A comparative study of physical and chemical methods for the separation of benzoic acid from industrial waste stream

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Certificate

This is to certify that work in this thesis has been carried out by **Rehan Khan** and completed under my supervision in School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

The project is dedicated to my ***beloved parents***, who nurtured me from childhood and not only prayed for my better future but even did struggle for while getting all troubles on their own heads.

In addition, i would also like to dedicate this project to **our** ***honourable and respected teachers*** who helped me in compiling this report.

Acknowledgments

I express gratitude and praise to ALMIGHTY ALLAH, The Creator of universe, who is beneficent and merciful, guided us in difficult circumstance, who endowed me with the will to undertake this thesis, Great respect to our Holy Prophet Hazrat Muhammad (SAW), who taught us to learn till lap of grave.

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Last but not the least my appreciation also goes to my family and friends for their encouragement, love and support throughout my life.

Abstract

Phthalic anhydride is manufactured by the partial oxidation of ortho xylene in the presence of V_20_5/TiO_2 catalyst. In the residue, maleic acid, benzoic acid (BA), toluic acid and traces of other organic compounds are present in the byproduct stream. The waste stream is in the form of slurry at high temperature and is solidified at room temperature. Benzoic acid was selectively removed from the solid waste of phthalic anhydride production industry.

In the present work, the separation of benzoic acid from crude sample has been performed by using physical and chemical techniques. In physical methods re-crystallization (RE), liquid-liquid extraction (LLE) as well as re-crystallization followed by liquid-liquid extraction (RE, LLE) and liquid-liquid extraction followed by re-crystallization (LLE, RE) have been studied. In another attempt chemical derivatization (CD) has been performed for the purification purposes. The operation has been carried out at the atmospheric pressure with operating temperatures of 100°C and 25°C in physical processes (RE) and (LLE) respectively while in chemical derivatization it ranges from 72°C to 100°C. The characterization of the samples was accomplished by melting point determination, Gas chromatography (GC), Mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) . RE technique gives high recovery with compromised purity.CD is found to be generating high purity but with only 58% recovery. While LLE is associated with optimized purity and recovery. Almost 99% of the purity was achieved by CD , LLE , RE followed LLE and LLE followed by RE.

Key words: Re-crystallization (RE), liquid-liquid extraction (LLE), chemical derivatization (CD), esterification, separation, benzoic acid, phthalic anhydride.

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Chapter: 1 Introduction

1.1 Industrial Process

Phthalic anhydride was first produced in 1830 by Augusta Laurent [1]. Naphthalene was the first feedstock and then o-xylene was used as feedstock after the world war for commercial production. In 2014 Chinese and north East Asia were the biggest producers of o-xylene in the world. Another feed stock can be (n-pentane).The n-pentane related process is still in development stages and require cheap material. The factors i.e. yield, cost, availability are considered during the selection of stock. Naphthalene and n- pentane are expensive as compare to o-xylene. In petrochemical industry, catalytic cracking is one of the fundamental process in which the heavy hydrocarbons are broken down to lighter hydrocarbons. The light hydrocarbons are usually of more importance. One of the examples of such process is the partial oxidation of o-xylene in the presence of air in a fixed bed reactor to produce phthalic anhydride. It is catalytic process in which Vanadium oxide based on Titania is used. The surface area of this catalyst is $10m^2$/gram and this catalyst can also be supported on ceria and silicon carbide. The surface area of the catalyst is not much high so that it would reduce diffusion and increase the residence time. The 63% of exothermic conversion is done in the first reaction, 7% and 5% done in second and third reaction respectively. The major units are distillation column, heat exchangers, vessels, heaters, compressors pumps, and cooling system. Air and o-xylene are feed to heater for the vaporization. The fixed bed reactor is used in this process, that is running at 1-3 bar pressure and 300 to 400 ^{o}C.The cooling should be done in order to avoid increase in temperature and is done by heat exchanging system. The top outlet stream from the reactor contains light gases and some quantity of water. It is sent to the treatment process. Water, phthalic anhydride and o-xylene are present in the bottom stream. The bottom stream is sent to distillation column to recover phthalic anhydride PA.The by products is sent to other distillation column for the recovery of o-xylene for recycling. Recently the feed for phthalic anhydride production has been converted from naphthalene to o-xylene. The heat transfer medium is usually fused salts and sodium or potassium nitrate. The ratio adjustment of o-xylene and air is adjusted in such away to avoid the explosion. This process is highly exothermic in nature with (-264 kcal/mole) heat released. O-xylene is in the feed stream along with air should not exceed 1%.The low ratio of the tube to the particle diameter avoid hot spots and deactivation of the catalyst because of the instant removal of the heat. Insufficient oxidation is the cause due to which the temperature rises from 245 to 480°C and the yield of phthalic anhydride reduces. As a result by product like BA , methyl maleic anhydride, o-toluic acid, CO_2, CO, water and traces of other organic compounds are produced [2].Phthalic anhydride is an intermediate product of flexible poly vinyl chloride,poly ester resin and also used as modifier for rubber and polymer.

The phthalic anhydride is produced in fixed bed vertical tube reactor in the presence of Vanadium oxide Titania catalyst by the reaction of air and o-xylene. Beside phthalic anhydride some byproducts are also formed like BA, maleic acid and other oxidative products [4,5].

1.2 Flow Diagram of Phthalic Anhydride Plant

Distillation column 1(D1), Distillation column 2(D2), Phthalic anhydride (PA), Maleic acid (MA), ortho-xylene (O-xy)

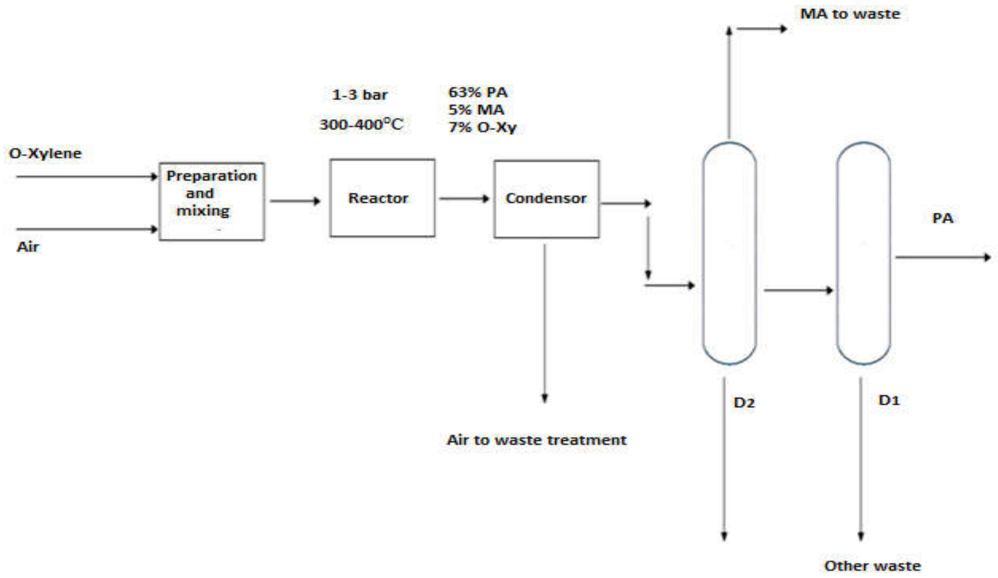
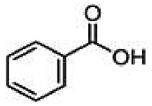


Figure1-1: Phthalic Anhydride Production Industry's Flow Sheet

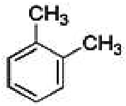
1.3 Main Reaction

The partial oxidation of O-xylene takes place in order to produce phthalic anhydride. Similarly in the same situation due to the insufficient oxidation, the side reactions take place.

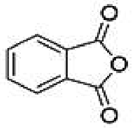
Structures of the important chemicals



$C_6H_5(COOH)$; *Benzoic acid*



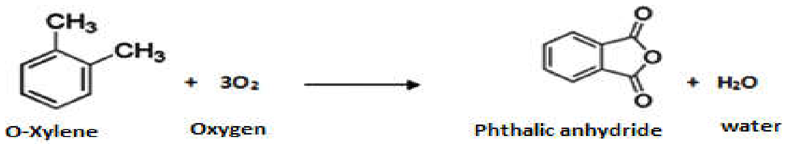
C_8H_{10};*O-xylene*



$C_6H_4(CO)_2O$; *phthalic anhydride*

1.4 Possible side reactions with the main reaction

During the side reactions, benzoic acid , maleic acid, maleic anhydride, water and other minor impurities are produced. Along maleic anhydride, benzoic acid is produced in more amount.



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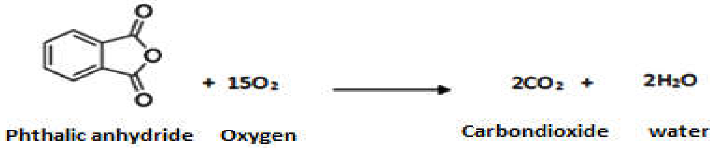

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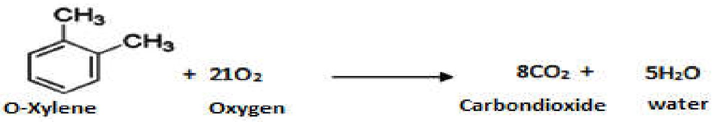

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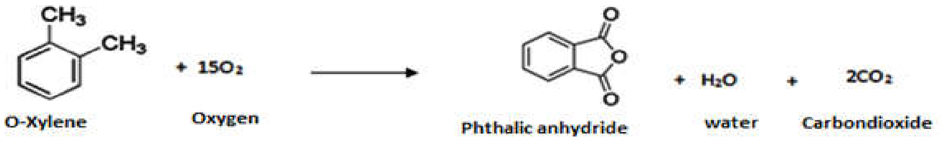

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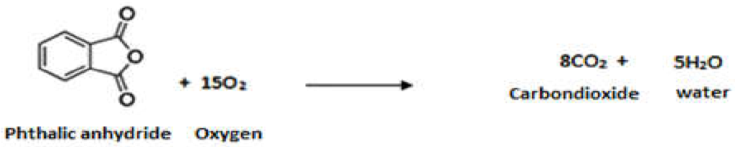

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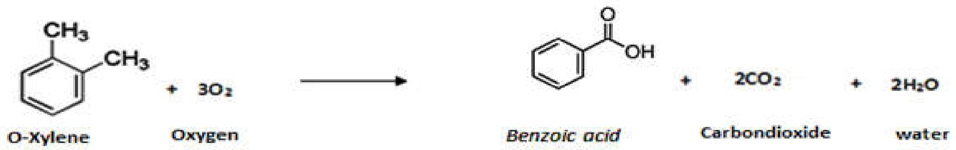

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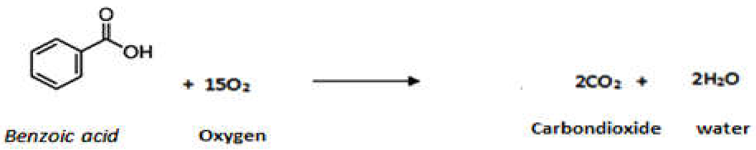


(1.8)

1.5 Reactions Kinetic for phthalic anhydride

Rate = K_1 P_{02} $P_{O\text{-}XYLENE}$ ....(1.9)

K_1; The rate constant of reaction for ortho-xylene

$P_{O\text{-}XYLENE}$ =The partial pressure of o-xylene in atm.

P_{0_2}= T he partial pressure of oxygen in atm.

The constant K1 is defined as

$\ln K_1/K_0 = -27000/RT + 19.837$

Where K_0 = 1 kilo mole/(kg catalyst)(hr)(atm)

R= 1.987 Cal/Mol,

T=In Kelvin

Table 1-1: Crude sample composition

Compound	Percentage composition
Benzoic acid	60%
Maleic anhydride	7%
Phthalic anhydride	30%
Citraconic acid and minor impurities	3%

Table 1- 2: Physical properties of Phthalic anhydride

Property	Value
Substance type	Organic
Physical type	White flake, needle
Melting point	131.6^{0}C
Boiling point	284.5^{0}C
Density	1.527 gm/cm^3
Water solubility	16400 gm/liter

Table 1-3: Characteristics of phthalic anhydride and its safety

Lower explosion limit	**1.70% volume**
Upper explosion limit	**10.50% volume**
Flash point	**152^{0}C**
Auto ignition temperature	**580^{0}C**
Lower flammable limit	**1.2%**
Upper flammable limit	**9.2%**

It is harmful if swallowed. In the presence of moisture, possible burn and cause problems to eyes. It may be the cause of irritation in respiratory track. PA has the ability to react with oxidizing agents .It can slightly react with moisture while incompatible with nitric acid, sodium nitrite and copper oxide. It should be stored in separate place outside the main building .it is protected from physical damages. It is stable at normal temperature and pressure. Heat and other ignition sources are avoided [4].

Table 1- 4: O-xylene properties and the safety

Lower flammable limit	**0.90%**
Upper flammable limit	**6.7%**
Flash point	**17.22^{0}C**
Auto ignition temperature.	**465^{0}C**

1.6 Objectives of the project

[1] Purification of Benzoic Acid By Physical And Chemical Methods.

[2] Purification of crude sample by recrystallization and liquid-liquid extraction.

[3] Purification of crude sample by Chemical derivatization.

[4] Characterization of the purified samples , GC-MS, FTIR, and melting point determination.

[5] Comparison of the experimental techniques in term of purity and recovery.

Chapter: 2 Literature survey

2.1 Benzoic Acid Purification by Pressurized Water

The literature survey was conducted on the separation of BA from the industrial waste by different techniques. One of the ways is pressurize hot water extraction of benzoic acid (BA) and phthalic anhydride (PA) from industrial waste through modified supercritical fluid extractor. It is for the first time used for the extraction of BA and PA. BA and PA can be selectively removed from the petrochemical waste by pressurize hot water extractor technique. The design is based on semi-continuous extraction. The selective extraction of BA and PA is achieved from the mixture of phthalic acid, aldehydes, toluic acid, maleic acid and other minor impurities. The pressure ,temperature, flow rate and extraction time required are 60-220 bar,60-140^{0}C ,0.2-1 ml/min, 5-45 min respectively [4].In present days environmental pollution is a serious issue which can`t be overlooked anymore and can be reduced by the implementation of modern technologies in the existing processes. There is intense need for economical, safe, effective, environmental friendly systems. Supercritical CO_2 has also been used for the purification in the same circumstance. It is observed that the supercritical water is no more of less importance in the isolation and purification process. At room temperature ,the polarity of water may have the ability to act as solvent for hydrophilic organic compounds, while at high temperature the water is good solvent for hydrophobic substances as it becomes less polar at elevated temperature. The degradation of compound take place at 374^{0}C, the critical temperature of water, so it is appreciated to operate the purification process at low temperature to preserve the integrity of important chemicals and avoid physiochemical changes. The PHWE, pressure hot water extraction is one of the methods tending to accomplish the process at temperature below critical temperature of water with more competence. The solubility of the pressurized water can be changed for hydrophobic substances, by altering temperature and pressure. Surface tension, dielectric constant and viscosity of water are reduced at critical temperature than it has at standard temperature and pressure, thus the mass transfer rate is increased and the extraction time is reduced [5].

Table 2-1: Composition, rate of production and concentration of each component [5]

Composition	**Rate of production (kg/h)**	**Concentration (w/w%)**
Phthalic anhydride	**15.6**	**51.7**
Toluic acid	**6.4**	**21.5**
Benzoic acid	**2.3**	**7.7**
Phthaldehyde	**1.2**	**4.0**
Maleic acid	**1.1**	**3.7**
Aldehydes	**0.1**	**0.3**
Minor impurities.	**3.3**	**11.1**
Total	**29.8**	**100%**

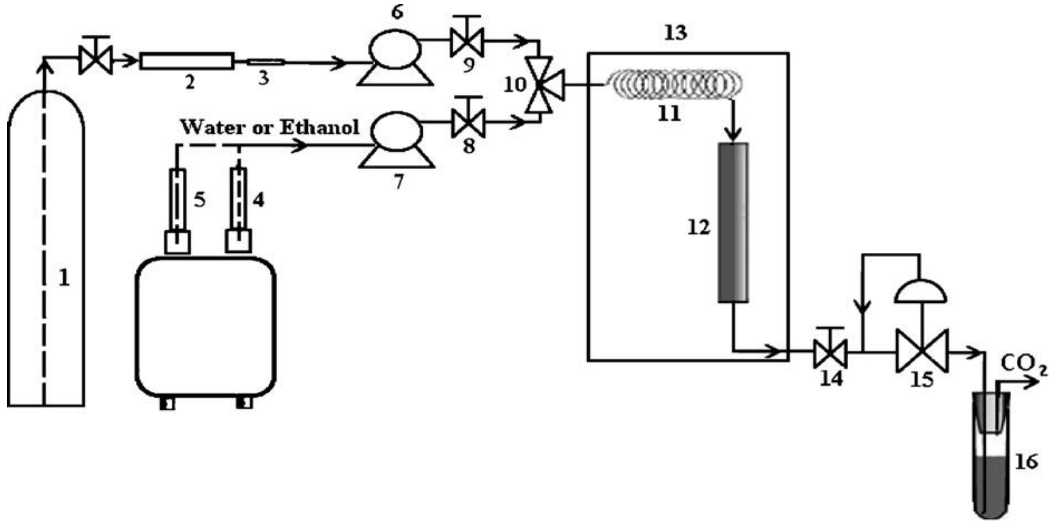


Figure 2-1: Schematic diagram of pressurized hot water extraction unit. [8]

In the figure (2-1) the following numbers are related to the respective parts of the diagram.(1) CO_2 tank; (2) molecular sieve filter; (3) 2 m pore size filter; (4) water tank; (5) ethanol tank; (6) carbon dioxide transfer pump; (7) high-pressure piston pump; (8, 9, 14) two-way needle valves; (10) three-way valve; (11) preheating coil; (12) extraction cell; (13) thermo stated oven;(15) back-pressure regulator and (16)sample collection tube.

It is easier to deal with supercritical water than supercritical CO_2, because CO_2 require liquefaction before it is pumped to the extractor. The advantage of the process (PHWE) is dealing with water in liquefied form than dealing with gases. Organic and inorganic modifiers can be used for enhancing the analyte separation. It increases solubility of compounds in the water. It also reduces the critical temperature of water**.** The main summary of this investigation is that, the separation of about 98% BA is accomplished by PHWE procedure. And the required parameters are as under [6].

Required parameters for PHWE purification procedure

Temperature:	**140^0C**
Pressure:	**118 bar**
Flow rate of water:	**0.9 ml/min**
Extraction time:	**29 min**

2.2 Adsorption of Benzoic Acid

On the same way adsorption of BA by hydrotalcites and their calcined products has also been studied and results were observed. BA is a common pollutant and is a toxic chemical with injurious effects on human body. It is a threat to human ecosystem and recovery of BA is an environmental friendly process [7].Hydrotalcites (HTs) and its calcined (CHTs) products have excellent ability to absorb BA from polluted water. The adsorption of the specie had been observed at different PH values of water. Understanding pH value is related to know about the dissociation of BA .pH value effect the ionization of BA and the more the ionization of BA, the more is adsorption on the surface of adsorbent.

The changing amount of the adsorbent and its effect on the adsorption was observed. Similarly the effect of the altering temperature on adsorption was studied. The phenomenon is actually related to the adsorption of anion that is formed after dissociation of BA. The regeneration was performed by recalcination at 500^0**C.**pH adjustment has significant role in the adsorption of sample over the surface of adsorbent. The investigated range of pH was between 4.5—9.5.The absorption of BA at different pH was observed and the adsorption was found to be dependent over it. The equilibrium adsorption quantity at pH 4.5 on HTs and CHTs were maximum, because of maximum ionization, while at pH 5.5 and pH 9.5, the adsorbent was low due to incomplete dissociation. The equilibrium adsorption quantity of CHTs is more than HTs at same pH value.

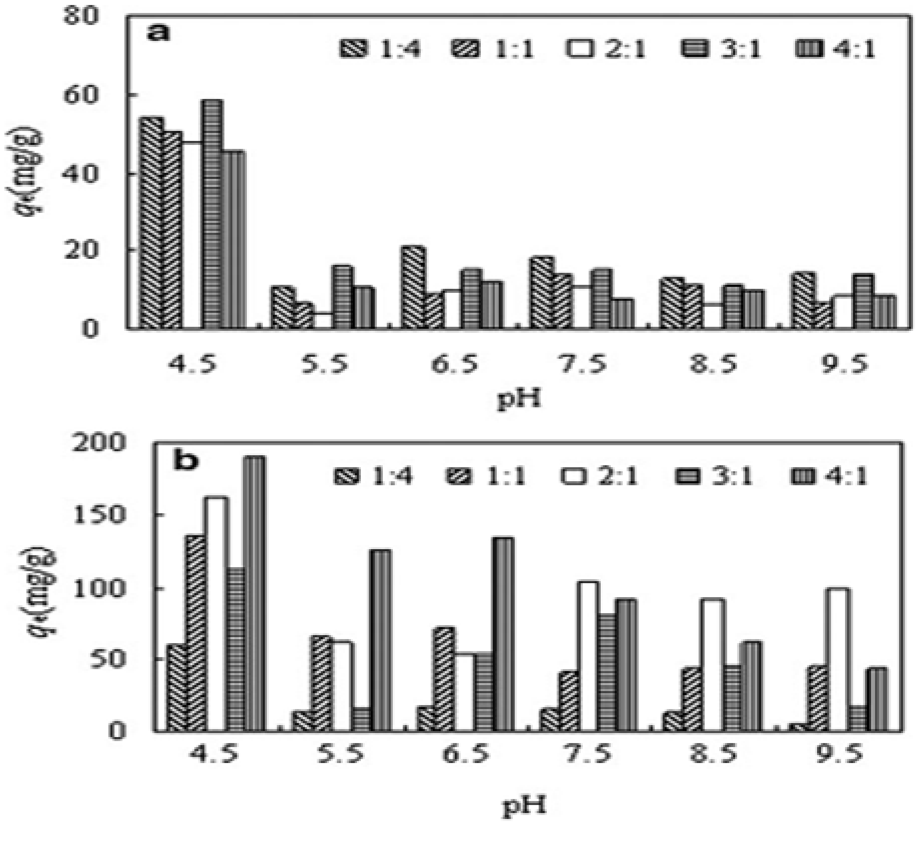


Figure 2-2: Adsorptions of BA over (a) HTs (b) CHTs at different pH at 293K, adsorbent amount; 0.02gm, initial concentrations; 220mg/l of BA [15].

The effect of Mg/Al ratio has been observed and extracted the conclusion that it has no effect on the adsorption of BA over surface, but adsorbent dosage is affecting adsorption.

The equilibrium adsorbent quantity is inversely proportional to the adsorption. At the lab scale test 0.01 gm is the suitable dosage for maximum adsorption on the surface. The quantity of dosage is associated with the unsaturation of adsorption site. The adsorption sites remain unsaturated when dosage is increased and thus leads to less adsorption. The problem associated with the process is the adsorption of very low quantity of benzoic acid [8].Temperature has its unique effect on the adsorption of BA on HTs and CHTs .in the case of HTs adsorption show inverse relation with temperature and in case of CHTs the higher temperature is responsible for the enhanced adsorption [17].

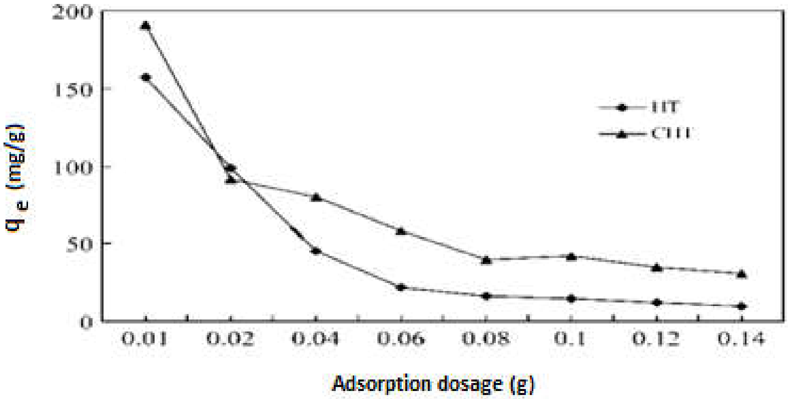


Figure 2-3: Recovery of BA on HTs and CHTs with molar ratio of Mg/ Al 2:1 as function of adsorbent dosage at 293 K, at pH 4.5,initial concentration 250 mg/lit

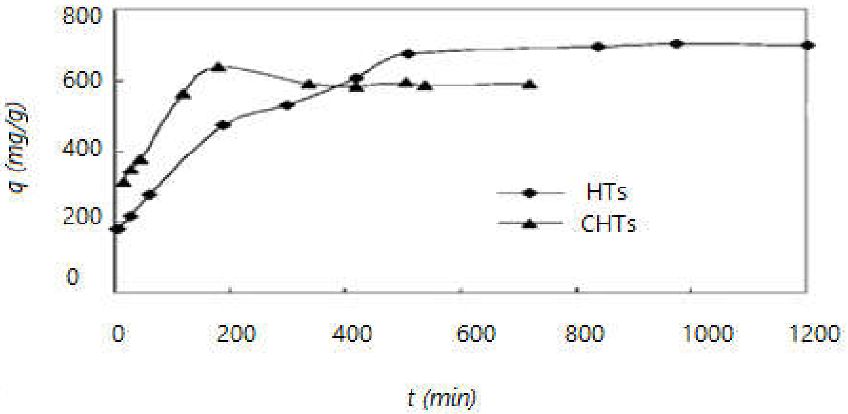


Figure 2-4: Adsorption of BA on Hts and CHTs Adsorbents with an Mg/Al molar ratio of 2:1 as function of contact time (initial pH4.5)

Adsorption equilibrium time is 600 min and 180 min in HTs and CHTs respectively.Equalibrium adsorption quantity of BA on CHTs was more than on HTs at the same temperature. Adsorption equilibrium is established between the adsorbate in solution and adsorbate on adsorbent surface.

2.3 Vacuum Distillation for the Purification of Benzoic Acid

Combination of High efficiency evaporation and vacuum distillation has been used for the recovery of BA from the industrial residue. The residue contains BA, flourenone, benzyl benzoate and other minor impurities and is obtained from caprolactum industry. The separations of heavy components like flourenone and benzyl benzoate were accomplished through high efficiency evaporation method by controlling the parameters i.e. temperature at 260 ^{0}C and pressure at 16 kpa.

Table 2-2: The composition and physical properties of the components of residue

Name	**Mass fraction %**	**Melting point / ^{0}C**	**Boiling point / ^{0}C**
Benzoic acid	21	122.4	249
Benzyl benzoate	42	21	323
Fluorenone	16.56	84	341
Benzophenone	1.38	45	305.3
Phenyle methanone	1.12	165	311
Others impurities	17.23	220	400

Evaporation was performed in rising and falling film evaporators. In the evaporation section the BA in the residue was increased about 60% and then sent towards the vacuum distillation unit. The rising film evaporator has 16m^2 heat exchange area while falling film evaporator has 22 m^2 .The evaporator chamber are filled with heating pipes and the heat transfer medium is oil that are kept at 320 ^{0}C.The BA in the storage tank are at 120 ^{0}C and then pumped to the rising film evaporator. After the heavy components separation the residue has increased BA about 63% and sent to the vacuum distillation unit. The BA and crude benzyl benzoate are separated here. BA is obtained at the top while benzyl benzoate is obtained at the bottom of the column. The temperatures at the top and bottom of the column are 181—186 ^{0}C and 240--250 ^{0}C respectively while the reflux ratio is kept at 3:1. Reflux is the ratio of liquid condensed and return to the column, divided by the liquid obtained as product. Controlling all these parameters 98% yield of pure BA at the top of column is obtained.

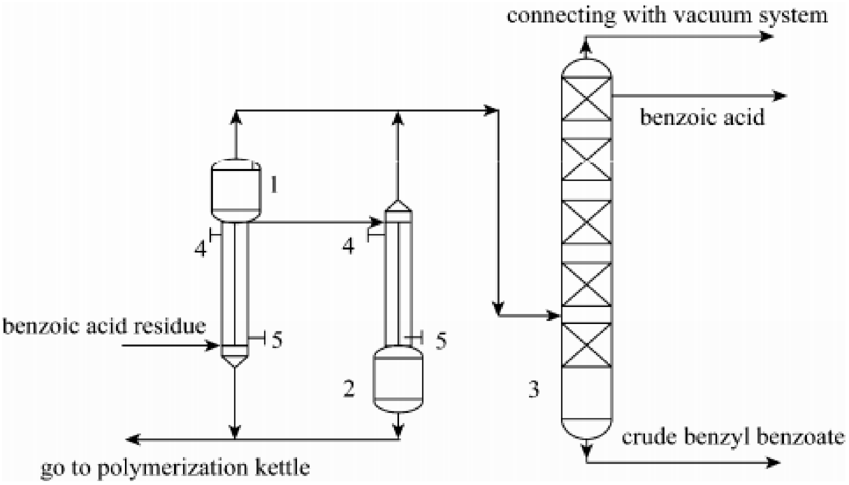


Figure 2-5: Plant Diagram of the evaporating system and distillation column distillation

In the figure (2-5) the different parts of the distillation systems are shown by their respective numbers. 1- rising film evaporator; 2- falling film evaporator; 3- benzoic acid vacuum distillation column; 4- heat conducting oil outlet; 5- heat conducting oil inlet.

Three kinds of streams are obtained in the whole process. The crude benzyl benzoate, BA stream, and the heavy residue that was further sent to polymerization unit for the coumarone resin production. The reason of not selection common distillation process is the blockage of apparatus by BA.While the vacuum distillation makes the process to be done at low boiling points. The vacuum column has 64 stages inner dia of 800mm and height of 25m.the collection of pure BA was 35 kg/hr [12,13].

Table 2-3: Reflux Ratios and Temperatures [14]

Reflux ratio	Bottom temperature^{0}C	Top temperature^{0}C	Purity of benzoic acid
1	250	186	94.5
2	250	186	96.1
3	251	186	98.1
5	251	186	98.7
6	251	186	99.1
8	251	186	99.3

2.4 Adsorption of Benzoic Acid on Bentonites Surface

Adsorption of BA from aqueous solution by three kinds of bentonites has also been carried out with appreciating results. In water treatment plant, removal of toxic chemical is important step. Actually different kinds of bentonites i.e. natural bentonites (Na-Bent),hydro aluminum pillared bentonites Al(OH)-Bent,octadecyl trimethyl ammonium chloride bentonites OTMAC-Bent ,and combination of octadecyl trimethyl ammonium chloride and hydroxyl aluminum modified bentonites (Al(OH)-OTMAC-Bent) has been used for adsorption and their adsorption capabilities has been observed. General bentonites are presented by Al_2O_3 SiO_2 .H_2O.The adsorption was achieved at different temperature in batch process. The adsorption of (Na- Bent),Al(OH)-Bent was not appreciating while the appreciating results were showed by and Al(OH)-OTMAC-Bent) ,OTMAC-Bent .The optimum condition for the adsorption of the last two types were pH of 3.5, 0.04 g/ml adsorbent amount and contact time of 90 min.The adsorption is endothermic and is directly proportional to temperature. Activated carbon has tremendous ability for the adsorption of BA but the matter is high cost, it is expensive as compare to bentonites. Due to natural abundance and low cost its usage has been increased [10].

Table 2-4: Bentonites Specifications

Adsorbent	**BET Surface area(m^2/g)**	**Pore volume(cm^3/g)**	**Average pore diameter (nm)**
Natural bentonites	10.15	0.03071	3.515
Na-Bent	31.67	0.06075	7.672
Al(OH)-Bent	167.3	0.1215	8.794
OTMAC-Bent	26.70	0.08663	10.53
Al(OH)-OTMAC-Bent	71.54	0.1005	9.261

These experiments were performed by observing the adsorption of BA on the different bentonites at different pH, temperature, contact time and adsorbent concentration. The adsorption of BA ON (Na- Bent), Al(OH)-Bent ,OTMAC-Bent,(Al(OH)-OTMAC-Bent) has been accomplished with fixed 10ml,5mmol/l BA solution. Effect of pH over adsorption was observed. The graph demonstrates that at pH 3.4 adsorption was inflated and it was trivial especially in case of OTMAC-Bent, Al(OH)-OTMAC-Bent) while in case of (Na- Bent), Al(OH)-Bent adsorption was insignificant. The reason of enhanced adsorption at 3.4pH was the complete dissociation of BA in the solution. Similarly adsorbent concentration affects the adsorption of BA specially altering the concentration of OTMAC-Bent and Al(OH)-OTMAC-Bent) at fixed pH .The adsorption increases up to specific value and then no more increase occur. Contact time has its own affect in the adsorption phenomenan.The equilibrium in adsorption was achieved at about 90 min.And the adsorption is directly proportional to the contact time until equilibrium is achieved.

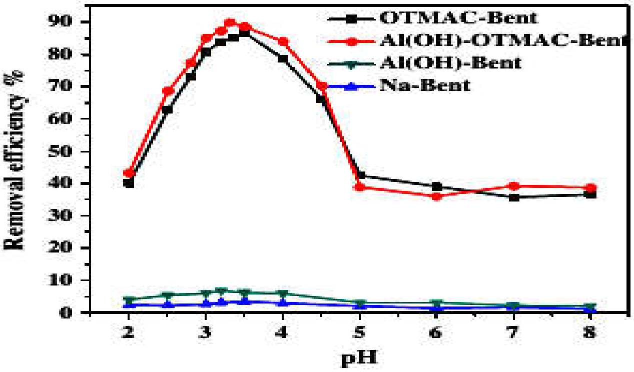


Figure 2-6: pH Effect of Benzoic Acid Adsorption on the Adsorbents

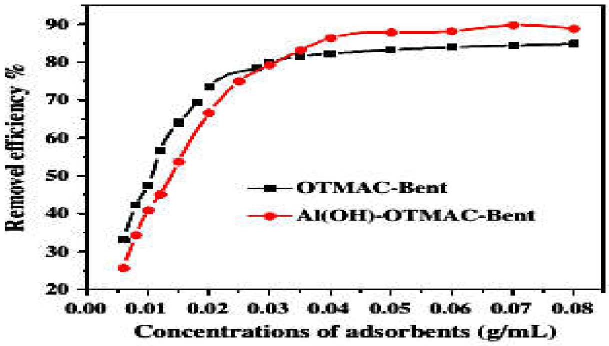


Figure 2-7: Concentration`s Effect on the Adsorption of Benzoic Acid on Adsorbents

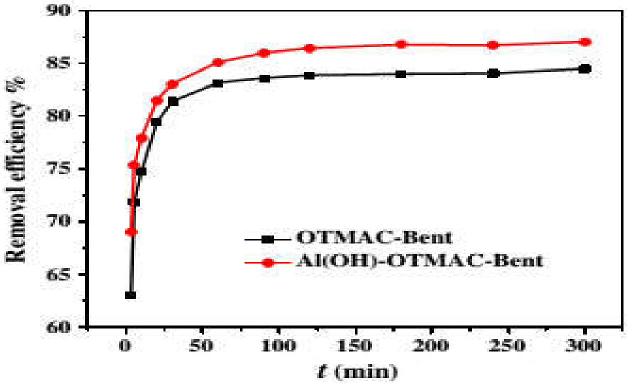


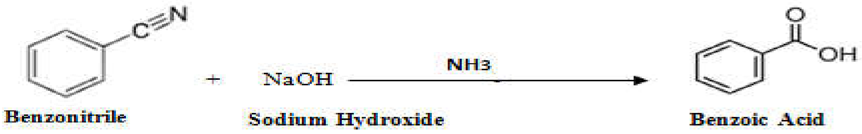
Figure 2-8: Effect of Contact Time on Benzoic Acid Adsorption Over OTMAC-Bent, (Al (OH)-OTMAC-Bent) [10]

2.5 Methods of benzoic acid preparation

Benzoic acid is an organic compound with molecular formula C_6H_5COOH. BA is produced commercially by the reaction of oxygen with toluene at about 200 ^{0}C temperatures in liquid phase in the presence of catalyst. It was first discovered in sixteenth century through the dry distillation of gum benzoine by Nostradamus (1556) and subsequently by Alexis pedemonetanus (1560) and Blaise dewignere (1596) Justus, Won, Liebig and Friedrich determine the structure of BA [16]. Catalyst used for the reactions are cobalt and manganese salt. Dry distillation is the process in which the solid substances are heated to produce gaseous products (which may be condensed into liquid). This process usually requires high temperature .It is used for extraction of liquid fuels from wood or coal. It can also be prepared by the oxidation of benzene with sulfuric acid or carbon dioxide in the presence of catalyst. Almost 90 % of the commercial BA is converted to phenol and caprolactum. It is used for the synthesis glycol benzoate. Other methods involve the oxidation of benzyl alcohol, benzalaldyehyde, cinnamic acid also by hydrolysis of benzonitrile, benzoylchloride. BA naturally present in many plants. BA is an important chemical for the synthesis of many organic compounds. The salt and esters of BA are known as benzoate. The first industrial process was related to the reaction of benzotrichloride with $Ca(OH)_2$ in water by using iron catalyst or iron salt. The reaction produced calcium benzoate. The resulting calcium benzoate was then converted to BA by the reaction of hydrochloric acid [16,17].

2.6 Hydrolysis of Benzonitrile to Benzoic Acid

Reaction



………(2.1)

In the scheme (2.1) the reaction of sodium hydroxide and benzonitrile was carried out in the reflux condenser. The reflux is detached to remove NH_3. The reaction mixture is then reacted with HCl (3 molar) to precipitate out BA.

2.7 Preparation of Benzoic Acid from Benzyl Alcohol

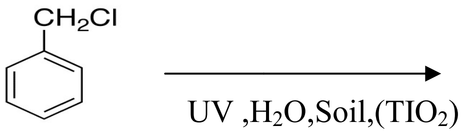
Reaction

……(2.2)

In the scheme (2,2) reaction takes place into steps. The benzyl chloride is converted to benzyl alcohol by reaction with sodium carbonate then the benzyl alcohol is reacted with potassium permanganate to form BA. The temperature required for this reaction is in the range of 70 to 100 ^0C in the reflux condenser.

2.8 Benzoic Acid Preparation from Benzyl Halides

Reaction



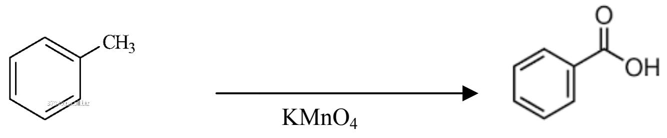
…………. (2.3)

Benzyl halide **Benzoic acid.**

In the scheme (2.3) conversion of benzyl halide (chloride) can be achieved by the oxidation reaction of halides in the presence of water and ultra-violet radiations. This is carried out in open atmosphere. Titanium oxide addition to the soil enhances the yield.

2.9 Benzoic Acid Preparation by Oxidation of Toluene

Reaction



+ H_2O ……………… (2.4)

Toluene **Benzoic acid** **Water**

Direct oxidation of toluene to BA with molecular oxygen can be achieved in the presence of cobalt catalyst. The molar ratio of oxygen to toluene, temperature, reaction time, catalyst loading values were found to be 2,157 ^{0}C, 2 hour, 0.57 gram/L respectively, for the optimum production of BA. The reaction can be liquid or gas phase [17].

2.10 Applications of benzoic acid

Benzoic acid has a lot of applications in the daily life and is very important chemical. It is used for the production of phenol by the oxidation of decarboxylation at 300--400 ^{0}C.The temperature of the reaction can be lowered by using catalyst of copper salts. The phenol can be used for the synthesis of nylon by converting it to cyclohexane. Benzoate plasticizers such as triethyleneglycol ester, glycol-triethyleneglycol are produced by transesterification of methyl benzoate with diols.transesterification is the way in which the exchange the organic (R) group of an ester, with the organic group of alcohols. These types of reactions are catalyzed by acids or bases and lipase enzymes. On the other hand BA and its salts are used as preservatives .BA prevents growth of yeast, molds and some kind of bacteria. It is added directly or reacted with sodium, calcium or potassium salts. The BA absorption occurs into the cell. If the intercellular pH changes to 5 or goes lower, the anaerobic fermentation is decreased by 95%.food like soft drinks, pickles, juices (citric acid) and other acidified foods are preserved by BA and its salts. There are chances up to some extent of benzene production if the BA and its salts react with the ascorbic acid present in soft drinks.About 0.05—0.1% of BA is used for the preservation process. Food with BA can be used and allowed by the international food law. It is used for the production of Whitefield ointment which is used for skin treatment to prevent fungal attack, ringworm and athlete foot .BA is also a major chemical in tincture of benzoine and Fairs balsam. These products are used as topical antiseptics and inhalant decongestants. Benzyl chloride is one of the product synthesized from BA is used as artificial flavor.

2.11 Benzoic Acid Safety

Benzoic acid is not the dangerous chemical found in the working place but however proper handling is still needed to avoid any problem. It is non toxic and stable at ordinary conditions. No occupational exposure limits has been still established for it. But still it have some health risks therefore safety work practice should be followed.

- Washing hands after handling it.
- Use in well ventilated area.
- Dust generation and accumulation should be minimized.
- Eye contact, skin, clothing should be avoided.
- Wash cloth before reuse.
- Breathing dust is avoided.
- Eliminate all the ignition sources during handling BA.
- When BA is spelled then the area should be washed and left well ventilated.
- BA should be stored in well ventilated, cool, dry place away from heat, peroxide (oxidizing agent), strong acids and bases.

2.12 Short and Long Term Effects of Exposure to Benzoic Acid

After exposure to BA the following effects can occur.

- Eye damage
- Skin irritation resulting in a rash, redness, burning feeling.
- Irritation in throat, nose, lungs if inhaled in vapor form and may cause coughing and shortness of breath.

2.13 Benzoic Acid Exposure Management

- In case of eye contact one should immediately flush eyes with large amount of water for at least 10 minutes.
- After inhalation one should move toward fresh air and after injection one should rinse mouth 4 or 5 times with water [18].

Chapter: 3 Experimental

3.1 Separation of benzoic acid by Re-crystallization

It is one of the significant organic chemistry experiments for the purification of sample with impurities. The dissolution of solid in solvent is accomplished in a specific approach. The solvent should be suitable for the solid that is to be purified. Heating the solute and cooling it are the main steps. Cooling the solution cause the yield of crystal.

Water is the best solvent for benzoic acid Re-crystallization because at 10 ^{0}C only 2.1 gram of BA dissolves in one liter of water while at 96 ^{0}C the solubility reaches to about 67 gram per liter. The substance should be less soluble in the solvent at room temperature. While near the boiling point range the required substance should have high solubility in the selected solvent. The nature of the solvent correspond the nature of solute. For example the common solvents for the re-crystallization phenomenon of BA are ethanol, methanol, cyclohexane acetone, benzene and water. Heating is the factor that dissolves the crystal in solvent while at room temperature it remains undissolve. Ethyl alcohol can also be used as a solvent for BA but due to ethyl benzoate formation the solvent is avoided. Similarly benzene can also be used as solvent but need high purity and more is expensive compared to water.

The cooling process has more importance in the purity if the product. The cooling rate alters the purity. The slower the cooling, the slower is the formation of crystal and of higher the purity. An inverse relation exists between the rate of cooling and product purity. It is usually achieved at room temperature. Sometimes the yield of crystal is less. It can be increased by scratching inside the flask with glass rod. Scratching actually provide more rough surface. The cooled solution is filtered. Mostly Erlenmeyer flask is used for the process. When the solution is heated, the solvent may evaporate and thus the small neck of the flask prevents the solvent loss. The amount of crystal causes the variation in the flask size. Usually the flask size is 2 to 3 times the value of solvent used. The solvent usage should be minimum to prevent it, the sample should not be dissolve at the temperature below boiling point. Some of the impurities are insoluble so avoid the solvent addition for dissolving them. Removal of impurities is an important step and is accomplished by gravity filtration.

3.2 Material Required

Hot plate, 125ml Erlenmeyer flask, stirring rod, Buchner funnel, 50ml beaker, boiling stones, weighting paper, 25ml graduated cylinder, melting point apparatus, filter paper.

3.3 Procedure

Crude benzoic acid (BA) of 5 gm was taken and put in specific amount of water. The solvent is water as it is considered as best solvent for the Re-crystallization. The amount of water taken was about 500ml in the flask. Heating the flask until the crude sample was dissolved and the solution became clear. Sometimes the sample has some impurities that would not dissolve in it thus the addition of more solvent is avoided. After dissolving the sample the solution is cooled at room temperature. The crystal appears in the solution after 2 or 3 hours. But we can keep it for whole night. The needle structured crystals are observed. Filtration is done in order to separate the BA crystals from undissolve impurities. After the dried crystals were obtained, were weighted. Re-crystallization separation is based on difference in the solubility of the solute in the solvent [19].

3.4 Observations and calculations

Recovery = weight of pure sample/ weight of sample of before Re-crystallization * 100

Initial weight taken =5 gram

Yield = 4.25/5 = 85 ± 5%

Recovery of benzoic acid assuming 60% in crude sample 100% but the presences of impurities were detected.

3.5 Melting point determination after Re-crystallization

Testing of the purified BA is performed by determining its melting point. Its melting point is about 121.1^{0}C.

$T_1 = 120.9\ ^{0}C$, $T_2 = 121.3\ ^{0}C$

T average = $121.1\ ^{0}C$

The temperature of solid at which its state changes from solid state to liquid state is called melting point. Difference substances have different melting points. Determining the melting point is one of the methods of inspecting about the purity of the substance. For example the melting point of BA is 122 ^{0}C in the literature but in the impure state the value of melting is lesser than the literature value. It is actually the physical property of compound. The difference in the melting points of compounds is due to the different structure. Melting point is insensitive to pressure and no pressure correction is needed while in the boiling point it matters. Melting and boiling point can be useful in the identification of substance.

The melting point of the pure is greater than impure substances. The impurities have the ability to disturb the lattice of the compound and the weak lattice can be easily broken with less energy. While in the case of boiling point, it is increase by the presence of the impurities which don't allow the molecules of the liquid to escape. In pure sample the main point is that the atom or the molecules are attached in regular pattern. And there exists strong forces. And thus high temperature is needed for melting them. Due to the presence of impurities the regular Pattern or repeating pattern of the molecules is disturbed, so the melting point is depressed and less energy is required for melting. The determination of the melting point is accomplished by melting point apparatus. The organic compound is taken in small amount in power form. The sample is put in the capillary tube. The capillary tube is attached to the thermometer that is located in the heating path. Gentle heating is done. The melting point of the required component is obtained from the literature. In the standard procedure the upper limit is adjusted. Then the increase in the temperature occurs according to the slope adjusted. When the temperature of the apparatus reaches to the melting point of the required sample, the keen observation is needed to note the two kinds of temperatures on the display. Temperature is noted at two situations, at one point where the vapours appear and at other point the complete melting of the sample is achieved. The capillary tubes are put in the trash can. Hot capillary tube may burn tissue if touched immediately removed from device.

T_1 = Temperature at which vapors appear

T_2 = Temperature at which substance is completely melt

T average = $T_1 + T_2 / 2$

Melting point of crude sample:

T_1= 108 ^{0}C ,T_2 = 117 ^{0}C

T average = 112.5 ^{0}C

3.6 Separation of benzoic acid sample by Liquid-liquid extraction

The type of separation in which one or more solute in a feed is transferred to another immiscible liquid .The mass transfer phenomenon is dominated in the process. Extracting is drawing or pulling something from something. In chemistry liquid extraction is getting compounds from solid or liquid by liquid solvent. It is also called solvent extraction. The main principle in the process is the difference in solubility of solute in two different immiscible liquids. It is the main procedure used in chemical laboratories [20].The main equipments used are separation funnel, counter distributation equipment. In the separating funnel, densities of the two immiscible liquids are responsible for the separation of the layers. The dense layer is at the bottom while less dense is above the dense. While in counter current chromatography, two immiscible liquids with no solid support are operated. One of them acts as stationary and the other as mobile phase. The movement of the components in this process is relative to the mobile phase.

Physical and chemical processes are taking place in it. It is also referred as partitioning .Solvent extraction also means to separate specific components from mixture of components by dissolving in suitable solvent [21].

3.7 Distribution Constant

The ratio of the concentration of solute in organic phase divided by its concentration in aqueous phase. It is the property that measures the extraction level in two phases. It shows how better the extraction is. Amount of extracting solvent and other parameters are responsible for effecting the distribution constant. It is denoted by K.

The Equation related to the liquid -liquid extraction

$$[A]_i = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^i [A]_o \quad \text{...........}\mathbf{(3)}$$

Ai: Concentration of (A) remaining in the aqueous solution after extracting Veq.

A_0: Original concentration of species A

V org: Volume of the organic solvent used

K: The distribution constant of the system.

The general method for it is to use solvent in small amount in each turn than using it in the bulk at once. The equation (3) above is related to the fact that the extraction shows good results when carried out in several steps as compare to do it in one step by consuming all the extracting solvent at once. It is used in the condition when distillation process in uneconomical or insufficient to extract the pure of components. It is suitable in azeotropic mixture separation and for the heat sensitive components [22].

3.8 Limitations of Liquid-Liquid Extraction

The solvents should be immiscible. Emulsion formation is discouraged. In some processes large amount of toxic solvents are used, that create disposal problems. The disadvantage of this process is also the wastage of time as it is more tedious and slow phenomenon.

Liquid -Liquid Extraction Application in Industries

1) Petroleum industry
2) Fine chemical industry
3) Bulk chemical industry
4) Biotic chemical industry
5) Pharmaceutical industry

3.9 Liquid-Liquid Extraction

The type of separation in which one or more solute in a feed is transferred to another immiscible liquid .The mass transfer phenomenon is dominated in the process. Extracting is drawing or pulling something from something. In chemistry liquid extraction is getting compounds from solid or liquid by liquid solvent. It is also called solvent extraction. . The main principle in the process is the difference in solubility of solute in two different immiscible liquids.

Material Required:

- Separating funnel , beaker 100ml
- Spatula , stand , filter paper
- Flask 125ml, funnel, Crude BA,
- Sodium bicarbonate, 3 molar HCl.

3.10 Experimental Procedure

Crude benzoic acid (BA) of 5 gm was taken and dissolved in 40 ml of ethyl acetate in (1 flask)**.**50ml of 1molar sodium bicarbonate was added to flask 1 and mixed well. The layers were allowed to separate and two types of layers were observed. Upper one layer is clear and the lower has blur appearance. The upper layer is poured in flask 1 and the lower layer to flask 3.Now 3molar of HCl about 20ml was added slowly drop wise with gentle shaking the components in the flask 1.after short time after addition precipitation was observed. Filtration of the precipitate was performed and then kept overnight for drying. The dried sample was tested in gas chromatography device and also the melting point was determined [23-25].

Experimental Data and Observations

Amount of ethyl acetate used= 40ml

Amount of 1 molar $NaHCO_3$ sodium bicarbonate = 50ml

Amount of 3 molar HCl = 20ml

The amount of crude sample = 5 gm

Recovery = weight of purified sample/ weight of benzoic in the crude sample * 100

Initial weight taken =5 gram

Yield = 2.7/5 = 54 ± 4%

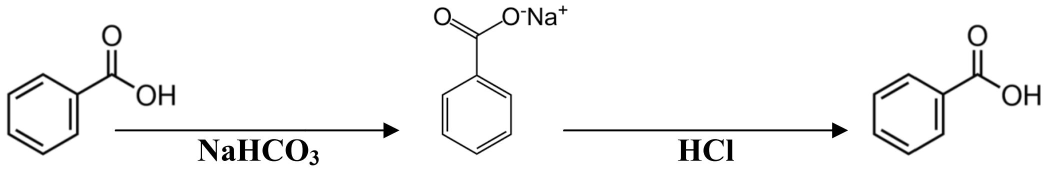
Recovery of benzoic acid by assuming 60% in the crude sample = 90± 5%

Melting point =122.6^{0}C

Literature value of BA melting point= 122.41^{0}C

3.11 Chemical Equation of the Liquid-Liquid Extraction Process

Conversion of impure BA to sodium benzoate and convert later to BA again.



Benzoic acid step 1 **Sodium benzoate** step 2 **Benzoic acid** **… (3.1)**

3.12 Re-crystallization followed Liquid-Liquid Extraction

Re-crystallization followed by liquid-liquid extraction was performed. By the combination these two types of experiments, purity was appreciated but there is compromise on the recovery. The recovery in this case was almost 65---66% [22].

Material Required

- Separating funnel, beaker 100 ml ,3 molar HCl
- Spatula, stand ,filter paper ,Sodium bicarbonate
- Flask 125 ml, funnel, Crude BA.

3.13 Experimental Procedure

Benzoic acid (BA) of 5 gm was taken and put in 350 ml of distilled water. The mixture was heated for almost 15 minutes. The temperature of the mixture was kept constant at 100^0C.After some time the crude BA disappears and the transparent solution is obtained. The water is then allowed to cool for almost 3 to 4 hours. The needle structures were observed after cooling. The crystals formed are separated from the water and impurities by filtration. The crystals of BA are obtained on the filter paper while the impurities are removed along with water. The crystals of BA were washed with cold water several times to remove remaining minor impurities [24].

In this process we get the recovery almost 85—90%.

Liquid – liquid extraction was carried out after the Re-crystallization step. The same procedure was followed as in experiment 2 with almost 68 %.

Measurements and Observations

Initial weight taken =5 gram

Amount of distilled water =350 ml

Amount of ethyl acetate used= 40 ml

Amount of I molar $NaHCO_3$ sodium bicarbonate = 50 ml

Amount of 3 molar HCl = 20 ml

Recovery = weight of purified sample/ weight of the crude sample * 100

Yield = 2.4/5 = 46 ± 3 %

Recovery of benzoic acid by assuming 60% in the crude sample = 76 ± 3%

Net Recovery= 76 ± 3%

3.14 Liquid-Liquid Extraction followed by Re-crystallization

Liquid-liquid extraction followed by Re-crystallization was performed. The same procedures were followed almost with the same amount of BA. Recovery is almost equal to the recovery of the 3rd experiment.

Initial weight taken =5 gram

Amount of distilled water =350ml

Amount of ethyl acetate used= 40ml

Amount of 1 molar $NaHCO_3$ sodium bicarbonate = 50ml

Amount of 3 molar HCl = 20ml

Recovery = weight of purified sample/ weight of benzoic acid in crude sample* 100

Initial weight taken =5 gram

Yield = 2.45/5 = 46 ± 3 %

Recovery of benzoic acid by assuming 60% in the crude sample = 77 ± 3%

3.15 Separation of benzoic acid Chemical Derivatization

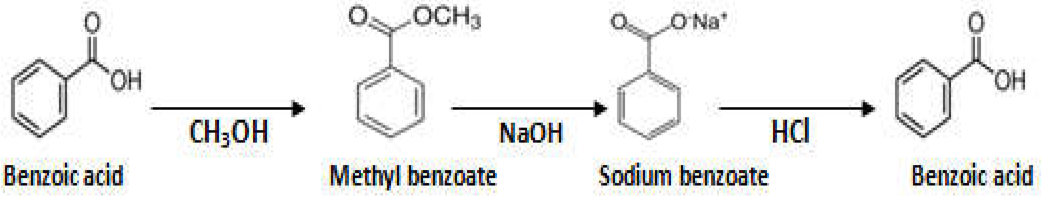
Chemical derivatization (CD) is one of chemical method used for the purification of BA. The method is about the conversion of carboxylic acid to ester. These reactions are commonly catalyzed by an acid that speeds up the reaction between the two reactants. The Keq equilibrium constant for these reactions is 4 for the most of the reactions and thus the ratio of the two reactants is 1:1 with almost 67% yield. Excess of alcohol can increase the yield by shifting the equilibrium to the right Side of the equation. The process is also called fisher esterification reaction. The yield may reach to the 95% by the use of excess amount of alcohols [25].

Reaction under reflux condenser is the way to maintain constant elevated temperature. The reflux condenser has two parts. One is the reaction flask usually round bottom flask and the other part is a condenser attached to the reaction flask. During heating the solvent evaporates and then come down back to the reacting flask after being cooled by the circulating water. In this process the volume of the solvent does not change because no solvent is allowed to go out of the flask. The cooling is done by the circulating water around the condenser. The circulating adjustment is done in such a way that it enters at the bottom of condenser and goes out at the top of condenser. At the start the flow rate of the circulating water is kept high for 2 –3 second and then the rate is reduced so that the trickle of water is required [26]. The circulated water is adjusted before the reaction is started. If the heating rate is correctly adjusted, the condensed drops can be observed. The high flow rate of water in the condenser may pop off the tubing and will spray all over. During the reaction boiling stones are put in the flask to avoid bumping of solvent. Reflux condenser is usually used for heating mixture for extended time and to prevent boiling away of solvent. Most of the organic reactions do not take place at room environment so the reflux heating adjustment becomes necessary for it i.e. the reaction between BA and methanol [27].

Drying agent is a chemical, used for the removal of water from the organic substances. When an organic compound is in contact with aqueous solution, there is possibility that some of the water will be dissolved by the organic phase. Different organic compounds have different tendencies of dissolving water. Many organic compounds are immiscible with water but however they can dissolve some amount of water due to its polar nature like diethyl ether dissolve water 7% of its weight. The more polar the compound the more it has the ability to dissolve water [28].The dissolved water form bond with the organic phase .Similarly in the present experiment one of the species (methyl benzoate) has the dissolving ability. The removal of water in these types of reactions is necessary because it may alter the rate of reaction [29]. During the reaction between methyl benzoate and sodium hydroxide, the presence of water associated with methyl benzoate may change the required concentration of the sodium hydroxide solution. Water can decrease the concentration of sodium hydroxide solution by the addition of more water molecules per volume. When the solution contains aromatics, the best drying agents for it are, $MgSO_4$, $CaCl_2$, and $P_4O_{10.}$ But in all these three $MgSO_4$ is considered the best for the present case of drying because of its fast action and more surface area. Liquid drying agents can also be used like acetone, acetic acid, aniline [30, 31].

One should carefully add drying agents because product loss may occur after adding too much of it. After adding it, the mixture is allowed to stand for some time until it is fully transparent. When the mixture is translucent, there is still drying agent flowing around in the mixture. Solid drying in (CD) reaction is considered best due to economics and efficiency while the liquid drying agents are expensive and also the separation of the layers may reduce the recovery of the BA [32].

3.16 Chemical equation of the chemical derivatization process



(3.2)

In this process the crude BA is converted to methyl benzoate, methyl benzoate to sodium benzoate and at the end sodium benzoate to pure benzoic acid.

3.17 Chemical Derivatization

Chemical derivatization (CD) is one of chemical method used for the purification of BA. The method is about the conversion of carboxylic acid to ester. These reactions are commonly catalyzed by an acid that speeds up the reaction between the two reactants. Reaction under reflux condenser is the way to maintain constant elevated temperature. Drying agent is a chemical, used for the removal of water from the organic substances. When an organic compound is in contact with aqueous solution, there is possibility that some of the water will be dissolved by the organic phase.

Apparatus required

- Reflux condenser, separating funnel,
- Heating plate, funnels, filter paper,
- Round bottom flask, rotary evaporator, physical balance, beakers.

Chemical required

- Methanol, crude BA
- Magnesium sulphate, sulfuric acid
- Sodium bi carbonate, ether, water.

3.18 Experimental Procedure

Crude BA of 5 grams was taken and mixed with 45ml of methanol in the round bottom flask. The amount of methanol can be varied but the suitable amount in this case is 25ml.The reaction was catalyzed by the addition of 1.2ml H_2SO_4.The reactants were mixed and attached to the reflux condenser [33]. The mixture was heated almost for 2 hour by keeping temperature at 70^0C. After reflux the reactants, methyl benzoate and some of the unreacted BA and sulfuric acid were poured in the separating funnel. It was mixed with 75ml water for the washing purpose. Rinsing the reaction flask with 35ml ether is done and it is also poured into the separating funnel . The removal of water from the reaction during methyl benzoate formation can shift the reaction towards the formation of more methyl benzoate. After shaking the lower aqueous layer was drained that contained unreacted methanol and acid [34]. The remaining ether layer was washed with 15 ml water and drained. The ether layer was again washed with $NaHCO_3$ (0.5M) solution to remove the untreated BA .During the washing cautiously shaking was necessary to get more progress in reaction. The CO_2 produced in the process can create pressure inside the separating funnel. The drying of the ether layer is achieved by $MgSO_4$ [35].Methyl benzoate was retained and the ether was evaporated by rotary evaporator at 36^0C.The methyl benzoate was then refluxed with NaOH saturated solution at 100 ^{0}C with almost the same volume as methyl benzoate. The reactants were refluxed for 2 hour and the stopped. Sodium benzoate was produced in this process which was then converted to BA by the addition of 3 molar HCl to the sodium benzoate almost double the volume of it. The precipitation occurs that was the conformations of the presence of BA [36].

Esterification reaction is the chemical conversion between alcohols and carboxylic acids. This reaction occurs in the presence of sulfuric acid as catalyst. During the reaction methyl benzoate and water is produced**.** The water in product has the tendency to react with ester and form alcohol back. To avoid the back reaction, sulfuric acid is added as catalyst.

Carboxylic acids have fewer tendencies to transfer protons. Therefore H_2SO_4 was used to protonate the reaction mixture and speed it up. Due to the presence of water in the reaction product, the reaction has more chances to get the reactants back. In other term the reaction is more reversible without catalyst. As the sulfuric acid has dehydrating ability so the water produced in reaction is absorbed by acid and thus avoid the back reaction. In fact the sulfuric acid doesn't participate in the reaction by itself but remain unconverted. The other reason of adding the catalyst was to carry out the reaction at low temperature, because the Esterification reactions are usually taking place at high temperature. Usually small amount of acid s are used in the reaction while using it in large amount may be uneconomical. Similarly adding more acid may lead to complexity during separation. The addition of hydrochloric acid (HCl) to the sodium benzoate, affect the amount of the final product BA. The more the addition of HCl the more is the production of BA via precipitation process. During the reaction the sodium chloride was also produced. The NaCl was then removed by washing the final product with cool water. Because salt is soluble in water while the precipitate BA remains [37].

……….. (3.3)

Benzoic acid is less soluble in water at room temperature than sodium benzoate and thus precipitates out.

3.19 Experimental conditions and Observations

In the observed chemical conversion associated to the purification of benzoic acid, it is noted that the sample has appreciating purity but low recovery

Initial weight taken =5 gram

Amount of methanol =50 ml

Amount of sulfuric acid = 2 ml

Amount of ether = 35 ml

Amount of water used = 75 ml

Amount of NaCl solution used = 15 ml

Amount of magnesium sulphate = 2 gm

Amount of NaOH = 10 ml

Amount of (3 molar) HCl = 15 ml

Melting point of the purified sample by chemical Derivatization = 122.1 ^{0}C

Recovery = weight of purified sample / weight of benzoic acid in crude sample * 100

Yield = 1.75/5 = 35 ± 5 %

Recovery of benzoic acid by assuming 60% in the crude sample = 58± 5%

Net Recovery: 58 ± 5%

Table 3-1: Melting Points of the crude and purified samples

Purification processes	**Melting point**
Literature value of benzoic acid melting point	**122.4^{0}C**
Crud BA	**112 . 1 ± 2^{0}C**
Sample purified by (Re)	**121.1 ±1^{0}C**
Sample purified by (LLE)	**122.3±1^{0}C**
Sample purified by (LLE) followed by (RE)	**122.4 ±1^{0}C**
Sample purified by (RE) followed By (LLE)	**122.3 ±1^{0}C**
Sample purified by (CD)	**122.1 ±2^{0}C**

Chapter: 4 Results and Discussions

4.1 Characterization of Samples

The characterization of the sample has been done by gas chromatography, mass spectrometry (GC-MS) and Fourier transforms infrared (FTIR) analytical instruments to check the purity of the refined sample.

4.2 Fourier Transform Infrared (FTIR) Instrument

FTIR is a powerful technique for the identification of pure organic and inorganic compounds. The interactions of radiations occur with those substances which possess permanent or induced dipole moments and excitation of vibrational state exist. The discrete level of vibrational energy should be in these kinds of molecules. It actually detects the vibration characters of different chemical functional groups. The compound must have dipole moment during vibration. Dipole moment is the property that is related to net measure of molecules polarity. The gases like O_2,N_2,Cl_2 and chiral compounds are not detected by the technique.IR have enough energy to cause induction of vibrational and rotational states while for the electronic excitation it has not enough energy .IR adsorption not only occur in organic compounds but also in covalent bonded metal complexes. There are different kinds of vibrations like stretching and bending vibration. The adsorption frequency depends on the force constant of bonds, relative atomic mass of atoms and geometry. Wave number presents the IR band position, which is the reciprocal of wavelength with unit (1/cm). Value of force constant (dyne/cm) for single bond is 5×10^5 dyne/cm while for double and triple bond the value is two and three times of the given value respectively. In former the bond length changes while in the last one bond angle changes [38].

Different ranges of IR radiations [39].

Near IR=0.75—1.4 µm, **Mid IR** =3--8 µm , **Far IR** =8--15µm

Main components:

- IR source
- Interferometer
- Sample chamber
- Detector
- Signal processing.

4.3 Powder Sample Preparation

In this method pressing of the powder in pellet form is done. There exists the flexibility of selecting different matrixes for different application. KBr, KCl or diamond dust can be used for mid IR range, high density polyethylene is appropriate for far IR testing and KBr can be used for near IR .the KBr pellets formation is done in such a way that the powder of the sample and KBr sizes are reduced to less than 5mm in diameter otherwise at large size the scattering of radiation may occur and that would cause deviation in readings. The reduction of the size is done by putting the substances I the grinder. The sizes are reduced until no more crystallite exist. Small amount of sample powder about (0.1—2%) of KBr amount is taken. It should be enough to cover the tip of the spatula. The grinding is usually done for 2 to 3 minutes. The powder is then pressed to pellets to specific diameter. This analysis is done in less than 10 minutes.

Spectrum: It is actually the plot between transmittance and the vibrational frequency.

The covalent bond range =600—4000 cm $^{-1}$

Finger print range = 600—1400 cm $^{-1}$

Functional group region= 1400--- 4000 cm $^{-1.}$

4.4 Gas Chromatography – Mass Spectrometry (GC-MS)

It is an analytical instrument combining gas chromatography with ability of separation, with mass spectrometry ideal in elucidation structure of separated components. This technique is usually used for the volatile organic components. In these kinds of equipments there exists equilibrium between stationary phases, which is responsible for the separation .The separation of the mixture depends upon the solubility of vapor phase (sample) in a liquid stationary phase. In the whole scenario first the GC is understood then MS is considered. After the background study one can analyze the readings provided by GC understanding the process is related to the situation of a pile of different balls with different weight. An attempt is made to move the balls with leaf blower. Some of the balls will move with high speed and some with low speed. The difference in the movement depends on characteristics of balls. The lighter will move faster than heavier one and some may take more time due to their shape. And also interaction of balls with each other is responsible for early or delay movement. It means some of the interaction may delay movement and some of them will accelerate the movements [41].

Similarly GC is separating chemical substances. Physical and chemical natures of molecules make them to travel with different speed in a column. The molecules with low weight will move swiftly. Also the shape of molecules may affect the time to exit column. There are more chances for different molecules to spend more time in the column than if they were if same kind of molecules [42].The carrier gas is usually an inert gas which carries the solute through column. This carrier gas is also called mobile phase (N_2, He) with 1-2 ml/min flow rate. The components having more affinity for the stationary phase elute later and travel slow. In other terms the separation is based on the affinity of components for stationary phase not mobile phase. A constant gas flow rate is maintained for the process. In most of the cases helium is used. The injection of the sample is usually done by using hypodermic needle or syringes o measuring specific amount of sample. The sample injected is in micro liters. The injection port is covered with silicon rubber septum or replaceable neoprene. The injection port is maintained at the temperature at which the sample immediately vaporized. The sample spreading in the column is curved or forming a plug. Some of the substances sticking to the column and some pass undisturbed. The detectors used are usually flame ionization detectors, thermal conductivity detector, electron capture detector. And flame emission detector. The flame ionization detector destroy the sample, argon detector needs argon as carrier gas while thermal detectors are sensitive.

The amount of time retained by the component in a GC column is called retention time. The retention time of component is noticed until it exits. Sometime retention time is enough to ensure the identification of compounds but it is not reliable way to identify the compounds. Because different compounds may have same retention time. There are thousands of substances that have same retention time, peak shape, and detector response.

Tuning and calibration is necessary before the analysis is carried out. This is performed by running the sample with known concentration. If the instrument shows deviation from the original concentration, it is recalibrated. GC separating accuracy is checked by running blank sample .Blank sample has no detectable component. If the detector indicates the presence of any component, then there is any residue from the previous analysis. The spectral peaks should be symmetrical, narrow, not overlapped and made with smooth lines. The GC result may be suspected if the peaks are overlapped and broad. The presence of water in the sample is indicated by poorly shaped, long and drawn out tail. The sample injection is done smoothly and rapidly for the good separation. The slow injection may lead to poorly shaped, overlapped and broad peak. Thin and twin peaks appear due to hesitation during injection. The twin and thin peaks appearance is also the evidence of running two samples consecutively.

Along with the advantages it has some limitations as the injection port septum should be replaced after 100—200 injections. High temperature shortens the life span of injection port. Sensitivity of the GC is affected by the leakage from the septum and this make errors in quantitative analysis as oxygen and hydrogen may alter the results. Because oxygen may react with sample and the GC would show the presence of other product.

While presence of water may affect the results therefore the analyte should be free of water. The temperature should be in a suitable range. If the temperature is too low there is no peak development or very poor peak and if the temperature is too high it may change the structure of analyte due to which other compound will appears in the result [43].

When H_2 gas is used as carrier gas it is necessary to know about the reaction affinity of analyte with hydrogen. Broad peaks result due to the hydrogen reaction. Care should be taken while using thermal conductivity detector because false peaks may appear. This phenomenon occurs if the thermal conductivity of carrier gas is comparable with the thermal conductivity of any component. A carrier gas should be pure otherwise the drifting of the base line will be observed. Regularly changing filter may prevent impurities.

4.5 Mass Spectroscopy

Mass spectrometry is the method to identify substances by charging the sample molecules and accelerating them toward the magnetic field and detect different charges on the basis of charge to mass ratio. The spectral plot is obtained and we can identify components by using component`s mass spectrum for qualitative analysis.

Pure gas is required for the mass analyzer. The temperature of sample inlet is about 400^0C.The sample should be in gas form. The sample then enters in the ionization chamber. The charged particles produced by high speed electrons are placed in a magnetic field and adopt in curved path. One value of voltage is for the one mass accelerating and reaching the detector. The range of the masses is covered in the variation in applied voltage, so that all the fragments reach the detector. The MS portion draws an array of peaks called mass spectrum. This peaks show the value of fragment mass. The mass spectrum of the unfragmented mass is usually a greater mass detected and called “parent mass”. Determination of the parent peak and molecular mass of the specimens are the most difficult analysis.

“Resolution” the term used for the ability of an instrument to distinguish between two substances closely related. The MS with greater resolution has usefulness for the analysis .MS shows more accurate mass for the large molecules when running with high resolution. Instrument with high resolution is preferred for analyzing body fluids because they have high molecular masses. Interior pressure may cause errors in the readings. Because if the pressure is high the different fragments will have more chances to collide and make new masses due to which different masses will be appeared in the detector while low pressure minimize collusion and new mass formation .the best spectra is obtained at low pressure .Sometimes it is difficult to find parent peak and then parent peak is for determining the parent mass. The parent peak is usually not observed in high molecular weight specimens like body fluids. This situation makes the qualitative analysis difficult. High speed scanning means analyzing the specimen rapidly. But when it is running with high speed it loses its ability of getting it with high resolution. In other terms we can say that the speed of scanning is inversely related to resolution of the process. Speed scanning is related to unreliable quantitative measurement. It is highly reliable if used in sufficient resolution in all cases the sample of known composition should be run. Because of high sensitivity of MS, traces amount of impurities can be detected .There should be run of “background” spectrum an analysis without specimens before analyzing the specimens. No personal opinion should be given but proper observation is needed in computerized data for possible compounds [44,45].

4.6 Detectors of the GC-MS

4.6.1 Flame Ionization Detectors (FID)

It is one of the most used detectors for the gas chromatography (GC) it has wide range of applications i.e. checking of petrol for aero planes, kerosene etc. GC FID is also used for food checking .The food wrapped in polystyrene, is contaminated with hydrocarbons after some time, so these contaminations are determined by this instrument. And the process is beneficial for the food safety. GC FID is more suitable for analyzing hydrocarbons like ethane, methane, and acetylene and also for other organic volatile compounds.

In FID the sample undergoes combustion process in the presence of hydrogen synthetic air flame. Free electrons and ions are formed in the flame. The charged particles produce current between the electrodes that is measurable .these electrodes are located inside the detector. The resulting current is of greater strength as compare to the strength of pure carrier gas and fuel gas flame alone. The differential provides information about specimens. Information are directly proportional to the current which depends on the composition of separated sample. Different separated portion of compound have its own specific value of current. It is destructive technique but sensitive and wide range of applications.

4.6.2 Thermal Conductivity Detector (TCD)

Thermal conductivity detector is also called Katharometer. It is commonly used in chromatography. TCD is responsible for detecting the change in thermal conductivity of column effluent and compare it to the reference flow of carrier gas. Most of the compounds have less thermal conductivity than carrier gas.

Operation: The detectors are composed of the heated filament in the temperature controlled cell. Stable heat flow exists during normal conditions between filament and detector. The filament is hotter than detector body. The temperature of the filament is kept constant and the carrier gas is allowed to pass through it. The filament needs power to keep the temperature constant but when the sample is added the temperature changes. When the sample and carrier gas pass through the filament the power difference is measured and recorded.

It is not destructive technique. This detector can be used in series with flame ionization detector.FCD has low sensitivity and low resolution than flame ionization detector. The filament is made of tungsten-rhenium that is chemically passivated to oxygen damage. However compound like acids and bases and halogenated compounds may damage the filament. Due to the damage a permanent change in sensitivity may arise [43].

4.6.3 Electron Capture Detector

Electron capturing detector is a device that detects atoms and molecules in gas through the attachment of electrons via electron capture ionization. It is used for the substance having high electro negativity like halogenated compounds.

Radioactive beta particles (electron) emitter is used in ECD it is in conjunction with makeup flowing gas through detector chamber. The emitter has 10 mill curie of radionuclide (Ni) ^{63} held by metal foil (I curie = 3.7. 10^{10} decay/second, non- Si- unit of radioactivity). Nitrogen is a makeup gas because it is easy to remove electron from nitrogen gas. The emitter electrons collide with the molecules of carrier gas and create more free electrons. These electrons create current that is towards anode [45].

As the sample is carried by the carrier gas to the detector, electron absorbing analyte absorb electrons and reduce the current. The reduction in the current is recorded and the concentration of the sample is directly proportional to the reduction in current. It is mostly used for halogenated compounds, nitriles, nitro compounds and other organomettalic compounds. It is 100—1000 times more sensitive than FID. While in comparison to FCD, it is million times sensitive.

MAIN COMPONENTS OF GC-MS

1. Carrier gas cylinder
2. Injector
3. Oven
4. Column
5. Detector

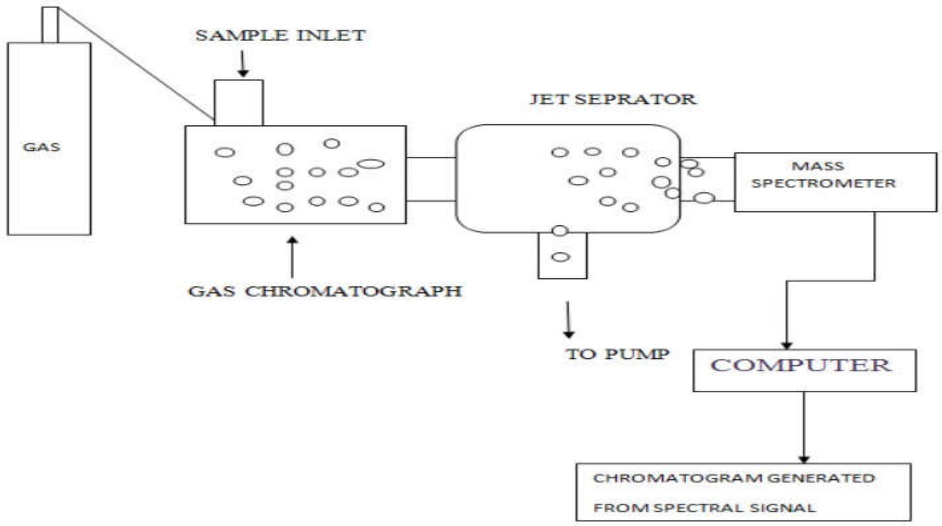


Figure 4-1: Block Diagram of GC-MS

It has a tube which has the stationary phase and is called column. The column can be made of glass, stainless steel. Different chemical mixtures can be separated by changing stationary and mobile phase. The refinement of the process is done by changing temperature and pressure for different processes. Usually the column is coated with stationary phase (solid) 5% phenyl 95% dimethylsilixane polymer.

4.10 Sample Preparation

Preparation of the sample is accomplished by dissolving the chemical in a suitable volatile solvent. The concentrations are kept in the range of 10—20 ppm. The solvent used should have less or moderate polar nature, like ethyl acetate, n-hexane, acetone and pentane, water is avoided as solvent. The prepared sample is kept in a glass vial. The sample components should be volatile at the range of 300 ^{0}C otherwise contamination would take place. After elution from the column it goes towards detector. Detector creates electrical signal. The greater the concentration of component, the longer is the peak. The time passed from the zero to the completion of elution is called elution time or retention time. Each component has its specific retention time. Graph generation is done by computer called chromatogram. Each peak in the graph represents different components of the mixture. The peak position shows the type of component while the height of peak is presenting quantity. The x-axis and y-axis in the graph show relative time and abundance respectively. If the temperature and pressure are not altered, the components will have the same retention time. There are compounds which have same properties to each other also have almost same retention time, and then more information is required for the identification of compounds.

4.11 Mass Spectrometry

The small portion of the sample is vaporized by hitting it by high energy electron to ionize sample. The ions produced are detected based on the mass to charge ratio. The beam of electron should have enough energy to break the bonds. The fragmentation pattern is the characterization of compound. It means that the fragmentation pattern will remain the same for the specific substance, and therefore it is the finger print of the substances. It is related to the information of elemental composition and structure [42].

4.12 Main Components of Mass Spectrometry

1. Ionization chamber
2. Analyzer
3. Ion detector
4. Data system

4.13 Results and discussions

4.13.1Gas Chromatography Mass Spectrometry

The sample along with the impurities was tested by GC-MS. The chromatogram shows the presence of impurities like maleic acid-toluic acid, Pimide and other unknown organic compounds.

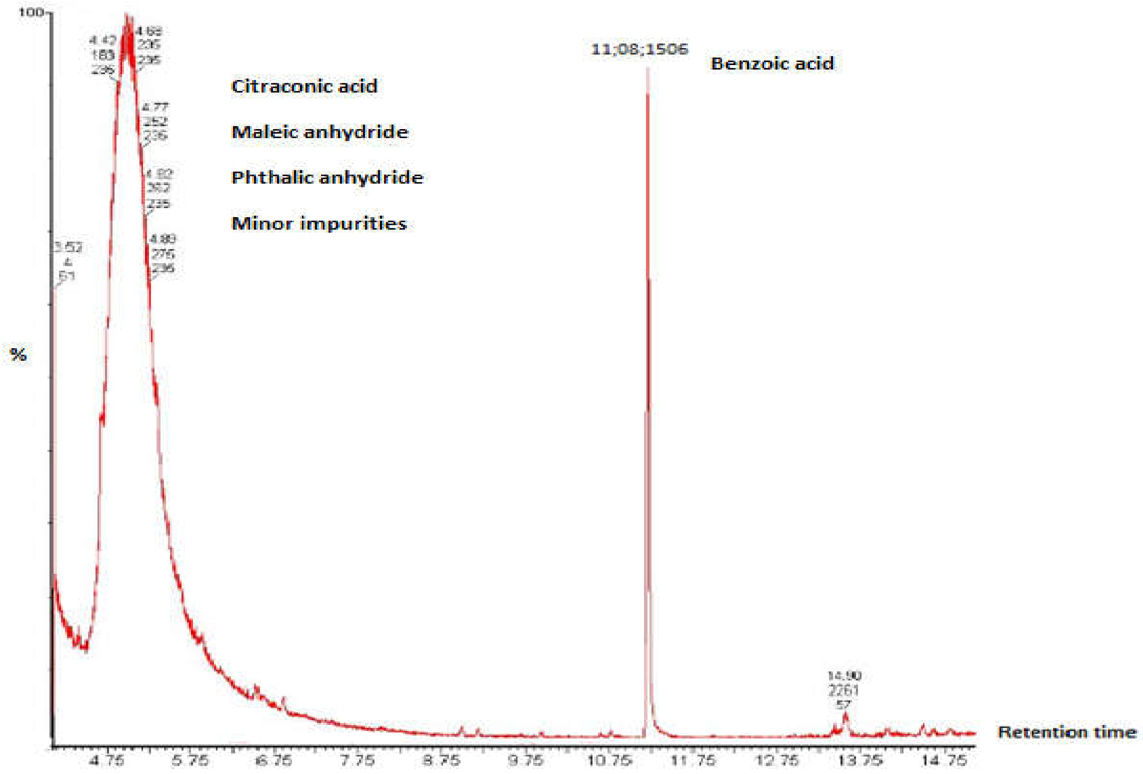


Figure 4-2: GC chromatogram of the crude benzoic acid sample

In figure (4.2) the peak of impurities appears at the range of 0 – 11 minutes retention time and in the same chromatogram the same peak of BA was also observed with low intensity at almost 11 minutes. The small peak of the BA is the evidence of the less amount of BA in the crude sample.

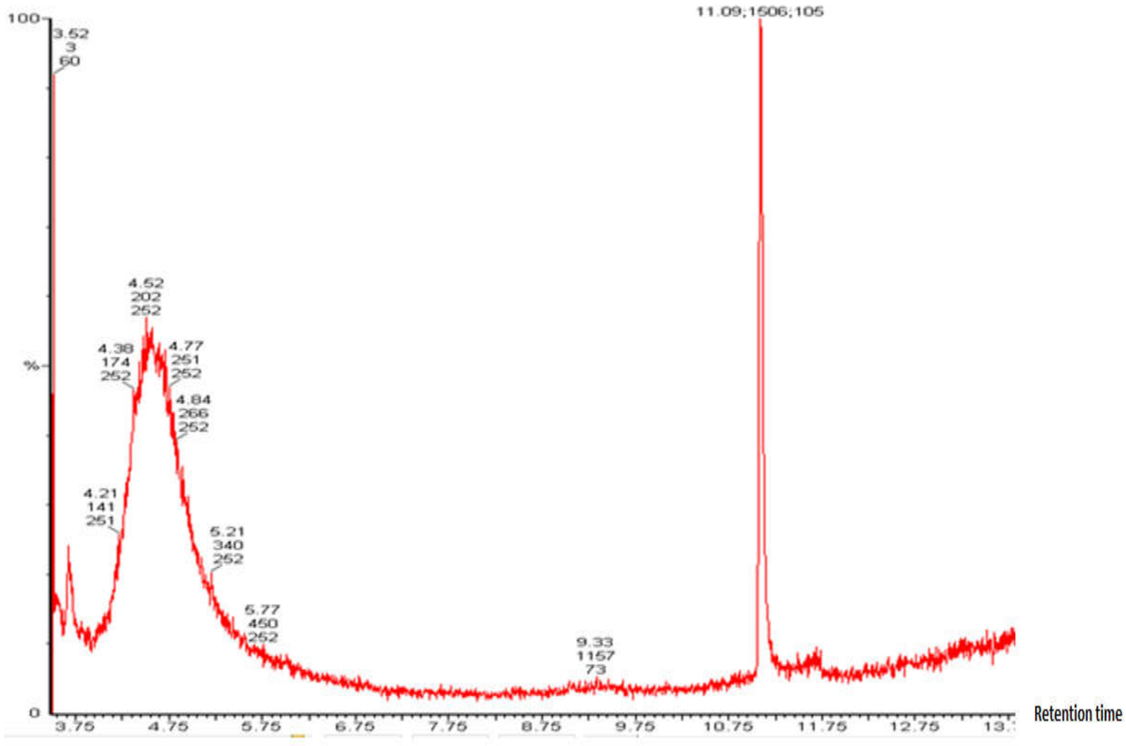


Figure 4-3: GC chromatogram result for sample purified by (RE)

The sample purified by the (RE) is not that much pure as compare to the sample purified by the other purifying methods. (RE) is not the better choice to purify the sample but in combination with (LLE) and (CD) is the best choice to get high purity. The sample purified by the (RE) method shows the result with low peak intensity in the chromatogram as compare to the peak representing impurities in the crude sample. In the chromatogram the peak of the impurities is still clearly visible.

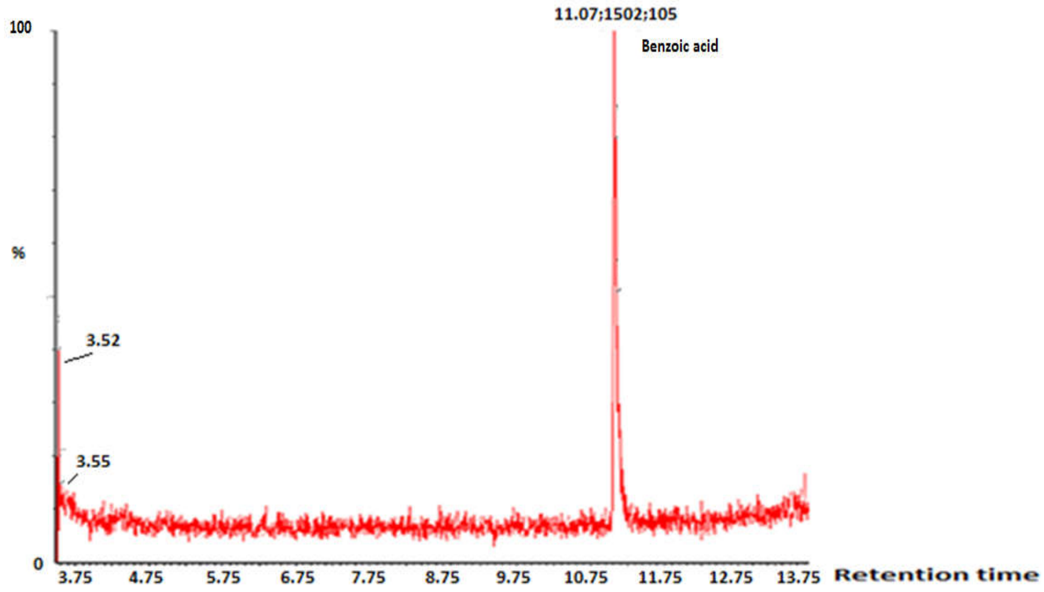


Figure 4-4: GC chromatogram result of the sample purified by (LLE)

In the GC chromatogram of these purified samples there is no such peak of impurities but only one peak of BA with high intensity. BA in the GC chromatogram can be identified by its retention time. The retention time varies for different components. Retention time of BA is almost 11 minutes.

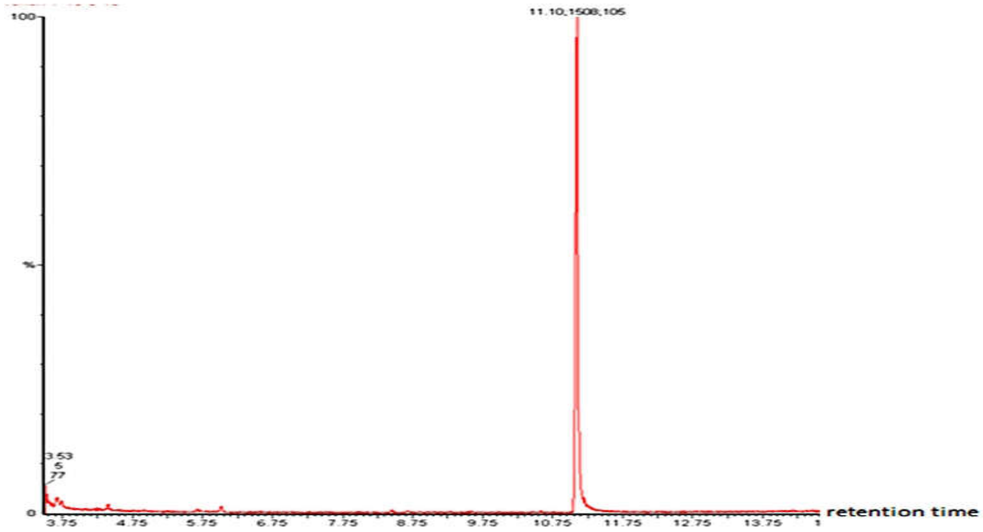


Figure 4-5: GC chromatogram of the sample purified by (RE) followed by (LLE)

The sample purified by the (RE) method shows the result with low peak intensity in the chromatogram as compare to the peak representing impurities in the crude sample. But in the same time the comparison of the sample purified by (LLE) and (RE),the clear view can be developed related to the purity of sample, as the peak associated with the impurities has been completely eliminated.

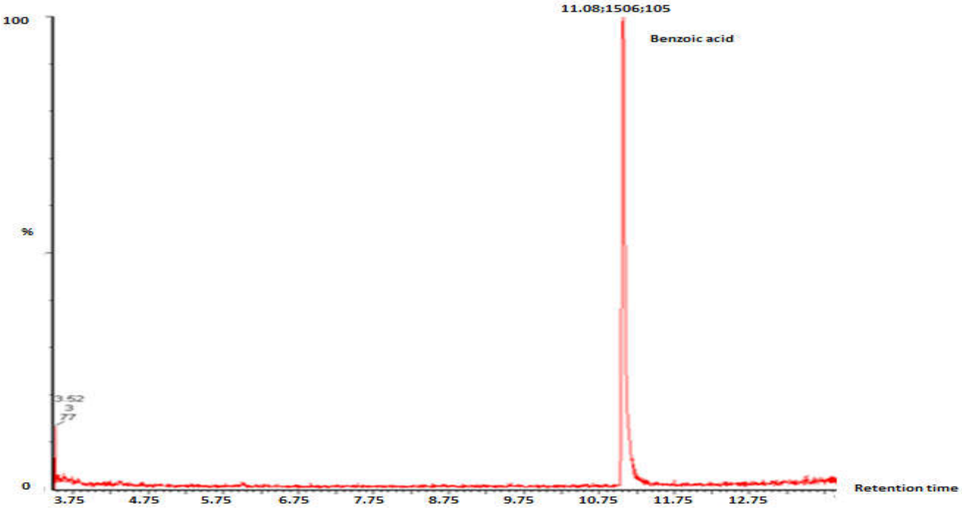


Figure 4-6: GC chromatogram of sample purified by (LLE) followed by (RE)

The same situation is observed in the figure (4-6) as in the chromatogram explained in the figure(4-4) and (4-5).the combination of the RE and LLE reduce the recovery of the benzoic acid up to some extent but it is also the suitable way to purify the sample.

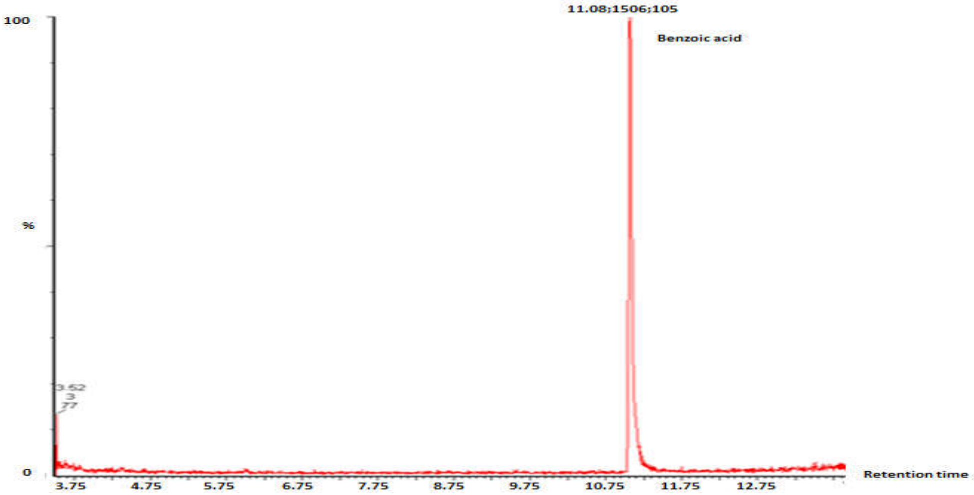
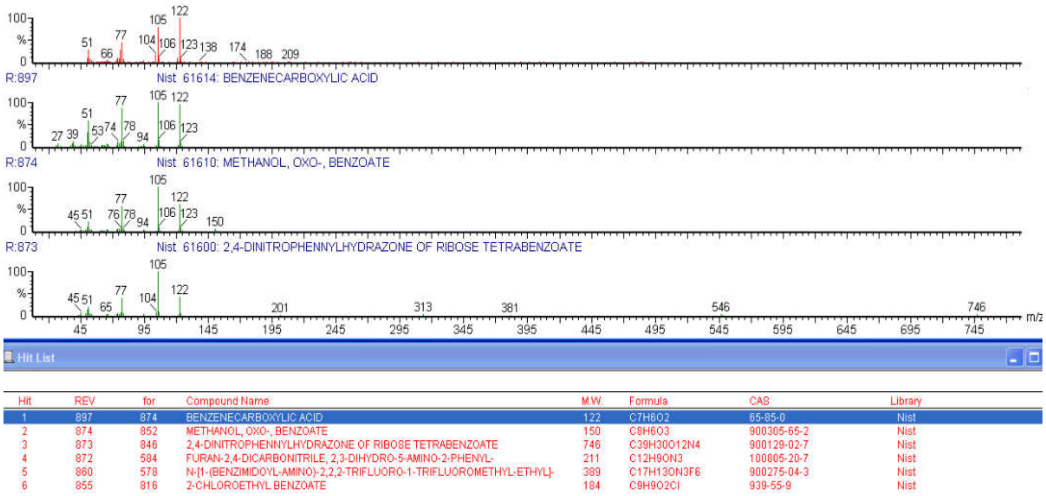


Figure 4-7: GC chromatogram of sample purified by (CD)

From the figure (4.4) to (4.7) samples purified by (LLE), (RE) followed by (LLE), (LLE) followed by (RE) and (CD) almost 99% pure. In the GC chromatogram of these purified samples there is no such peak of impurities but only one peak of BA with high intensity. BA in the GC chromatogram can be identified by its retention time. The retention time varies for different components. Retention time of BA is almost 11 minutes.

4.14 Mass Spectrometry Results



R:897 Nist 61614: BENZENECARBOXYLIC ACID

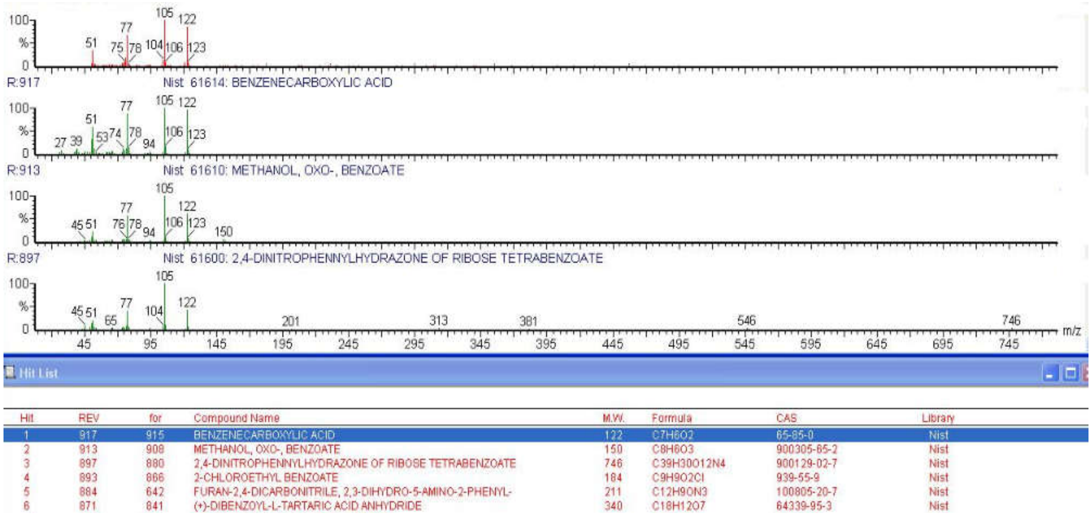
R:874 Nist 61610: METHANOL, OXO-, BENZOATE

R:873 Nist 61600: 2,4-DINITROPHENNYLHYDRAZONE OF RIBOSE TETRABENZOATE

Hit	REV	for	Compound Name	M.W.	Formula	CAS	Library
1	897	874	BENZENECARBOXYLIC ACID	122	C7H6O2	65-85-0	Nist
2	874	852	METHANOL, OXO-, BENZOATE	150	C8H6O3	900305-65-2	Nist
3	873	846	2,4-DINITROPHENNYLHYDRAZONE OF RIBOSE TETRABENZOATE	746	C39H30O12N4	900129-02-7	Nist
4	872	584	FURAN-2,4-DICARBONITRILE, 2,3-DIHYDRO-5-AMINO-2-PHENYL-	211	C12H9ON3	100805-20-7	Nist
5	860	578	N-[1-(BENZIMIDOYL-AMINO)-2,2,2-TRIFLUORO-1-TRIFLUOROMETHYL-ETHYL]-	389	C17H13ON3F6	900275-04-3	Nist
6	855	816	2-CHLOROETHYL BENZOATE	184	C9H9O2Cl	939-55-9	Nist

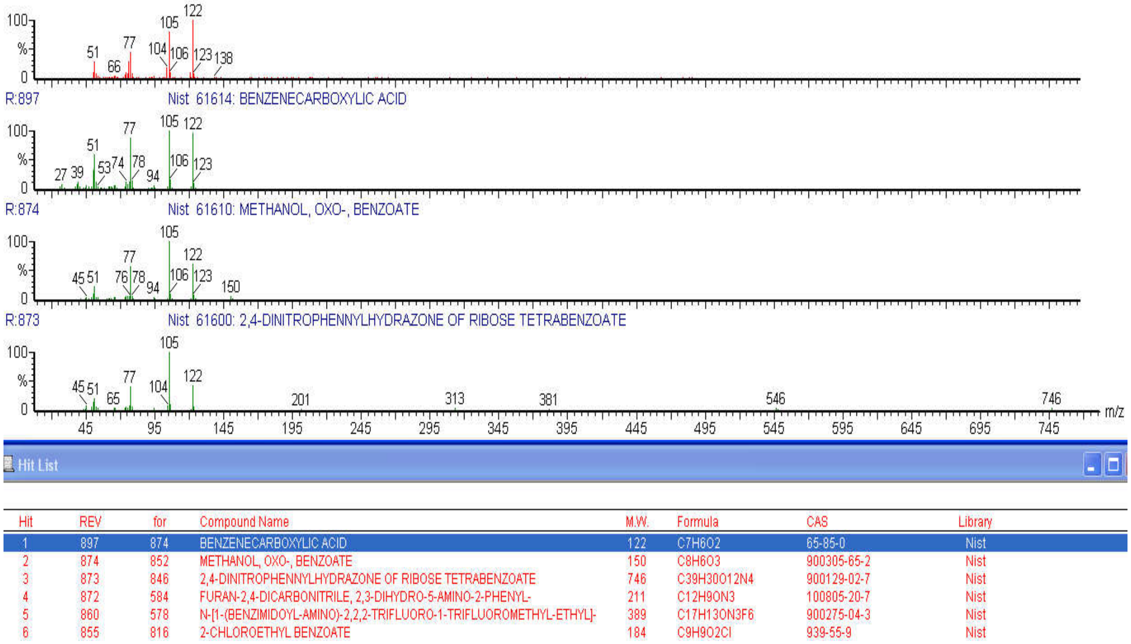
Figure 4-8: Mass library of crude benzoic acid sample

In the figure (4.8) of the crude benzoic acid ,peaks are observed other than the molecular peak of the benzoic acid because of the presence of the impurities in the sample.



Hit	REV	for	Compound Name	M.W.	Formula	CAS	Library
1	917	915	BENZENECARBOXYLIC ACID	122	C7H6O2	65-85-0	Nist
2	913	908	METHANOL, OXO-, BENZOATE	150	C8H6O3	900305-65-2	Nist
3	897	880	2,4-DINITROPHENNYLHYDRAZONE OF RIBOSE TETRABENZOATE	746	C39H30O12N4	900129-02-7	Nist
4	893	866	2-CHLOROETHYL BENZOATE	184	C9H9O2Cl	939-55-9	Nist
5	884	642	FURAN-2,4-DICARBONITRILE, 2,3-DIHYDRO-5-AMINO-2-PHENYL-	211	C12H9ON3	100805-20-7	Nist
6	871	841	(+)-DIBENZOYL-L-TARTARIC ACID ANHYDRIDE	340	C18H12O7	64339-95-3	Nist

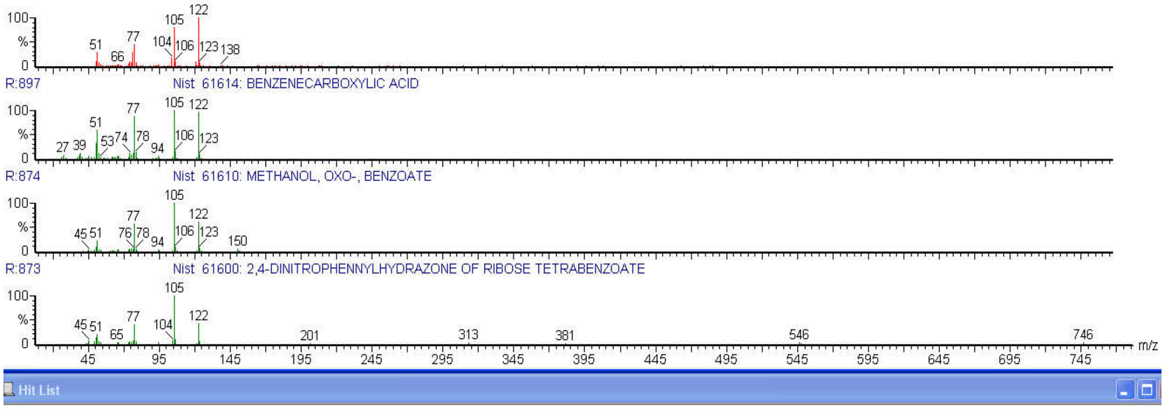
Figure 4-9: Mass library of the sample purified by (RE)



Hit	REV	for	Compound Name	M.W.	Formula	CAS	Library
1	897	874	BENZENECARBOXYLIC ACID	122	C7H6O2	65-85-0	Nist
2	874	852	METHANOL, OXO-, BENZOATE	150	C8H6O3	900305-65-2	Nist
3	873	846	2,4-DINITROPHENNYLHYDRAZONE OF RIBOSE TETRABENZOATE	746	C39H30O12N4	900129-02-7	Nist
4	872	584	FURAN-2,4-DICARBONITRILE, 2,3-DIHYDRO-5-AMINO-2-PHENYL-	211	C12H9ON3	100805-20-7	Nist
5	860	578	N-[1-(BENZIMIDOYL-AMINO)-2,2,2-TRIFLUORO-1-TRIFLUOROMETHYL-ETHYL]-	389	C17H13ON3F6	900275-04-3	Nist
6	855	816	2-CHLOROETHYL BENZOATE	184	C9H9O2Cl	939-55-9	Nist

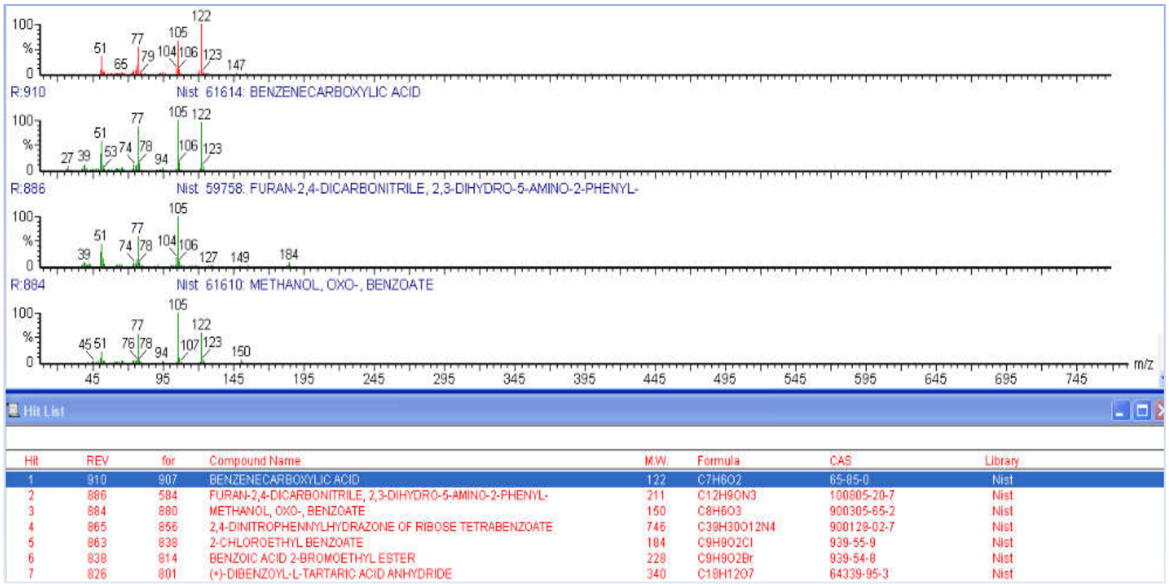
Figure 4-10: Mass library of the sample purified by (LLE)

The (MS) spectrums have the prominent peaks i.e. 122, 105, 77, 51.The peak at 122 mass to charge ratio (m/z) ratio is called parent peak.



Hit	REV	for	Compound Name	M.W.	Formula	CAS	Library
1	897	874	BENZENECARBOXYLIC ACID	122	C7H6O2	65-85-0	Nist
2	874	852	METHANOL, OXO-, BENZOATE	150	C8H6O3	900305-65-2	Nist
3	873	846	2,4-DINITROPHENNYLHYDRAZONE OF RIBOSE TETRABENZOATE	746	C39H30O12N4	900129-02-7	Nist
4	872	584	FURAN-2,4-DICARBONITRILE, 2,3-DIHYDRO-5-AMINO-2-PHENYL-	211	C12H9ON3	100805-20-7	Nist
5	860	578	N-[1-(BENZIMIDOYL-AMINO)-2,2,2-TRIFLUORO-1-TRIFLUOROMETHYL-ETHYL]-	389	C17H13ON3F6	900275-04-3	Nist
6	855	816	2-CHLOROETHYL BENZOATE	184	C9H9O2Cl	939-55-9	Nist

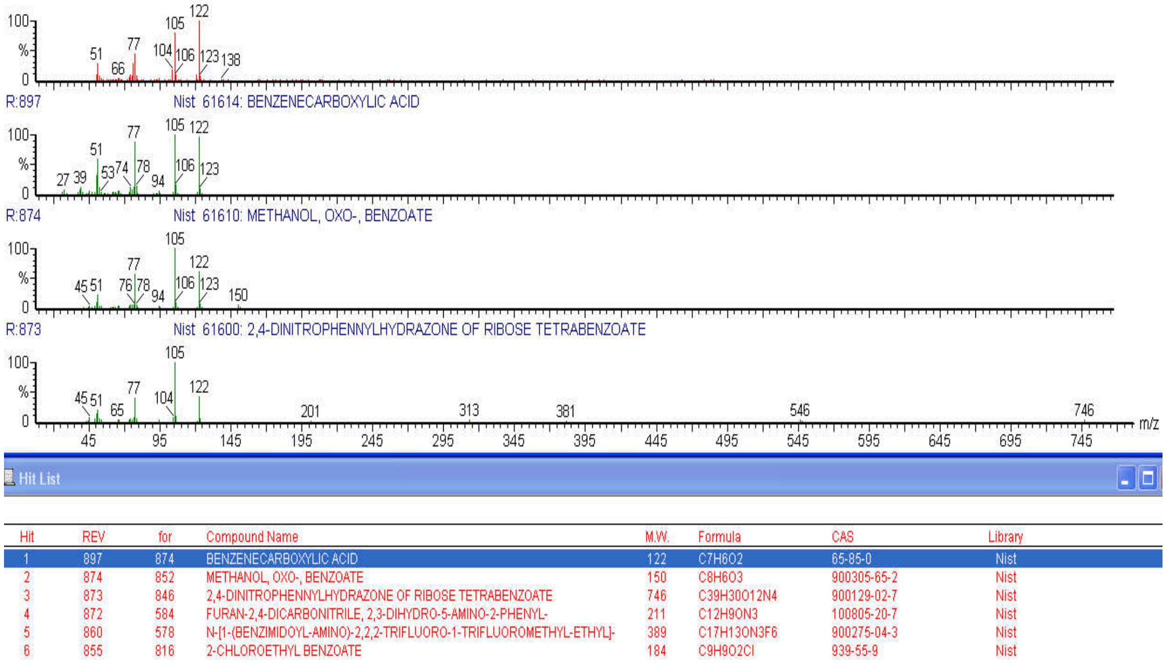
Figure 4-11: Mass library of the sample purified by (RE) followed by (LLE)



Hit	REV	for	Compound Name	M.W.	Formula	CAS	Library
1	910	907	BENZENECARBOXYLIC ACID	122	C7H6O2	65-85-0	Nist
2	886	584	FURAN-2,4-DICARBONITRILE, 2,3-DIHYDRO-5-AMINO-2-PHENYL-	211	C12H9ON3	100805-20-7	Nist
3	884	880	METHANOL, OXO-, BENZOATE	150	C8H6O3	900305-65-2	Nist
4	865	856	2,4-DINITROPHENNYLHYDRAZONE OF RIBOSE TETRABENZOATE	746	C39H30O12N4	900129-02-7	Nist
5	863	838	2-CHLOROETHYL BENZOATE	184	C9H9O2Cl	939-55-9	Nist
6	838	814	BENZOIC ACID 2-BROMOETHYL ESTER	228	C9H9O2Br	939-54-8	Nist
7	826	801	(+)-DIBENZOYL-L-TARTARIC ACID ANHYDRIDE	340	C18H12O7	64339-95-3	Nist

Figure 4-12: Mass library of the sample purified by (LLE) followed by (RE)

The removal of COOH group gives rise to peak at 77 m/z ratio. And the elimination of $C_2H_2COOH^+$ fragment from the BA molecule gives rise to peak at 51 m/z ratio [44].



Hit	REV	for	Compound Name	M.W.	Formula	CAS	Library
1	897	874	BENZENECARBOXYLIC ACID	122	C7H6O2	65-85-0	Nist
2	874	852	METHANOL, OXO-, BENZOATE	150	C8H6O3	900305-65-2	Nist
3	873	846	2,4-DINITROPHENNYLHYDRAZONE OF RIBOSE TETRABENZOATE	746	C39H30O12N4	900129-02-7	Nist
4	872	584	FURAN-2,4-DICARBONITRILE, 2,3-DIHYDRO-5-AMINO-2-PHENYL-	211	C12H9ON3	100805-20-7	Nist
5	860	578	N-[1-(BENZIMIDOYL-AMINO)-2,2,2-TRIFLUORO-1-TRIFLUOROMETHYL-ETHYL]-	389	C17H13ON3F6	900275-04-3	Nist
6	855	816	2-CHLOROETHYL BENZOATE	184	C9H9O2Cl	939-55-9	Nist

Figure 4-13: Mass library of the sample purified by (CD)

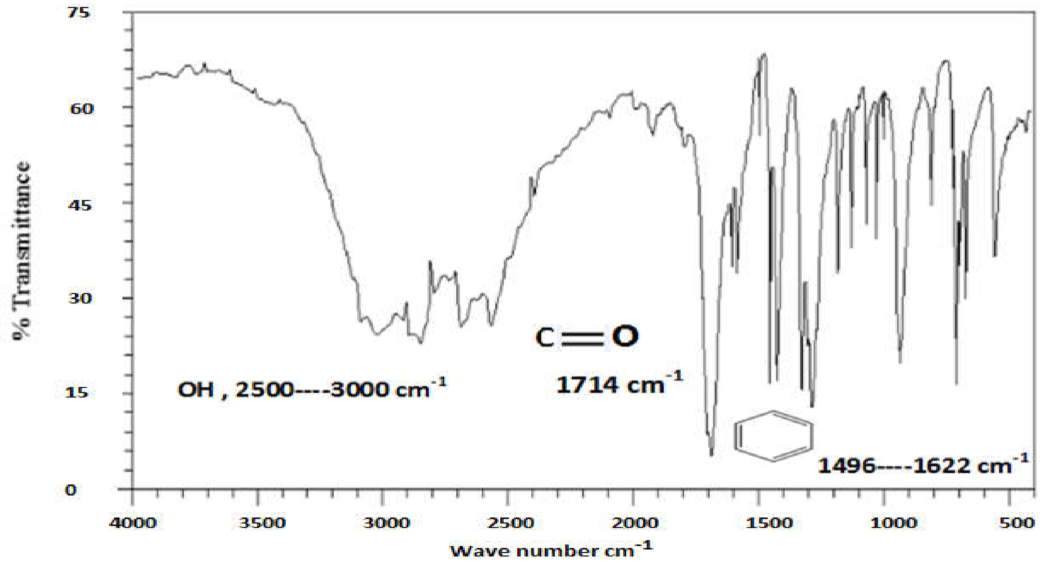
Similarly the study of MS can also leads to know about the compound under observation. From figure (4.9) to (4.13) the (MS) spectrums have the prominent peaks i.e. 122, 105, 77, 51.The peak at 122 mass to charge ratio (m/z) ratio is called parent peak. It actually indicates the molecular mass of compound. While other peaks were observed related to the fragments formed by ionization. The removal of the OH group from the main structure is responsible for the peak at 105 m/z. The removal of COOH group gives rise to peak at 77 m/z ratio. And the elimination of $C_2H_2COOH^+$ fragment from the BA molecule gives rise to peak at 51 m/z ratio [44].

4.15 FTIR Results

FTIR is a powerful technique for the identification of pure organic and inorganic compounds with the exception of few homonuclear molecules such as O_2,N_2,Cl_2.In addition every compound has unique infrared absorption spectrum. Therefore, an exact match between the spectrum of a compound of known structure and the spectrum of an analyte unambiguously identifies the analyte. Infrared radiation is generally not of sufficient energy to cause electronic transitions but can induce transitions in the vibrational and rotational states associated with ground electronic state of the molecules. The interactions of radiations occur with those substances which possess permanent or induced dipole moments and excitation of vibrational state exist. It actually detects the vibration characters of different chemical functional groups. The compound must have dipole moment during vibration. Dipole moment is the property that is related to net measure of molecules polarity [40-45] .

Table 2.5: IR absorption regions of some of the common bonds using Hook`s Law

Bond type	Force constant (f) (dyne/cm)	Observed (cm^{-1})
C-O	$5*10^5$	1300-800
C-C	$4.4*10^5$	1300-800
C-H	$5.0*10^5$	3000-2850
O-H	$7*10^5$	3800-2700



4-14: Literature spectrum of pure benzoic acid

FTIR is a powerful technique for the identification of pure organic and inorganic compounds with the exception of few homonuclear molecules such as O_2,N_2,Cl_2.In addition every compound has unique infrared absorption spectrum. The adsorption frequency depends on the force constant of bonds, relative atomic mass of atoms and geometry. Wave number presents the IR band position, which is the reciprocal of wavelength with unit (1/cm). Value of force constant (dyne/cm) for single bond is 5×10^5 dyne/cm.

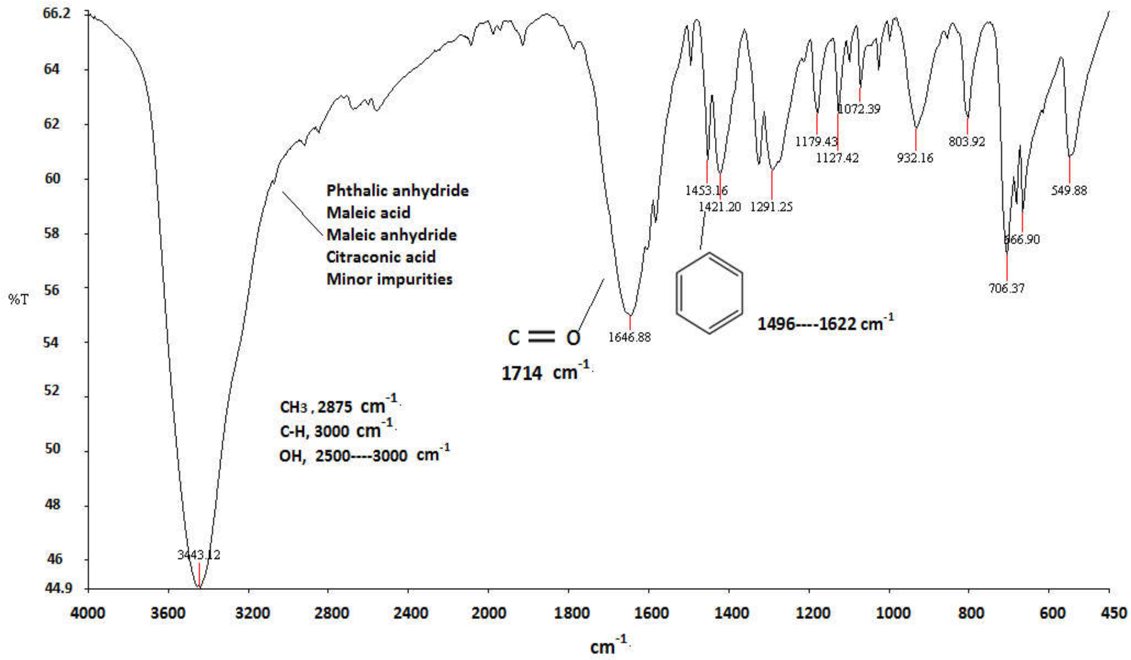


Figure 4-15: FTIR spectrum of crude benzoic acid

The spectrum of the crude benzoic acid and the sample purified by re-crystallization are not resembling the figure 4-14 literature spectrum of benzoic acid because of the presence of impurities like phthalic anhydride, maleic anhydride, maleic acid and other minor impurities. In the spectrum the 2500--3500 cm^{-1} is the region indicates the (OH) stretching bond. But due to the presence of CH_3 in the range of 2875 cm^{-1} is the cause of deviating the spectrum from the spectrum of pure benzoic acid. The 1715cm^{-1} range shows the presences of CO while the 1622—1496cm-1 is the range of aromatic ring.

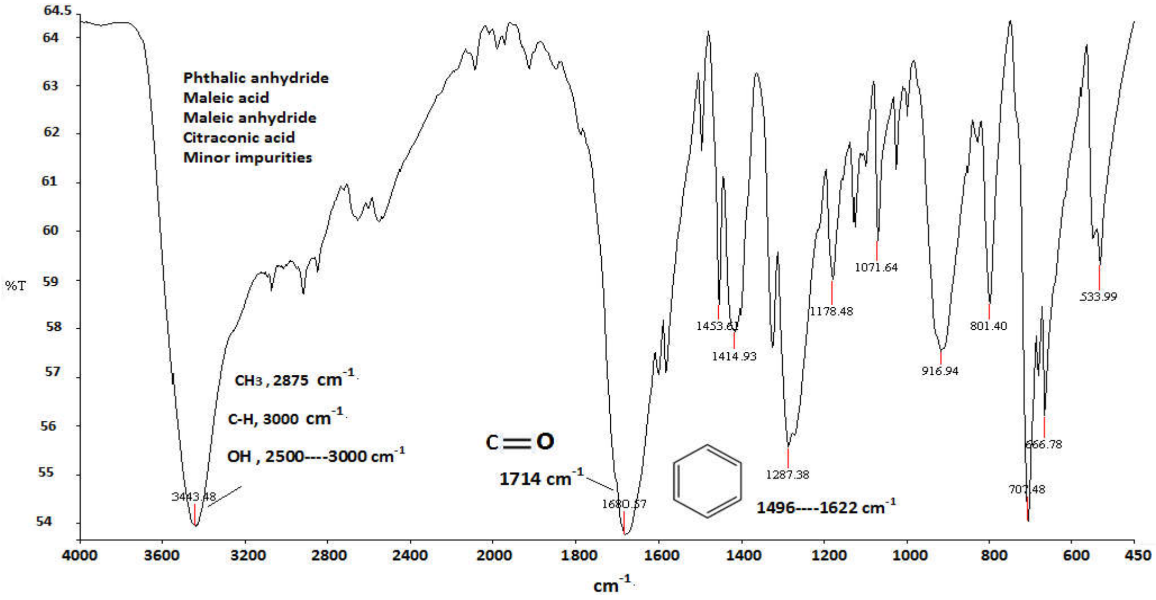


Figure 4-16: FTIR result of the sample purified by (RE)

In the spectrum of crude sample and the sample purified by re-crystallization has dominant inverted bell shape in the range of 2500----3000 cm^{-1} frequency due to the presence of a lot of OH groups associated with the impurities. In the figure 4-16 the reduction in the impurities can be noticed by the submissiveness in the shape of inverted bell. While in the figures from 4-17 to 4-20 there in no inverted bell shape in the 2500----3000 cm^{-1} range of frequency due to the elimination of OH groups associated with the impurities. In the spectrum of these purified samples, the frequencies of different bonds of benzoic acid resemble the frequencies ranges in the literature spectrum of benzoic acid.

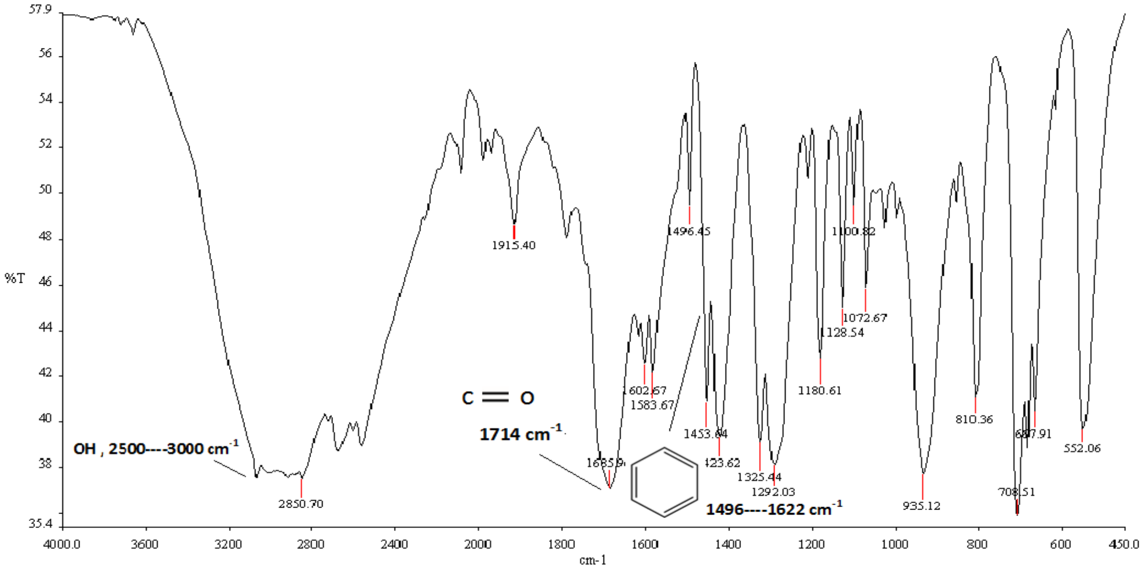


Figure 4-17: FTIR result of the sample purified by (LLE)

The purified samples' spectrums resemble the literature spectrum of the benzoic acid. In the spectrum the 2500--3500 cm^{-1} is the region indicates the (OH) stretching bond. The 1715cm^{-}range shows the presences of CO while the 1622—1496cm^{-1}is the range of aromatic ring. In the same spectrum there are two types of ranges classified on the range of frequency, the functional group region and finger print region. The functional group has the frequency range from 4000 to 1500 cm^{-1} while finger print has 1500 to 400 cm^{-1}.

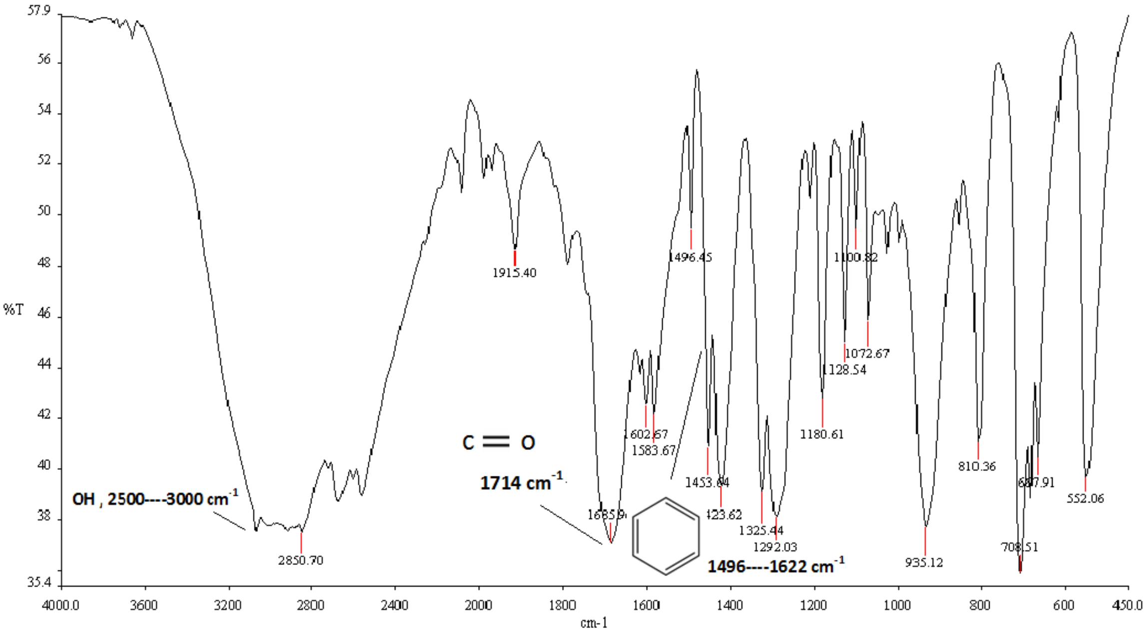


Figure 4-18: FTIR result of the sample purified by (RE) followed by (LLE)

The bonds associated with the benzoic acid have been observed at the same ranges of frequencies. The bonds present in the range of 1500 to 400 cm^{-1}are in the finger print region It is difficult to label them because of the bending vibration associated in the specified range of frequency.

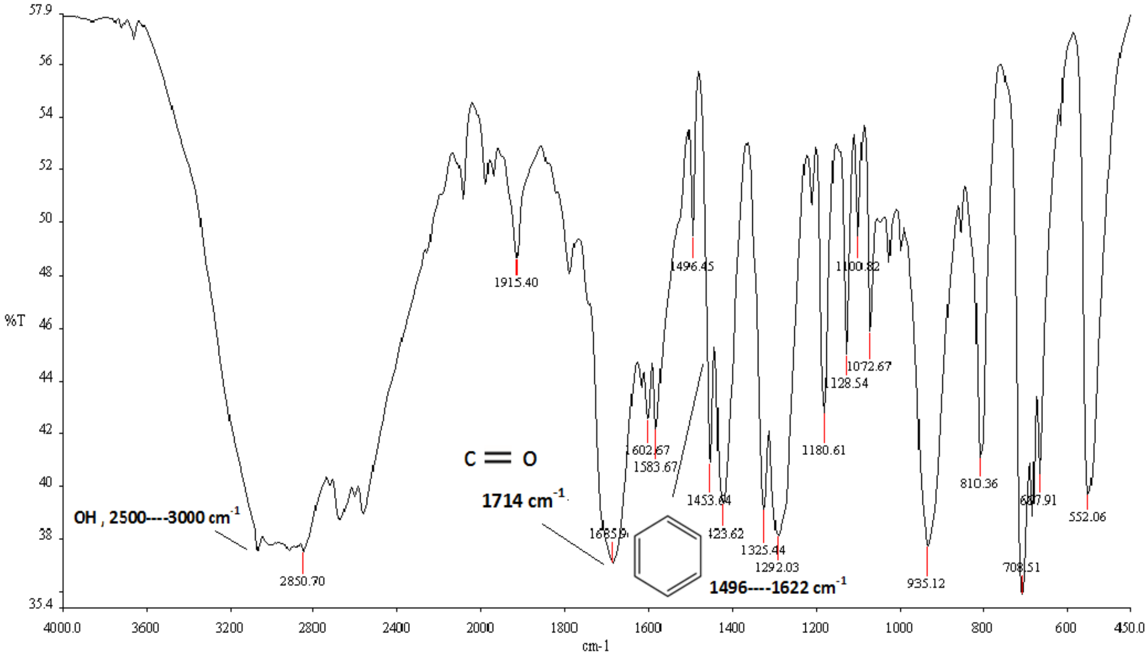


Figure 4-19: FTIR result of the sample purified by (LLE) followed by (RE)

It actually detects the vibration characters of different chemical functional groups. The compound must have dipole moment during vibration. Dipole moment is the property that is related to net measure of molecules polarity. The purified samples' spectrums resemble the literature spectrum of the benzoic acid. In the spectrum the 2500--3500 cm^{-1} is the region indicates the (OH) stretching bond. The 1715cm^{-1} range shows the presences of CO while the 1622—1496cm^{-1}is the range of aromatic ring.

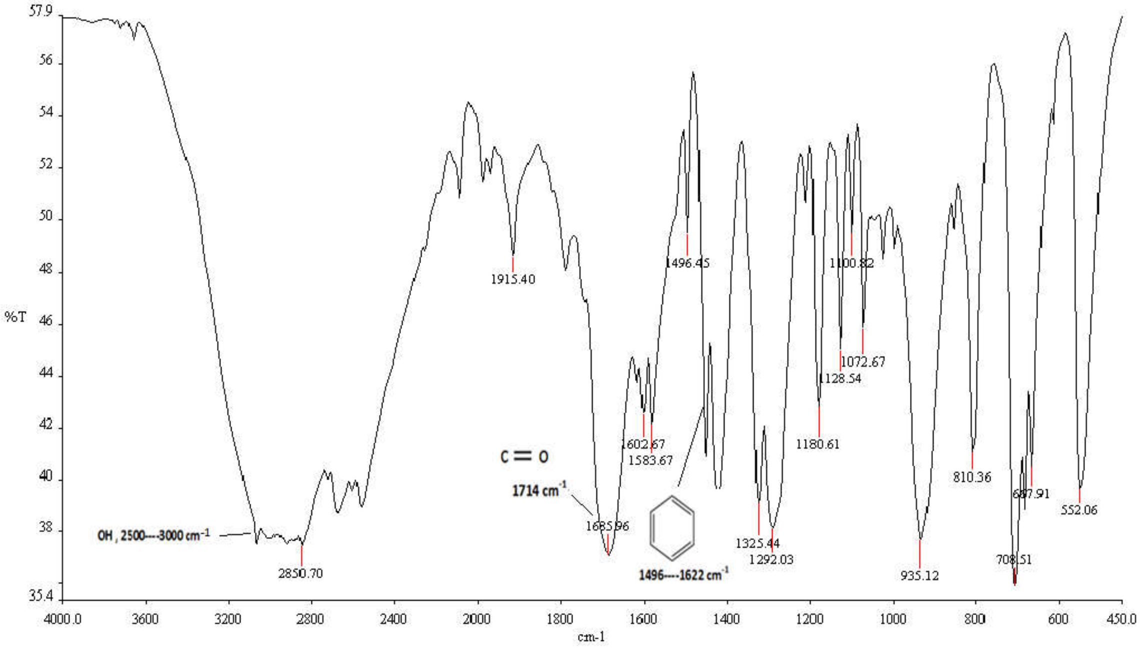


Figure 4-20: FTIR spectrum of the sample purified by (CD)

In the spectrum of the sample purified by chemical derivatization has outstanding purity that is evident from the resemblance of spectrum with the literature spectrum of benzoic acid. In the spectrum the inverted bell shape of the peak in the range of 2500--3500 cm^{-1} has been reduced by the elimination of the impurities with a lot of OH bonds.

4.16 Images of the crude and purified samples

Figure 4-21: Image of crude benzoic acid

The image of the crude solid sample of benzoic acid obtained from NIMAR industry. The crude sample should be in powder form before it is processed by any purifying technique.

4-22: Image of the sample purified by (RE)

The image of the sample purified by (RE). It is in the form of long needle crystals. The color of the purified sample has white appearance that can be distinguished from the color of crude sample.

Figure 4-23: Image of the sample purified by (LLE)

The image of the sample purified by (LLE). It is in amorphous form. The purified sample has white appearance. The physical appearance of this purified sample is different from the sample purified by (RE) process.

Figure 4-24: Image of sample purified by (RE) followed by (LLE)

The image of the sample purified by (RE) followed by (LLE). It is in amorphous form. The purified sample has white appearance. The amorphous nature of the sample is because of the precipitation process of sodium benzoate to benzoic acid by the protonation.

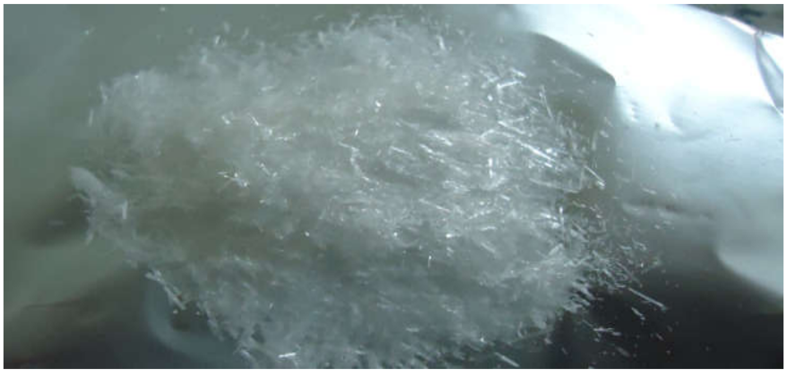


Figure 4-25: Image of sample purified by (LLE) followed by (RE)

The purified sample is crystal because of the (RE) performed after (LLE).in the (LLE) followed by (RE) the recovery of purified sample is less due to the loss of benzoic acid in the two purifying techniques.

Figure 4-26: Image of sample purified by (CD)

The sample purified by (CD) is also amorphous in nature due to the absence of recrystallization step while the protonation of sodium benzoate by HCl is responsible for the fast precipitation step of obtaining benzoic acid .

Chapter: 5 Conclusions and Future Recommendations

5.1 Conclusions

The benzoic acid has been successfully purified by using physical and chemical processes from the crude sample. The purification accomplished by re-crystallization yield benzoic acid with 85±5 yield with recovery but the cause of not considering it a best way is the incomplete elimination of impurities from the sample of the as shown in the GC chromatogram in the figure 4-3.The peak associated with the impurities can be clearly observed at 3.75--5.75 min range of retention time.

Liquid-liquid extraction is considered the best way of decontaminating the sample with 54±4% yield with the benzoic acid recovery of 90±2% with outstanding purity. The figure 4-4 indicates a clear intensive peak of the only benzoic acid almost at the retention time of 8 min after it is injected.

Re-crystallization followed by liquid-liquid extraction had almost 80±3 recovery of benzoic acid. And liquid-liquid extraction followed by re-crystallization had 81±2% recovery of Benzoic acid with appreciating effects on the purity of crude sample. In the figure 4-5 only one peak exists, associated with the benzoic acid while figure 4-6 shows the same result at the retention time of 10.75 min. In the chemical method of purification, the chemical derivatization was performed, had 58±5 recovery of (BA) but leads us to high purity.

5.2 Future recommendations

The simulation of all the purification techniques by Aspen plus would help to estimate the energy required and the cost of the processes.

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