

Effect of Plastic Ingredients synthesis Using Nuclear Magnetic Resonance

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Abstract

The research reviews focused on investigation of methods used for organic production. The condensation reaction of phenol with acetone in the presence of sulfonic catalyst (P-toluene sulfonic acid) PTSA studied with the influence of significant factors.

Using NMR as a tool is one of the paper advantages and introducing alternative catalyst that brings the stability compared to ion-exchange resin such as Amberlyst or DOWEX, and the solubility that enhance the rate of reaction to give better selectivity and productivity. As a result, catalytic reaction has the potential of producing bisphenol A (BPA) at lower production costs. Also the study cover other aspects relevant to the process such as engineering processes include: solubility, diffusivity, chemistry of the reagents and the reaction mechanism.

Keywords: Organic, Reaction, Acetone, Phenol, Catalyst, Solubility, and Engineering, and Mechanism

1. Introduction

Bisphenol A (BPA) is the commercial name used in the United States for 4,4'-isopropylidenediphenol and other names are still used. Its commercial name indicates the preparation from two molecules of phenol and one of acetone. The molecule of BPA can be described as two phenolic rings joined together by a bridging iso-propylidene group (Kim et al., 1987). BPA is a chemical produced in large quantities for producing polycarbonates and epoxy. The BPA can be found in many applications associated with polycarbonates plastics such as drinking packaging, medical devices, and infant bottles, compact disc, food cans, bottle tops water supply pipes and etc.

Aleksandra Dianin is a Russian scientist, prepared bisphenol A for the first time in 1891 by a condensation reaction of acetone and phenol catalyzed by hydrochloric acid. The method was not patented until 1917 but was manufactured on an industrial scale for the first time in 1923 by a German firm, Chemischen Fabriken, to be utilized as an intermediate for producing coating resins (European Patent.2004). Since then, the production of BPA as an intermediate for epoxy resins continued to grow. Furthermore, some of the first large-scale producers were Firma Resin and Vernis Artificiels in France, Farben Fabriken Bayer in Germany. Dow Chemical Company, General Aniline and Film from 1941 – 1954, Shell Chemical Co., Monsanto Co. from 1956 – 1971, Union Carbide from 1960 – 1980, and General Electric Co since 1967 in the United States. Shawinigan Chemicals in Canada, Esquim in Mexico, Shell Chemicals U.K. and R.Grasser Co. in England, Ketjen and Shell in the Netherlands, Mitsui Toatsu Chemicals, Honshu Chemical Industries and Nippon Steel Chemical Co. in Japan .

Bisphenol A is generally used as a reagent for producing polycarbonates, epoxy resins, phenoxyresins, acrylicresins, polysulfonic resins, and other polyester. There are different BPA forms such as Halogenated forms which are used as flame retardants, and alkylated forms where used as stabilizers and antioxidants form for rubber and other plastics such as PVC. It is also used as a component of food-packaging adhesives, as a fungicide and as a component of dental filling compositions. BPA production in the United States, in 1974, was only 415 million (United States Patent, 1993). Now, the total production of BPA is one of the highest chemical productions in the world-wide. It is well known that for obtaining light-colored high molecular weight polymer via linear condensation, the purity of the monomer must be high. Although polycarbonates need a high quality of BPA, most epoxy resins formed by ordinary BPA. However, there are several methods of evaluating the quality of BPA. The most important parameter that characterizes the quality of BPA is its color and the technique that is most used for estimating the purity of BPA is the melting point [29]. The crude products have wide range melting point starting at about 140°C, melting point of the pure compound is 157 °C but good commercial grades melt at 154 to 155 °C .

Since obtaining high purity BPA is of great importance, improvement of the manufacturing process was continuously investigated by researchers and engineers. Either the yield or the selectivity of the reaction, or both were considered for improvement and several modification of the original method were studied before such as different catalysts, homogenous and heterogeneous, alternatives to acetone as feedstock.

The purpose of this investigation is to outline the basis of a research for alternative catalysts that could be utilized for mitigating the health effect of BPA production. Studying the condensation reaction of phenol with acetone in the presence of sulfonic catalyst (P-toluene sulfonic acid) PTSA will be discussed.

The major advantage of adopted catalyst is the stability compared to ion-exchange resin such as Amberlyst or DOWEX, where the solubility enhance the rate of reaction to give better selectivity and productivity. Also the potential of producing bisphenol A at lower production costs. The research reviews the current technologies for BPA process and focus on previous investigation on the feasibility of alternative catalysts that fit other technologies with low production cost and minimal health. Also, the study reviews the ability of producing bisphenol A (BPA) by using supercritical carbon dioxide (ScCO₂) as a reaction media and will cover other aspects relevant to the process such as solubility, diffusivity, chemistry of the reagents and the reaction mechanism.

Table 1: Chemical Structured Names of Bisphenol A

Bisphenol A Common Names	Bisphenol A Common Names
2,2-bis-4'-hydroxyphenylpropan	phenol, 4,4'-dimethylmethylenedi-
bis(4-hydroxyphenyl) dimethyl methane	phenol, 4,4'-isopropylidenedi-
2,2-bis(4-hydroxyphenyl)propane	propane, 2,2-bis(p-hydroxyphenyl)
4,4'-dihydroxydiphenyldimethylmethane	dimethylmethylene-p,p'-diphenol
p,p'-dihydroxydiphenyldimethylmethane	beta-di-p-hydroxyphenylpropane
Dian	bisferol A

<https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf> (updated Oct., 2021)

1.1 Bisphenol A production process

The aim of the chapter is to give an overview of the BPA production methods. General purification issues will be presented. The physical and chemical properties of BPA will be summarized.

1.2 Preparation of Bisphenol A

The BPA synthesis including mechanisms, possible reactions, by-products, and order of reaction discussed in the following sections,

1.2.1 Primary Reaction

The acid catalyzed condensation of acetone with two moles of phenol is the first process for forming BPA,

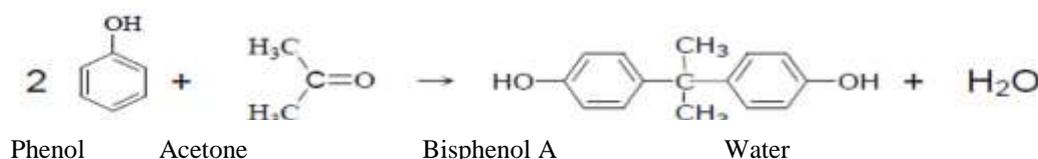
The heat of reaction, for reagents and products in their natural physical state at 25°C, is calculated from heats of formation as 19 kcal/mol and a molar ration of 1:2 acetone to phenol, is considered in the first stage of the research, in the presence of concentrated hydrochloric acid at room temperature. There was a claim of the present of small amount of water (10%) or less in the reaction mixture increases the reaction rate of the mixture catalyzed by hydrochloric acid [28]. Others suggest that processing the reaction by ion-exchange resin (sulfonic acid) modified with alkyl-SH groups enhance the reaction and decrease the amount of water 5% by weight in the mixture which decreases the yield of BPA. However, it was suggested by Jerabek et al. that to reduce the effect of water, dehydration by various water-binding agents (such as Calcium Chloride or phenyl acetate) or by azeotropic distillation can be used.

This reaction proceeds with an electrophilic attack of the proton from the acidic catalyst on the molecule of acetone. During this step, producing by-products or "impurities" might change the mechanism of the reaction by produce undesirable products as a result of acetone – acetone reaction or Dimerization. Thus, Mesityl oxide is formed and increasing the number of impurities that lead to further phenolic reaction and the process becomes more complicated.

2. Literature review

The review will be focused on Bisphenol A synthesis. BPA is produced by the reaction of phenol with acetone in the presence of heterogeneous or homogenous catalyst. The study will cover the recent studies and special attention will be given to the use of supercritical carbon dioxide as a reaction medium for BisphenolA (BPA) formation.

Main Reaction:



2.1 Bisphenol A Synthesis Methods

The most industrially used processes for making BPA in the United States and Western Europe are the acetone-phenol reaction, in homogenous as well as heterogeneous catalysis. Considering the cost involved and the net advantages the heterogeneous catalysis offers, the resin-catalyzed process is preferred, and it has been improved continuously. There are different methods for Bisphenol A production,

2.1.1 Conventional Methods

This method based on the type of the catalyst and solvent. It is also called Hydrogen Chloride-catalyzed process. The first production of BPA was made by Russian scientist, Dianin, in 1891. He used Hydrochloric acid to accelerate the reaction since it is hard to form BPA without strong acid. However, the process of obtaining BPA is also depending on the phenol to ketone (acetone) reaction ratio. Thus, there will be excessive phenol, approximately a ratio of (3-30):1 to ensure the reaction is processed (WO 2005/030687, 2005). Although the reaction gives high efficiency, the conventional methods of BPA production does not provide approximately high selectivity of the reaction of phenol with acetone and the required purity of the desired product. It also appeared that it is impossible to achieve the equilibrium state for some by-product of the reaction therefore the process cannot be performed for long time without production loss. In addition, because of the low concentration of BPA, high energy consumption will be resulting from the reaction. These disadvantages force engineers and scientists to look for better methods to form highly pure BPA product [4].

2.1.2 Alternative Methods

There are alternative methods to produce BPA by using different catalysts with/without promoters. This method is also known as the resin-catalyzed process. It gives better results in terms of selectivity, and purity of product. One of the catalyst that been used such as exchanger resin also improves the production of BPA. In addition, there are other catalysts have been used and modified to increase the BPA concentration and improve the phenol and acetone reaction, for instance, sulfonated ion exchange resin, DVB divinylbenzene, and polystyrene. Although the formation of BPA is improving continuously, still there is no answer for the variation in ratio of phenol to acetone.

2.2 Kinetics of the synthesis of Bisphenol A

The literatures and researches show that the reaction between phenol and acetone is too slow in the absence of catalyst, but it proceeds with formation of Bisphenol A (BPA) in the presence of acidic catalyst or any strong acid (Gates et al, 1974). However, the condensation reaction of phenol with acetone will be studied by using conventional hydrochloric acid and catalyzed by new and suitable catalyst. Although the BPA formation depends on the molar ratio of reactants (acetone and phenol), using a suitable solvent or catalyst will enhance the reaction ratio between phenol and acetone and improve the selectivity. There are different catalysts and solvents have been tested and their effects on the reaction rate and BPA yield also evaluated. However, water concentration was so low that the reaction became first order with respect to the acetone. As the reaction proceeded to increase the water concentration, the inhibition effect of water reduces the reaction rate and gives low yield. Therefore, increasing the yield and decreasing the water concentration will be one of the aims of the study.

2.2.1 Catalyst preparation

The reaction of BPA formation is reported to be first order in catalyst. This is the reason why it was recommended to run the process at several atmospheres [2] where the first catalyst used to produce BPA was concentrated hydrochloric acid. In addition, processes that use gaseous hydrochloric acid or acid ion exchange resin are operated in the United States. Although the process operated by ion exchange resin is slower and the product more difficult to purify than the hydrochloric acid catalyzed process, 75% concentrated sulfonic acid can be used as catalyst to reduce sulfonation. Also, sulfonic catalysts have many benefits and the main advantages of using sulfonic acid as catalyst for BPA formation are:

1. The apparatus is simpler and
2. The corrosion is less severing.

It is recommended that any acid with constant K_a greater than 10^{-3} will be suitable to be operated in the production process. Also, with SO_3H group which will be increasing the efficiency of the strong acid resin and stabilize it in the presence of water. However, the degree of neutralization will be very important in order to enhance the reaction rate and improve the final product. Effective catalysts are obtained by neutralization 15-20 percent of ion exchange capacity of a sulfonated aromatic resin having an initial exchange capacity of about 4.5-5.2 meq/g dry weight H^+ form, giving a modified resin having a capacity of about 3.6-4.4 meq/g dry weight H^+ form [9]. Therefore, a higher degree of neutralization impairs the catalyst efficiency. Since it is very slow without catalyst, required no catalyst separation, or washed with water, or distilled out only in the case of homogeneous hydrochloric acid catalyst because it can be easily recycled and the waste disposal problems reduced.

2.3 Chemistry of the Reaction

The BPA reaction consists of the electrophilic attack of a polar reactive intermediate, which can be a carbonium ion, on the aromatic ring. In the first step, the hydrogen bonds are formed between the carbonyl group of the acetone and the sulfonic group of the resin. The intermediate is expected to react with phenol in the non-polar surrounding medium, forming a tertiary alcohol, which transforms rapidly into a carbonium ion, the final step is the formation of bisphenol A molecule which take place through hydrogen bonds.

2.3.1 Electrophilic Reaction

The electrophile is something which carries either a full positive charge or has a slight positive charge on it. It is strongly attracted to the exposed electrons in the pi bond (π) to form new compound.

The selection of parameters depends on the specific compound. There are several important parameters need to be considering during the process:

1. Temperature
2. Pressure
3. Time
4. Particle size.

2.3.2 Reaction Order

The formation of BPA is a condensation reaction in two steps. First, a molecule of acetone reacts with a molecule of phenol, and then the product, or the corresponding ion, reacts with the second molecule of phenol. The reaction was reported as a first order in both acetone and phenol indicates that the first step of the reaction is slower than the second step; therefore, the slower step is the Rate Determining Step (RDS), (Ghosh and Saha, 1967). Another study showed that the catalyzed reaction was second order with respect of phenol. Furthermore, according to several studies, the reaction is reversible like most other electrophilic substitutions and its activation energy for the overall process is in the range of 11 – 19 Kcal/mol. However, the main by-product is the o,p-isomer made in the presence of an acid by increasing the temperature therefore temperature needs to be controlled as low as possible to maximize the BPA production (Ghosh and Saha, 1967).

3. Research Modeling

3.1 Mathematical Studying Model

The Production (%R) is equal to:

$$\frac{d[BPA]}{dt} = K[A][P]$$

$$\frac{d[BPA]}{dt} = -\log(100 - R), \text{ therefore,}$$

$-\log(100 - R) = Kt$, then, we are able to determine K as,

$$K = 2.303 / (P - 2a) t \cdot \log a(P - 2x) / P(a - x)$$

$$\text{Rate of Reaction} = kC_A C_P / (1 + K_A C_A + K_P C_P)$$

Kinetic equation including the effect of water:

$$\text{Rate of Reaction} = kC_A C_P / (1 + K_A C_A + K_P C_P + K_w C_w)$$

3.1.1 The Mass Balance Equation:

$$\epsilon_b \frac{dc}{dt} = -v \frac{dc}{dz} - k a(c - C^*)$$

Where:

A and T are the concentration of acetone and acid

K: Adsorption Coefficient (dm^3/mol) = $5.44 \cdot 10^{-4} \text{ m}^3/\text{mol}$

X: Concentration of Bisphenol A at time t in sec. mol/l

A: Initial concentration of acetone mol/sec

k : rate constant l/mol/sec

P: Initial Concentration of phenol mol/l

According to Arrhenius equation, the results obtained were temperature dependence, for the water adsorption coefficient, K_w . For the adsorption coefficient of acetone and phenol increased with the temperature, although, the rate constant of reaction is increased with temperature, the energy of between acetone and phenol is weaker.

$$K = 1470 \text{ Exp } (-59900/RT) [\text{m}^3\text{kg}^{-1}\text{s}^{-1}]$$

Temperature effect determined as first-order reaction rate constants plotted against the reciprocal of the reaction temperature Figure 1. It showed the temperature effect on the reaction rate constants. When the temperature decrease the constants value were decreased and increased with the increasing temperature.

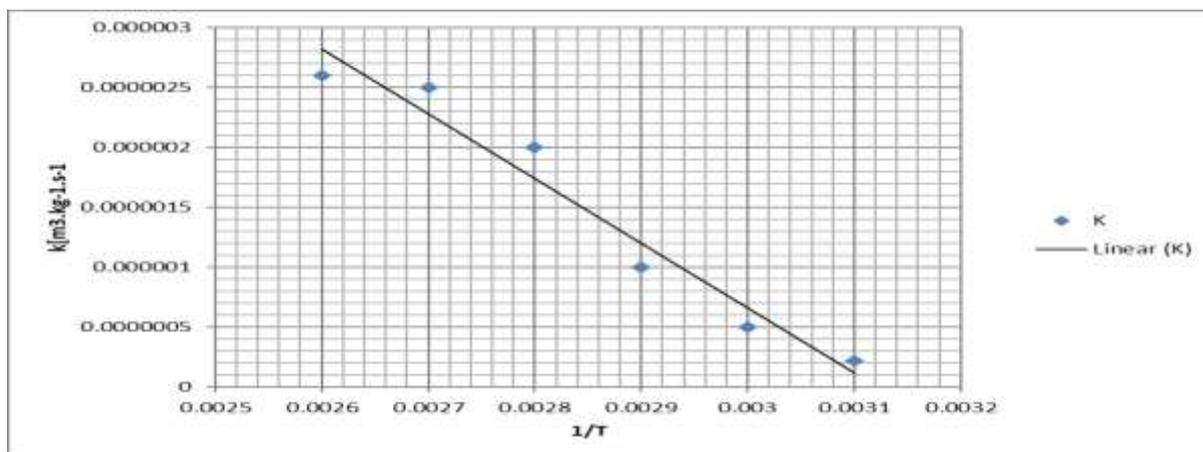


Figure 1: Arrhenius plot of the reaction rate constants.

3.2 Methodology

The experiment carried out in the chemistry lab based on the reaction of phenol-acetone reaction and also the reaction will be tested in different ways. Firstly, the reaction of acetone and phenol will be carried out. Secondly, the homogeneous catalyst will be added. Thirdly, the reaction will be processed in the presence of supercritical carbon dioxide, scCO_2 . The report will cover the first and second parts.

The main goal of the project is to use supercritical carbon dioxide as a reaction medium for the production of BPA and also for separation purposes to remove undesired products easily. Minimizing the effect of the undesired products on the BPA formation by using SCF will be another target for the study as an advantage of using green technology for BPA production and reduce the chemicals that emitted into the atmosphere and polluted the environment. This technique will be applied after synthesizing BPA by different methods to investigate and evaluate their results with/without using ScCO_2 technology.

P-Toluene sulfonic acid, acetone, and phenol were purchased from Sigma-Aldrich Company. An appropriate amount of an aqueous solution of chloroform was added to the solution at room temperature. Synthesis of bisphenol A (BPA) was carried out in the liquid phase under atmospheric pressure and 60°C in 1000ml two-neck round bottom flask equipped with a condenser and a magnetic stirrer. An 8.6g of PTSA catalyst put into the reactor with 23.5g of phenol, 2.9 g of acetone was added by a micro-syringe to start the bisphenol A synthesis. Yield was determined by a column chromatography. Furthermore, vacuuming the sample was applied after separation process to purify the final product from the residual solvents. Weights were measured before and after evaporation.

3.2.1 Characterization

Bisphenol A monomer synthesis from the condensation reaction of phenol with acetone will be analyzed by using Column Chromatography, NMR, GC-MS techniques. Spectroscopic analysis showed that BPA monomer was present in the product although significant amounts of compound formed during the reaction and residual starting material were still present.

After sampling and cooling down the samples at 0°C , evaporation was applied by using rotary evaporator for 10-20 minutes at 40-60 $^\circ\text{C}$. HNMR spectrum at 400 MHz was measured by a Bruker DMX500 with the following condition; Spinning rate 5 KHZ, Constant time 1.75 msec, interval 4 sec, accumulation 500 times, and glycine as an external standard of chemical shift. Before the measurement, the sample was cooled at -20°C .

3.2.2 Material and Equipment

Phenol and acetone as the main reactants of reaction brought from Sigma-Aldrich Company. P-toluene sulfonic acid-PTSA is available in the chemistry lab with chloroform, Methanol, Dichloromethane DCM, acetonitrile, (CDCl₃, DMSO were used as deuterated solvents for NMR) Silica gel and Sand were also available in the lab.

250 & 1000 ml two neck round bottom flask were used, rotary evaporator R-114, water bath B-480 & B-490 RE Buchi, condenser, thermometer

3.2.3 Process Selection

Condensation of phenol with acetone in the presence of p-Toluene sulfonic acid (PTSA) as a catalyst.

Acetone and excess phenol are reacted at a temperature of 60 °C and atmosphere pressure by condensation in p-Toluene Sulfonic Acid catalyzed reactor system to produce p,p-bisphenol A, water and various by-products are also formed in the reaction process. The crude distillation or chromatography column helps to remove water and unreacted acetone from the reactor effluent [9]. Acetone and unreacted materials will be sent to rotary evaporation process at 50 - 60 °C for more purification then mother liquor from purification system is cooled down at - 20.

Equipments Used:

- Reactor
- Oil bath
- Condenser
- Heater
- Chromatography Column (CC)
- Rotary Evaporator

Description:

- Components of a control System

The system is divided into the following components:

1. Process
 2. Measuring element
 3. Controller
- Controlling System Used:
 1. Temperature Control
 2. Stirring control
 3. Pressure Control

Temperature Control:

It is desired to maintain the temperature in the reactor by using a controller. If the measured temperature differs from the desired temperature, the controller senses the changes and modify at the required temperature.

Stirrer control:

Stirring can be control by using magnetic stirrer .In this experiment, IEC Magnetic stirrer was used with CAT No. : CH2090-001 STIR

Input: 220 / 240 V.AC. 50/60 Hz. 4 AMP.

Pressure control:

The pressure maintains at the atmospheric pressure [13].

3.2.4 Experimental Results and Discussion

The author has performed several experiments at the chemistry lab. Those experiments were carried out at 60 – 80 °C for all over variables where concentrations of both catalysts and reactants fixed at maximum yield level. At the end of the experiment, the reaction mixture was cooled down at room temperature and then stored at (-20) after dried and weighed. Then, the yield of reaction mixture was determined for each individual experiment using $X = 1 - (1 + 0/03t)^{-2.0}$

X: is fraction conversion of limiting component (mol/mol)

Table 2: The results of experiments

Sample	T(min)	Weight(g)	Yield (%)
1	60	16.45	7.21
2	120	38.12	16.69
3	240	65.42	28.65
4	300	125.64	55.04
5	360	139.5	61.1
6	420	140.5	61.54
7	480	140.12	61.37
8	540	140.02	61.33
9	600	135.62	59.4
10	660	130.54	57.18

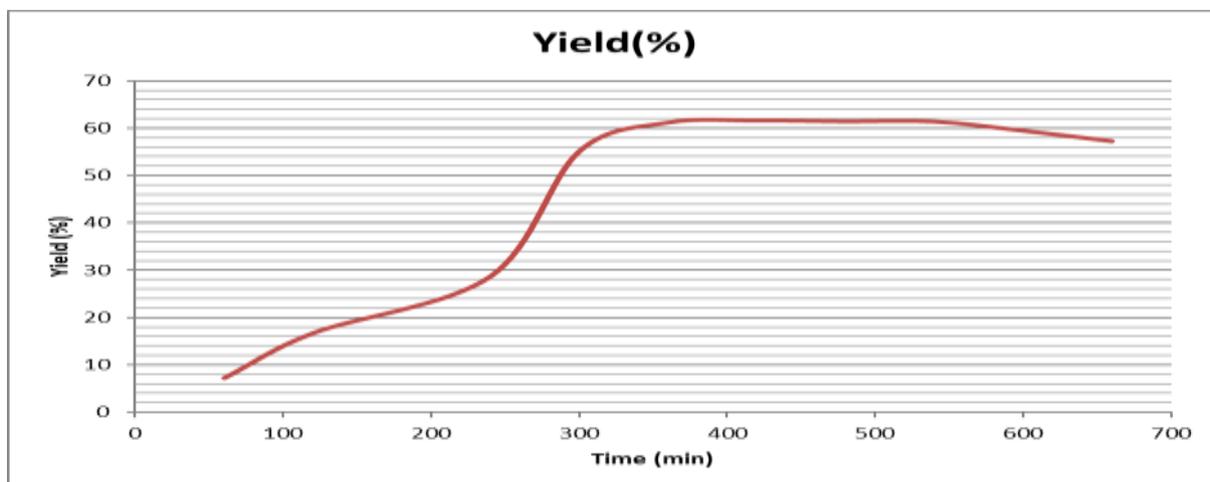


Figure 2: The plot of yield vs. time for Bisphenol A formation

The plot was generated based on experimental data. It is worthy to mention that the yield determined versus time and the maximum production are given based on

$$R : \text{Ratio Conversion \%} = R/(1+2R)$$

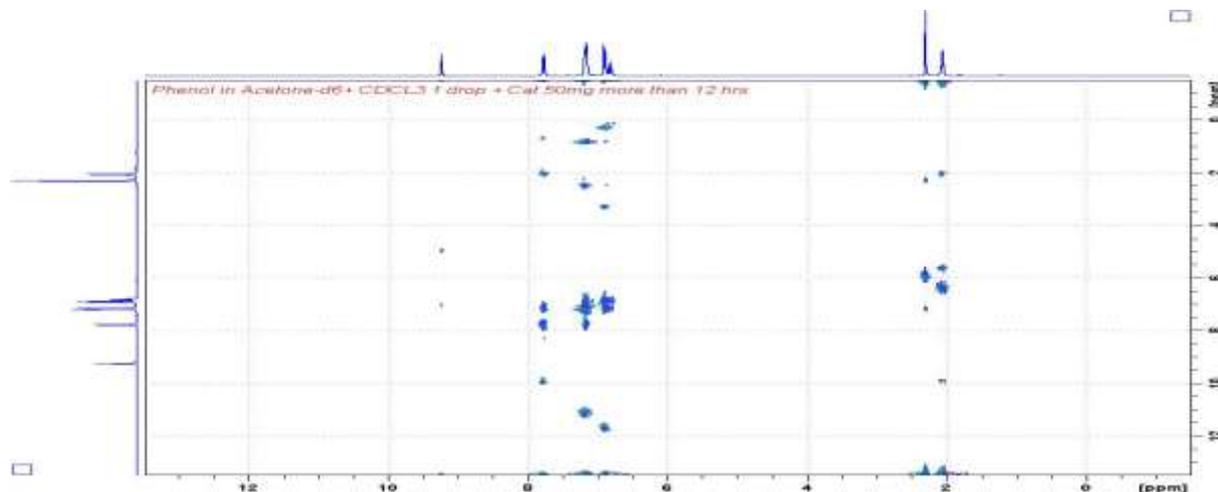
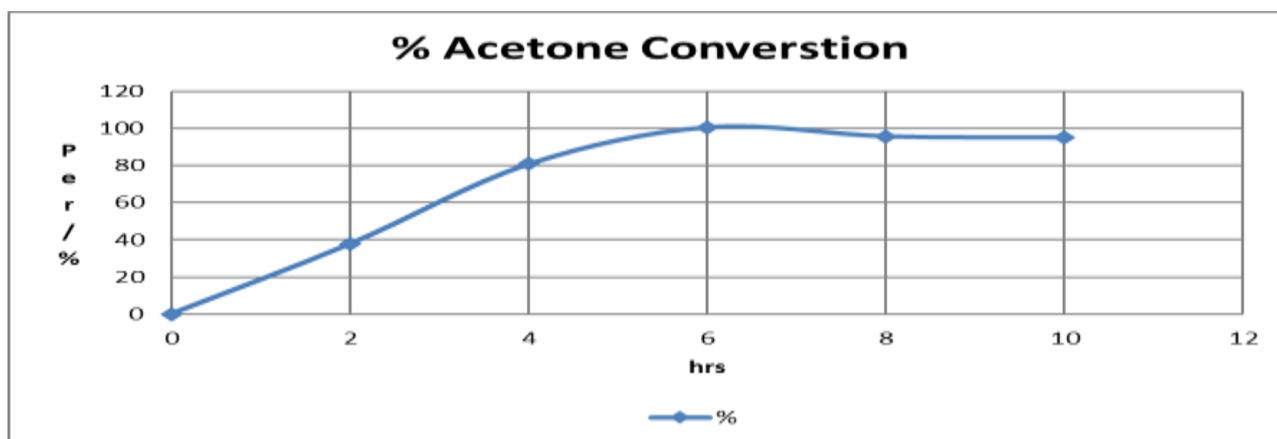


Figure 3: The reaction of phenol in acetone-D6 and CDCl3

Table 3: The time versus Conversion Data

Time	Ratio	Conversion
0	0	0
2	0.089001	0.075552548
4	0.23862	0.161531169
6	0.336909	0.20128163
8	0.31057	0.191575116



4. Statistical Analysis

The samples were analyzed by HNMR (Gyro and Flip Machines). Gyro system was used to analyze the structure of the product where flip was used for kinetic reaction purpose. All procedures and results of the analysis are described in the following sections.

The graph shows the total acetone converted to product and time needed for completion. It is very clear that after 6 hours of reaction, the whole acetone converted to products.

4.1 Design of Experiment (DOE)

The following section will focus on the experimental design to investigate and evaluate the individual and interaction effect. Using different techniques to deal with noise in an experiment, and make a good decision for the chemical process. To design an experiment by using engineering method or program, the following steps need to be investigated:

1. Response Variables
2. Factors
3. Randomization

4. Repetition and Replication

Response Variables are the variables that measured and the object of the characterization or optimization (Y's). However, defining the response will be the hardest part to design an experiment. To solve this problem, several questions have to be answered such as:

- How will the results be analyzed?
- How good is the measurement system?
- What are the baseline mean and standard deviation?

2. Factors:

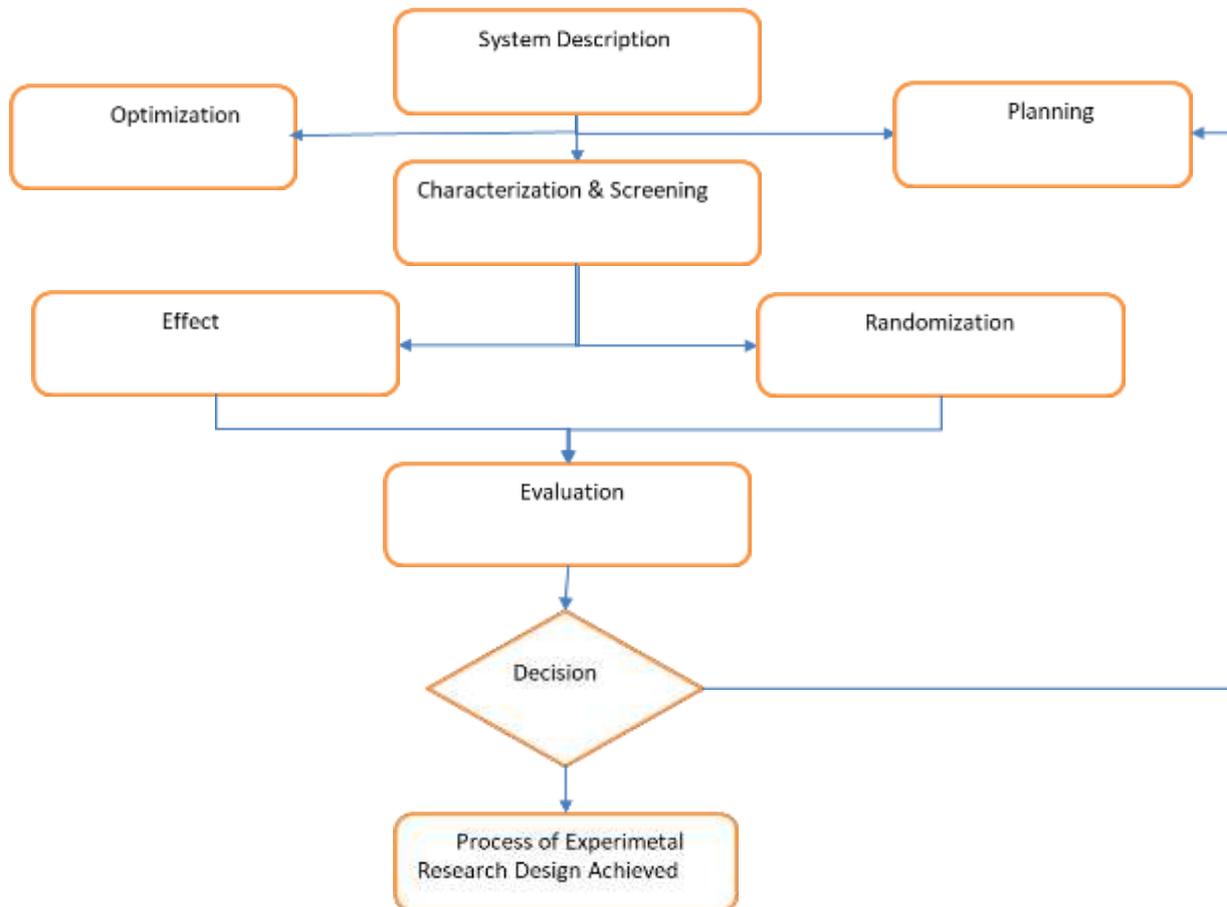
They are variables which controlled or varied in a systematic way during the experiment.

These two steps are important to design the experiment and evaluate or investigate the factors effect on the process.

The purpose of using an experimental design is to deal with different factors and make a good decision for an optimal production process. Before starting the design of experiment DOE, pre-experimental plan is recommended.

4.2 Experimental Design Methodology

Figure 5: The Protocol of Research Methodology



4.2.1 System Description

Define the scientific approach where one or more independent variables are applied to one or more dependent variables to determine their effect on the latter are important. In the methodology of any research, experimental design support physical, engineering, education and science. To describe your system, it is important to identify the important tools of the your system such as the research tools. In this research, an application of Nuclear Magnetic Resonance Spectroscopy known as (NMR). The

principle of NMR is based on the transferring the charges (energy) from a base energy to a higher energy level to study physical and chemical properties of the materials. It helps identify the structure of molecules. (I.e., medical uses).

The most industrially used process for BPA production are acetone-phenol process, in homogenous and heterogeneous catalysts. Considering the costs involved and the net advantages the heterogeneous catalysts offer, the resin-catalyzed process is preferred, and it has been improved continuously. A process which considers reacting acetone with very little excess phenol (1:4 or 1: 10) was reported by Azam and his group (Azam and Salwa, 2001). The reaction of this process consists of two steps. In the first step, the acetone is reacted with very little excess phenol in the presence of a resin catalyst to convert 20 – 60 % of acetone. In the second step, the reaction mixture from the first step will be reacted in the presence of hydrochloric acid as a catalyst. Although there were different processes using alternative feeds, by-products still come out with the product mixture.

4.2.2 Planning:

Before starting the computer program, pre- experimental planning needs to be done. The preparation requires before beginning experimentation depends on your problem. For example, you need to determine what influence factors are, what processing condition influence, thus careful planning can help to avoid problem that can occur during the execution of the experimental plan.

4.2.3 Processing Characterization (Screening)

In many processes development and manufacturing applications, potentially influential variables are numerous. Screening reduces the number of variables by identifying the key variables that affect product quality. This reduction allows focusing on the really important variables. Screening may also suggest the best or optimal setting for these factors. Then you can use optimization methods to determine the best settings and define the nature of the curvature.

Screening test by running a relatively small number of tests to isolate the most important factors.

4.2.4 Optimization:

The method of optimization helps to determine the best settings and define the nature of the curvature. The optimal values for experimental factors depend on the process objectives. The objective of this experimental is to reduce by-products and maximize the BPA Yield. The changes of concentration over time determined.

4.2.5 Randomization:

It can be done in many ways

- A. Run the treatment combination in random order
- B. Assign experimental units to the treatment combinations randomly

The advantage of randomization is to average out the effect of the extraneous factors (called noise) that may be present but were not controlled or measured during the experiment.

- C. Spread the effects of the noise across all runs
- D. These extraneous factors (noise) cause unexplained variation in the response variable (Yield).

Performance Equation

$$r_A V = \frac{dn_A}{dt}$$

$$n_A = V * C_A$$

$$r_A V = V \frac{dC_A}{dt}$$

Then:

$$r_A = dC_A/dt$$

Table 4: The randomization data

Run Order	Std order	Temperature	Time	Concentration
1	15	-1	-1	-1
2	3	-1	-1	1
3	13	-1	1	-1
4	18	-1	1	1
5	10	1	-1	-1
6	5	1	-1	1
7	9	1	1	-1
8	14	1	1	1
9	7	□	0	0
10	16	- □	0	0
11	4	0	□	0
12	11	0	- □	0
13	2	0	0	□
14	12	0	0	- □
15	1	0	0	0
16	8	0	0	0
17	17	0	0	0
18	20	0	0	0
19	19	0	0	0
20	6	0	0	0

Table 5: The conversion versus time

Time	C _{A0}	C _A	(C _A /C _{A0})	ln (C _A /C _{A0})	Kt
1	0.1	0.09978	0.997802418	-0.0022	-0.0022
2	0.2	0.199122	0.995609666	-0.0044	-0.0044
3	0.3	0.298027	0.993421732	-0.0066	-0.0066
4	0.4	0.396495	0.991238607	-0.0088	-0.0088
5	0.5	0.49453	0.989060279	-0.011	-0.011
6	0.6	0.592132	0.986886738	-0.0132	-0.0132
7	0.7	0.689303	0.984717974	-0.0154	-0.0154
8	0.8	0.786043	0.982553975	-0.0176	-0.0176
9	0.9	0.882355	0.980394733	-0.0198	-0.0198
10	1	0.97824	0.978240235	-0.022	-0.022

Time vs. Reduced (C_A/C_{A0})

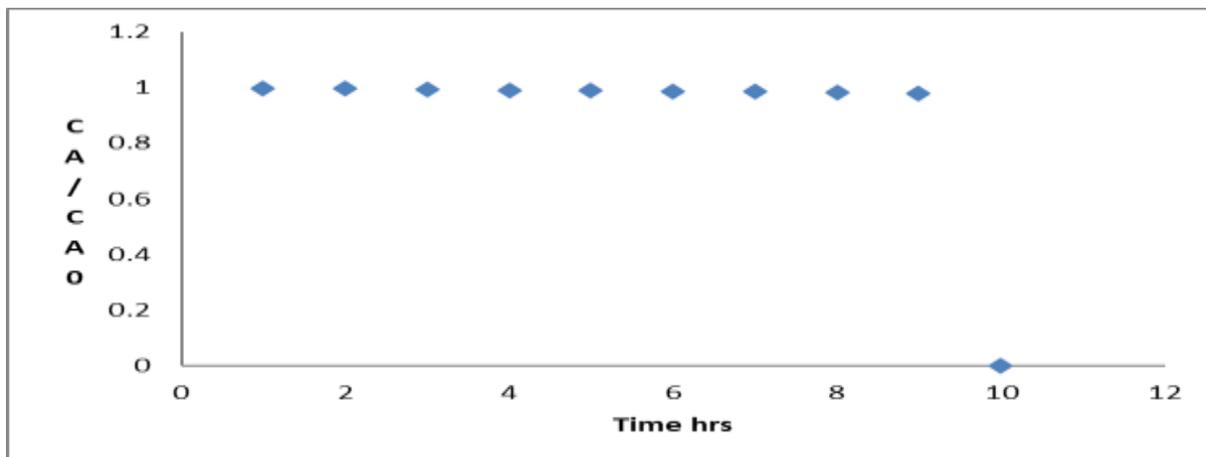


Figure 6: The trend of Time versus (C_A / C_{A0})

5. Effect

Individual effect of each factor as time, temperature, and catalyst, determined by following equation:

$$\text{Effects} = [(+Y/n) - (-Y/n)]$$

To assess the consequences of the reaction, using a reliable statistical program to determine the effect of variables on the assigned process. Minitab was performed. It enable us to identify the relationship between variables and making decision.

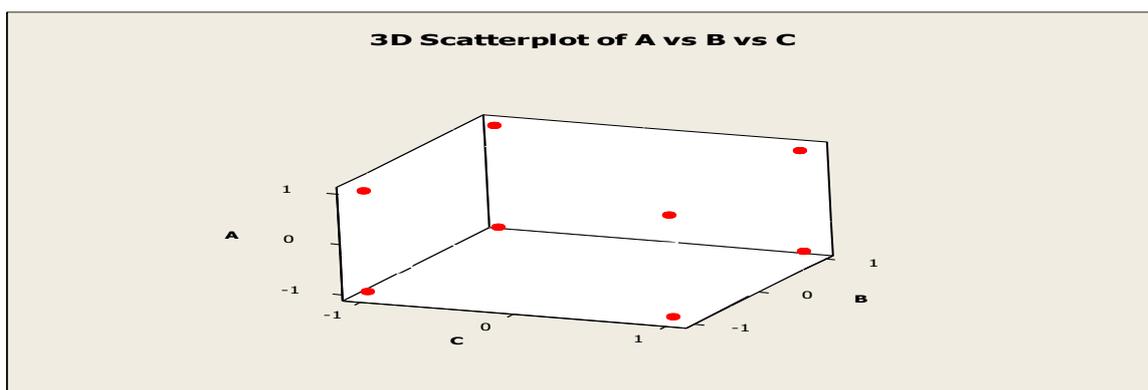


Figure 7: The cube chart of coded values of factors

Above cube chart shows the coded value of all factors from high to low values (1 to -1)

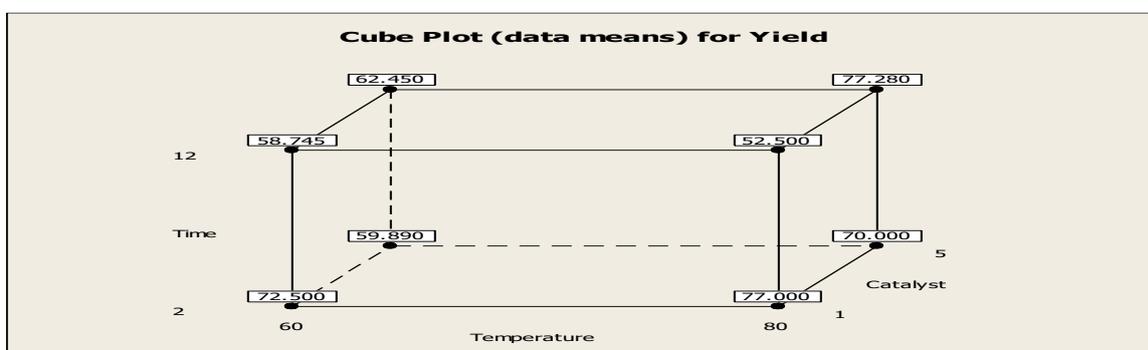


Figure 8: The cube chart of yield

5.1 Interaction Plot

In addition, the interaction effects of the different parameters on the process studied. The illustration of catalyst and time interaction presented a significant effect on the process. Thus, the time interval of the process and the type of catalyst are effective parameters. It followed by the interaction effect of catalyst and temperature then time and temperature interaction effect. However, heating may have a limited effect on the process which can be resulted from the behavior and physical properties of the materials. This can be explained by the interaction between temperature and time shown in the following figure. The separation between red and black segments was obvious therefore, the temperature and time interaction has slightly affected the process while the influence of temperature increased with catalyst.

Moreover, using Minitab to evaluate the significant factors with significant effects on the reaction process and eliminate all factors without real effect on the process. Also, it minimizes required time during the reaction.

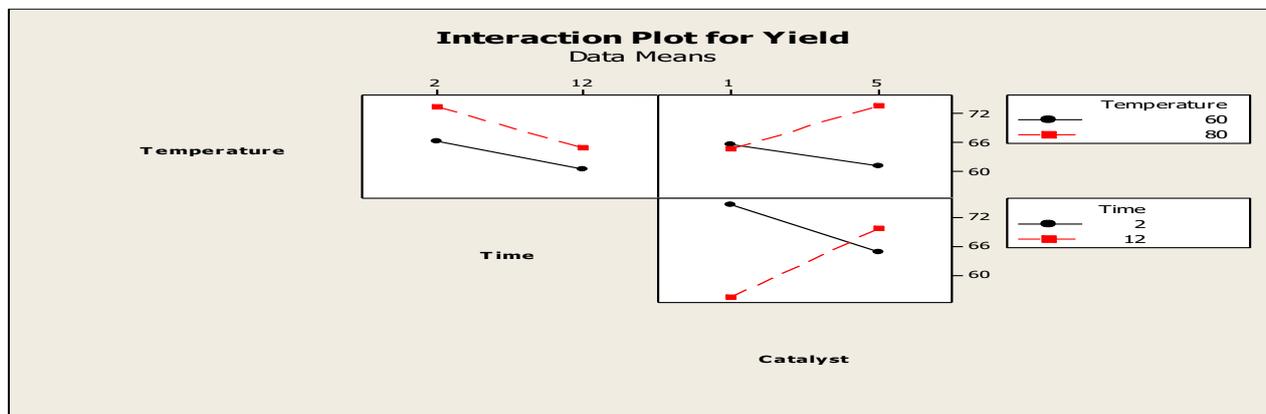


Figure 9: The relationship of the significant factors to the yield

6. Results and Discussion

General Linear Model: Yield versus Temperature, Time

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Temperature	1	777.7	777.7	777.7	1.94	0.201
Time	1	40.2	40.2	40.2	0.10	0.760

Factorial Fit: Yield versus Temperature, Time, Catalyst

Estimated Effects and Coefficients for Yield (coded units)

Term	Effect	CoefT	P
Constant	47.073	9.40	0.000
Temperature	-13.944	-6.972	0.201
Time	3.171	1.586	0.760
Catalyst	-11.146	-5.573	0.298
Temperature*Time	-0.969	-0.484	0.925
Temperature*Catalyst	-12.056	-6.028	0.263
Time*Catalyst	18.829	9.414	0.097
Temperature*Time*Catalyst	-17.031	-8.516	0.127

The results demonstrate the interaction effects of parameters on the process. The interaction between the process parameter presents a great effect on the reaction process. However, controlling such a process can be achieved by managing these parameters.

6.1 Discussion

The mechanism of bisphenol reaction from industrial starting material was studied. The obtained yield –time relationship was obtained .It was found that at about 62% can be obtained after 6 hours of reaction.

The experimental design detects the effects of different factors on the process. In addition, the experimental data shows the reaction rate of the starting materials and final products which is in agreement with the HNMR spectra results even though there were some experimental errors due to the equipments and measurement errors .In addition, designing the experiment by DOE presents the experiment by engineering way and save time and money for future research.

Although bisphenol A - BPA production process is continuously improved by different ways even by manipulating parameters, the complexity associated with the reaction stoichiometric ratio of acetone to phenol came from the variation between them (i.e., 1 -2 to 1 – 10 or 30), this may result in adding or increasing the requirement of number of process, and more processing procedure during purification. Thus, the reaction becomes more complicated.

The reaction is the industrial reaction to produce BPA by using ion exchange resin. The

Reaction shows that swollen ion exchange resin with SO_3H group attacks the aromatic ring to form BPA. Firstly, SO_3H group will react with carbonyl group (acetone) by less than completing proton H^+ and then acetone will react with phenol to give the final product of BPA, the two aromatic rings shown on the BPA structure describe the need of excessive phenol to react with one acetone to produce BPA and water. However, producing water decreases the catalytic activity of the resin. As water spreads towards the outlet, the acetone conversion decreases (Motoaki Kawase et. al., 1999). This accumulation of water prevents a long-term operation of the process; therefore, to stabilize the operation process, water must be removed. Producing water during the reaction, slow down the reaction and decrease the concentration of the product.



Figure 10: Acetone and PTSA reaction spectra 1



Figure 11: Acetone and PSTA reaction spectra 2

The analysis by NMR instrument shows that there are several products made by the reaction with small percentage, but Mesityl Oxide detected as the most by-product chemical. It is considered as a high reactive compound.

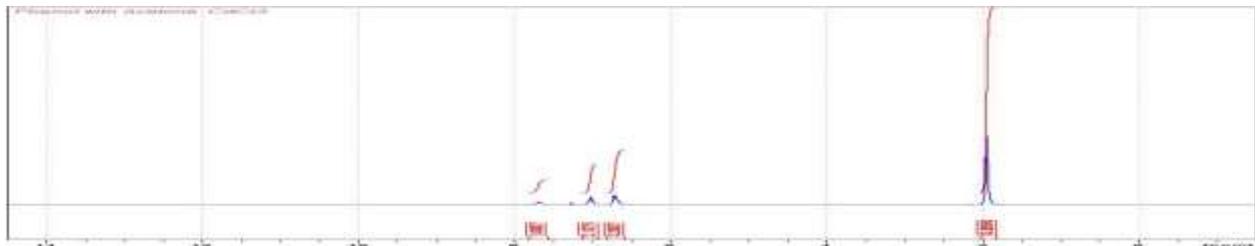


Figure 12: Acetone and PSTA reaction spectra 3

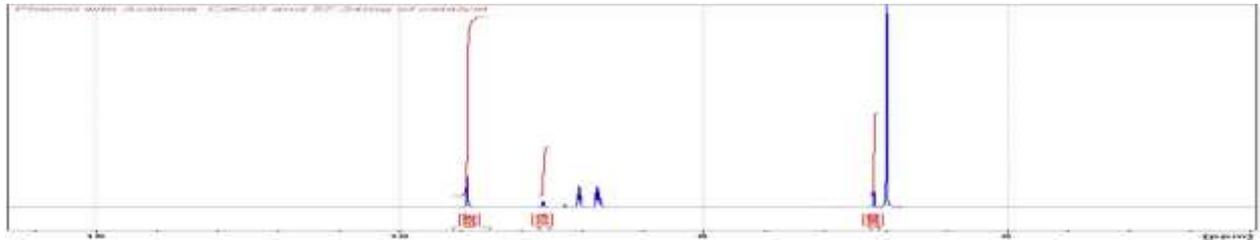


Figure 13: Acetone and PSTA reaction spectra 4

The analysis showed that the reaction of phenol and acetone in the presence of catalyst which produced bisphenol A. In addition, the development of the product while the reactant disappeared can be seen in the NMR Spectra.



Figure 14: Acetone and PSTA reaction spectra 5

7. Nuclear magnetic resonance - NMR

What is NMR?

A Nuclear magnetic resonance, known as NMR, is phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field. Most of the matter that can be examined with NMR is composed of molecules which are composed of atoms.

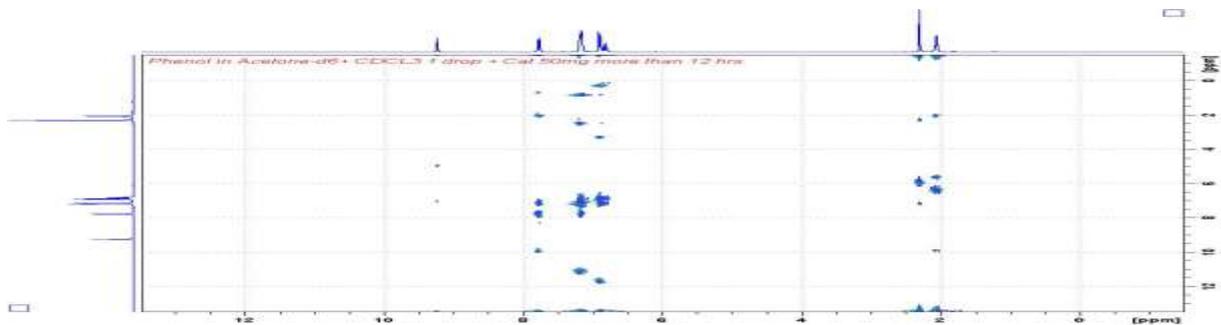


Figure 16: Acetone and PSTA reaction spectra 6

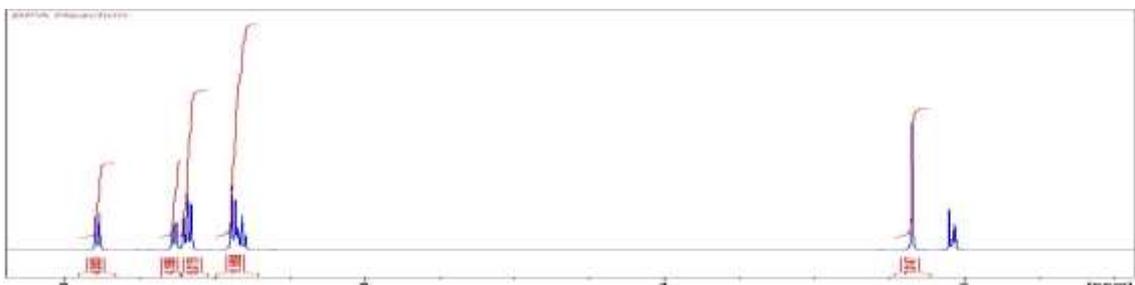


Figure 17: Acetone and PSTA reaction spectra 7

Table 6: Integration of BPA reaction

Time	A (Phenol)	B(Phenol)	C(BPA)	D(BPA)	(C+D)/8	(A+B)/5	Ratio
0	4	4	0	0	0	1.6	0
2	3.96	5.77	0.159	0.18	0.042375	1.946	0.021775
4	2.61	3.66	0.407	0.403	0.10125	1.254	0.080742
6	2.57	3.54	0.262	0.278	0.0675	1.222	0.055237
8	1	1.455	0.2029	0.2043	0.0509	0.491	0.103666
10	1.0208	1.424	0.021	0.0109	0.003988	0.48896	0.008155

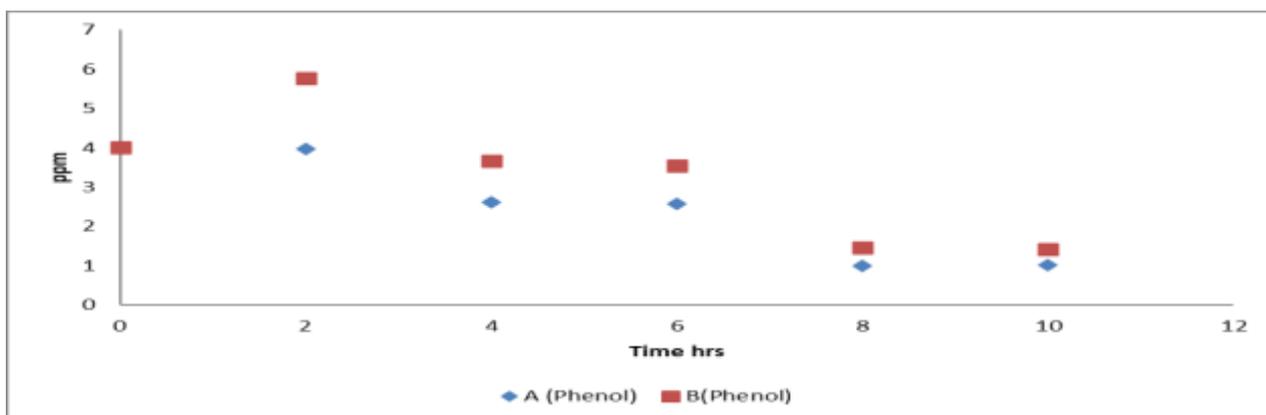


Figure 18: The ratio of conversion (Bisphenol A : phenol)

The graph illustrated the reaction rate of BPA. While the starting material phenol disappearance through the reaction time. The phenol protons (phenol A & Phenol B) decreased while the final products appear slowly during the reaction until the BPA formed. The gap between red and blue dots obvious at the beginning (i.e., $t = 0 - 2$), however, a reduction of the distance between the two dots was measured (i.e., $t = 4 - 6$). After eight hours the gap between dots was minimized and as the curve moved forward the gap between dots reduced. The following The curve shows the reaction of phenol during the reaction.

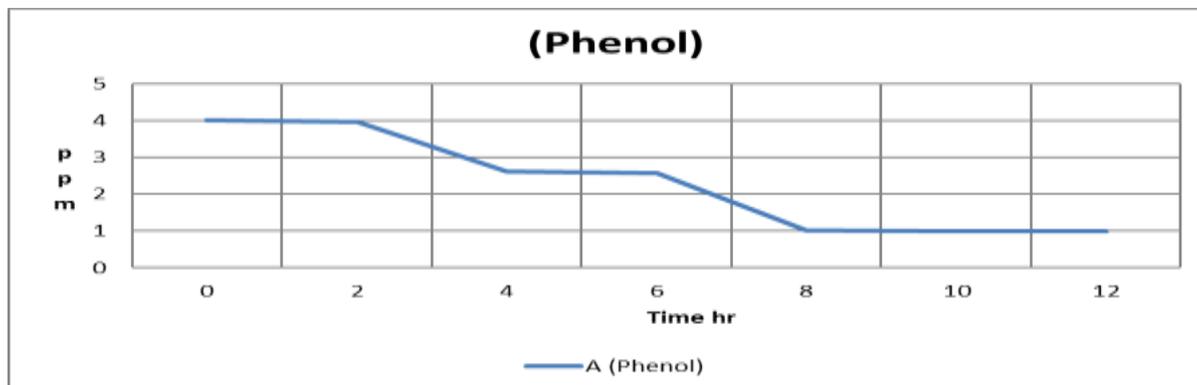


Figure 19: The starting material curve of phenol per time.

Aceton - Methanol + CO₂

The reaction modified by adding methanol. As the following table showed the expansion of acetone affected with the temperature and pressure in the presence of methanol. the reaction acetone with methanol in the presence of CO₂ performed separately due to the impurities associated with acetone. This reaction was taken at 60 °C. It is worthy to mention that acetone expanded as the pressure increased.

Table 7: Effect of Methanol-Acetone +CO₂ on the reaction process

Methanol-Acetone + CO ₂		T:		60
Run 1	V _{initial} (ml)		5	
P (bar)	Exp (mm)	Delta (mm)	V _{increase} (ml)	Expansion (%)
0.3	192	0	0	0
10	192.5	0.5	0.177705	3.5541
20	193.5	1.5	0.533115	10.6623
30.2	194.5	2.5	0.888525	17.7705
40.2	195.5	3.5	1.243935	24.8787
50.3	198	6	2.13246	42.6492
59.7	198.5	6.5	2.310165	46.2033
70	203	11	3.90951	78.1902
78.7	206.5	14.5	5.153445	103.0689
84.3	212	20	7.1082	142.164
90	222	30	10.6623	213.246
96.4	232.5	40.5	14.394105	287.8821

7.1 HNMR-Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Nuclear magnetic resonance spectroscopy is the use of the NMR phenomenon to study physical, chemical and biological properties of matter. As a consequence, NMR spectroscopy finds applications in several areas of science. NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Two-dimensional techniques are used to determine the structure of more complicated molecules. These techniques are replacing X-ray crystallography for the determination of protein structure also. Furthermore, the versatility of NMR makes it pervasive in the sciences. This is just a basic principle necessary to begin using NMR Spectroscopy. NMR Spectroscopy will be a useful technique to be used to measure the amount of BPA produced.

The experiment will be carried out in the chemistry lab to apply the reaction and measure all the factors, where other techniques such as HNMR, CC, and TLC will be explained in the following sections.

7.2 Reactor Loading and Set-up

1. Put on protective clothing, lab coat, goggles, and gloves. All the steps were performed in the fume hood.
2. Weigh the desired quantity of catalyst (10%) in a clean measuring dish.
3. Transfer the catalyst into the flask.
4. Weigh the desired quantities of phenol and acetone (4.7 g or 23.5 g of phenol and 0.58 g or 2.90 of acetone).
5. Add the measured quantities of reagents to the reactor.
6. Turn on cooling water to condenser
7. Turn on Magnetic stirrer
8. Turn on the heat and adjust the thermostat for the desired temperature

7.3 NMR Tube Reaction

1. Weigh a clean, empty NMR tube.
2. Weigh 0.05 g of catalyst in the NMR tube. To avoid transfer losses, the desired quantity was measured directly in the tube.
3. Prepare a mixture of acetone and phenol with ration of 1:2 acetone to phenol.
4. Take 40 µl of the mixture with Pipette and put them into the tube.
5. Add 600 µl of deuterated chloroform to the tube
6. Cover The NMR tube and seal carefully with parafilm.
7. Insert the tube in the appropriate spinner and adjust the depth using the sample depth gauge.
8. Turn on the air and position the tube in the magnet.
9. Lower the tube into the magnet by turning the air off.
10. Start the spinning air.

11. When the spinning rate reaches its set value, adjust lock power and lock gain.
12. Center and then lock signal.
13. Start heating the magnet by turning on the heater, setting the temperature at 343 K, and increase the air flow through the magnet.
14. Once the temperature is reached, shim the field, and start the routine for data acquisition.

7.4 Reactor Shut-Down and Clean Up Procedure

1. Put on protective clothing, lab coat, goggles, and gloves
2. Turn off the heater.
3. Turn off the magnetic stirrer.
4. Turn off the cooling water to the condenser.
5. When reactor is at room temperature, remove the reactor from the C-Clamp.
6. Distill it out by Rotary evaporator.
7. Take the weight of the sample
8. Put the sample in the fridge at -20°C
9. Then take analyze the sample.
10. Wash flask, the stopper, and the thermometer with acetone, then with water and soap, then with distilled water, and allow them to dry.
11. Rinse thoroughly the sampling syringe with acetone to remove any residuals.

7.4.1 NMR Tube Reaction

1. Remove the tube from the magnet.
2. Turn off the heater and set the temperature back to the room temperature value.
3. When the magnet cooled down, reduce the air flow through the magnet.

8. Summary

The paper covers important aspects and present a new way of producing a chemical/organic material, BPA, which is important as the main feedstock for polycarbonate production. However, there are gray areas among catalysts type that might be used during the reaction with high efficiency. The paper presenting a solution of using supercritical fluid as a green technology in order to produce bisphenol A (BPA), which can be used as an essential part of polycarbonate synthesis. To limit the use of conventional methods, reliable method has to be applied to produce BPA as a high chemical scale production.

The work presented in this study focused on effect of plastic ingredients processing by

1. Identify new suitable catalysts for BPA formation
2. Find appropriate reaction conditions
3. Determine the reaction conditions that significantly influence the process and explain their influence.

The analysis of experimental design shows that the interaction effect of temperature with catalyst has significant effects on BPA yields. Furthermore, the interaction effect of temperature with time has also a significant effect on the process but in the present of a strong catalyst with the optimal operating conditions for maximum yield. Whilst individual effects of time and concentration have minor impacts on the process.

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