benzene to phenol by Hydrogen peroxide over TS-1 catalysts”, Thai institute of Chemical Engineering (TIChE) International Conference 2011, November, 2011, Ref. No. cr-005

VITA



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