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Molten Salt Pyrolysis of Waste Polystyrene

Abdulaziz Mohammed Alamer
Worcester Polytechnic Institute

Muteb I. Awaji
Worcester Polytechnic Institute

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Molten Salt Pyrolysis of Waste Polystyrene

A Major Qualifying Project Report
Submitted to the Faculty of the
WORCESTER POLYTECHNIC INSTITUTE
in Partial Fulfillment of the Requirements for the
Degree of Bachelor of Science
in Chemical Engineering

By

Abdulaziz Alamer

Muteb Awaji

April 30, 2014

Approved by:

Professor Ravindra Datta, Advisor
Chemical Engineering Department, WPI

Professor Michael Timko, Co-Advisor
Chemical Engineering Department, WPI

ABSTRACT

In recent decades, the world has been concerned about the environmental impact of waste plastic, and researchers have been focusing on developing new methods to recycle plastic waste. The most common are mechanical recycling techniques, but they fail to treat the majority of waste plastics. Thus, recent studies focus on monomer recovery via thermal pyrolysis. The goal of this project was to develop a novel single pot pyrolysis technique by employing molten salts to attain good yields at varied conditions. The effects of temperature, salt composition and catalyst were studied, and the yield and the composition of liquid products were analyzed. The best temperature and salt composition that result in the highest liquid yield, monomer recovery and monomer selectivity, were identified.

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CHAPTER 1. INTRODUCTION

With the world's current population producing about 1.3 billion tons of solid waste yearly, management of Municipal Solid Waste (MSW) is becoming a major issue. In 2011, the MSW generated in the United States was more than 250 million tons, with plastics making up 12.7% of it, and only 8.3% was recovered while the remaining was discarded in landfills. Since the development of plastic in the early 1900s, it has become a very popular material used in everyday life. Plastic is used due to its cheap price, light weight, ease of fabrication and durability. However, the unique properties that make plastics attractive for use in consumer products are also the main concerns in the processing of their waste management, especially their being non-biodegradable, and requiring an ultra-violet light to break down. Figure 1 below shows a graph of yearly total MSW generation rates in the United States (Municipal Solid Waste in The United States, 2013).

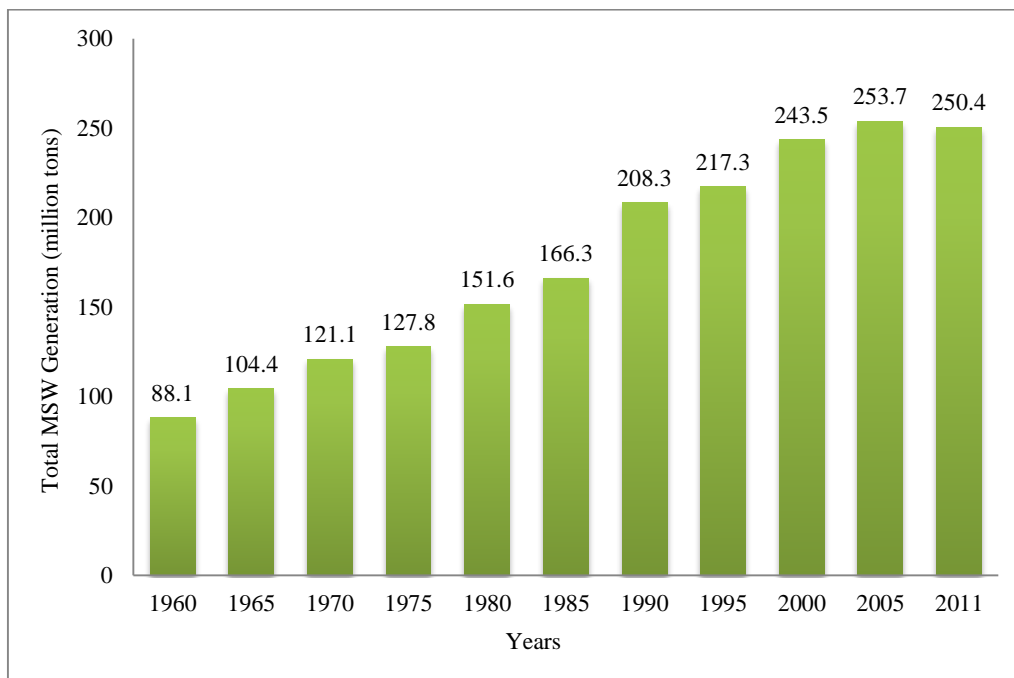


Figure 1: MSW generation rates from 1960 to 2011 (Municipal Solid Waste in the United States, 2013).

Due to its low density, plastics are used in applications where low weight is needed such as food containers; therefore, plastics are very commonly used. With 91.7% of plastics being discarded every year, finding disposal space is becoming very difficult. Plastics also have very long shelf life, and it would take them hundreds of years to naturally decompose. The disposal of plastic waste in landfills is not a method that is sustainable; instead more effort should be put into improving the available recycling methods. Currently, there are four main recycling methods, namely, primary, secondary, tertiary, and quaternary methodologies (Elsayed, 2003).

Primary recycling, also known as re-extrusion recycling, is a mechanical process in which plastics with similar features are extruded to produce products that are similar to the original products. This process require the materials to have similar properties and be partially clean, e.g., plastic bottles with processing defects, which makes processing postconsumer items difficult using this method. However, primary recycling is a suitable method for use with industrial plastic scrap (Al-Salem et al., 2009).

Secondary recycling is physically processing postconsumer items into a product of a lesser value than the original product, for example plastic bottles can be recycled into fibers that can be later used in carpets. This method of recycling can only be used with items made from the same polymer; hence plastic identification codes are used. The plastic waste is usually extruded after being milled and washed. Figure 2 outlines the stages of secondary recycling (Aznar et al., 2006).

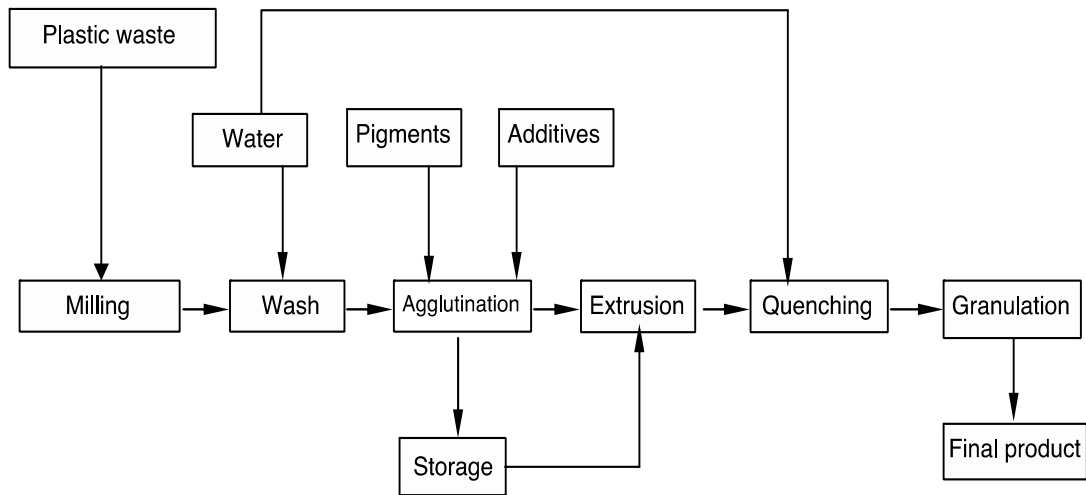


Figure 2: Overview of secondary recycling stages (Aznar et al., 2006).

There are many issues associated with recycling plastics mechanically, one of which is the degradation of the quality of the product. During the recycling process, stress can build up in the plastic as well as the possibility of occurrence of chemical reaction due to having different materials. The main issue however is the inability to mechanically process many of the plastics due to their properties. In fact, only 15-20% of plastics can be recycled effectively through mechanical means. The most common types are listed in Table 1 below.

Table 1: Total plastics in MSW by resin (Municipal Solid Waste in The United States, 2013).

Resins	Generation	Recovery		Discarded
	Thousand tons	Thousand tons	Percentage	Thousand tons
PET	4,280	830	19.4%	3,450
HDPE	5,590	550	9.8%	5,040
PVC	900			900
LDPE/LLDPE	7520	370	4.9%	7,150
PLA	50			50
PP	7,180	30	0.4%	7,150
PS	2,170	20	0.9%	2,150
Other resins	4,150	850	20.5%	3,330
Total Plastics in MSW	31,840	2,650	8.3%	29,190

Tertiary recycling is the process of breaking the polymer chain into lighter hydrocarbons and high value fuel feedstock through chemical depolymerization or thermal depolymerization. Chemical depolymerization is reversing the polymerization reaction to reduce the polymer into monomers. Only polymers that are produced by step-growth polymerization reactions, such as polyester, can be chemically depolymerized. However, the majority of plastic are produced by chain-growth polymerization and for this reason, chemical depolymerization is not considered an ideal way to treat plastic waste. Thermal depolymerization is a process of breaking down the complex hydrocarbon into light crude oil in a pressurized, heated and oxygen free environment. This process usually operates at a high temperature and it only breaks down long chain hydrocarbons, such as plastics (Elsayed, 2003).

Quaternary recycling is a process which converts plastic waste directly into energy source, such as electricity. This process is called incineration and it requires a very high temperature. One kilogram of plastic waste can generate 11,000 Kcal of energy whereas one liter of oil can only generate 10,200 Kcal (Elsayed, 2003). The exact amount energy generated by plastic waste depends on the type of plastic. For example: polystyrene can produce 16,082 kcal/kg while polyethylene can generate 18,720 kcal/kg (Elsayed, 2003). However, this form of recycling generates gases and some hazardous compounds which could result in air pollution.

Due to the fact that waste management has become a major issue in today's society especially with the limited landfills, research has turned its focus to different recycling methods. Improving the available recycling methods will help reduce air pollution as well reproduce newer products from plastics. Therefore, the purpose of this project was to develop a new method of ternary recycling plastic waste. This new method relies on improving the currently studied pyrolysis of polystyrene by using molten salt, specifically chloride salt. The experiment in this

project was conducted at moderate temperature in order to break down polystyrene polymer into lighter hydrocarbons. The obtained results showed that using molten salt increases the liquid yield and the selective production of styrene monomer.

This report starts with a literature review that focuses on the types and mechanisms of polymers, pyrolysis of polystyrene, and molten salts. This background research was then used to determine an appropriate procedure and experiment setup for each test done in this project. Since all of the tests were conducted in a Semi-Batch reactor, located in WPI's Goddard Hall Reaction Engineering Lab 222, then a layout of the reactor and its component were identified. Later, the results obtained from all of the tests were presented and discussed. Finally, conclusions based on the project's results were drawn, and a recommendation for future projects was presented.

CHAPTER 2. LITERATURE REVIEW

2.1 Polymers

Plastics are organic materials with very large molecules that consist of a repeated unit called mer. There are two main types of plastics, thermosets and thermoplastics. The molecule chains in thermosets are cross-linked together through primary covalent bonds. When heated, thermosets decompose and cannot be molded again, so they are molded while still in the gel stage of the polymerization reaction. Examples of thermosets include epoxy, which is used as a coating material. Thermoplastics are more common than thermosets and they are typically used for packaging. Some common types of thermoplastics are polystyrene, polyvinyl chloride, and polyethylene. The chains of thermoplastics are connected together by secondary bonds, so when heated, thermoplastics melt. Further heating will cause them to decompose into monomers and lighter hydrocarbons. Thermoplastics are molded or extruded from their resin form, i.e., after the polymerization reaction is complete (Sperling, 2006).

2.1.1 Types of Polymers

Thermoplastics can be broken down into two categories, vinyls and non-vinyls plastics, based on the mer structure. Two carbons connected by a single covalent bond make the main chain of the mer of vinyl plastics. Figure 3 Shows the mer structure of polyethylene; a typical vinyl polymer. The mer structure of non-vinyl polymers on the other hand can have many different forms. The functional group of the main chain contributes to most of the properties of the material, such as polarity and crystallinity. Figure 4 shows the mer structure of nylon 6,6, which has amide as the functional group (Sperling, 2006).

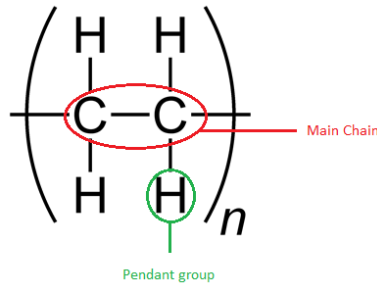


Figure 3: Mer structure of polyethylene (Wikipedia, 2014).

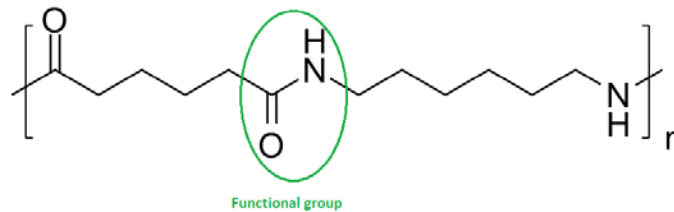


Figure 4: Mer structure of nylon 6,6 (Wikipedia, 2014).

The process in which monomers are linked via covalent bonds to make a large polymer molecule is called polymerization reaction. There are several types of polymerization reactions, the two most common types of polymerization reactions are addition polymerization, also known as chain growth polymerization, and condensation polymerization, which is known as step growth polymerization (Sperling, 2006).

Generally, addition polymerization is used to produce vinyl polymers. In this process, a free radical initiator such as benzoyl peroxide or an ionic compound is used to produce active growth sites where monomers link together. This step of the process is called the initiation step. The next step is called propagation, in which the molecules link together and grow rapidly. Finally, when the desired size is reached, the reaction is terminated. Ionic compounds can also be used as reaction initiators (Sperling, 2006).

In condensation polymerization, usually two different types of monomers combine to make a non-vinyl polymer without the need of using a free radical initiator. The process is slower than addition polymerization, and final molecular weight of polymer is much lower, but all polymer chains are close in molecular weight as opposed to polymers produced by addition polymerization, which generally vary in sizes especially in commercial plastics (Sperling, 2006).

There are many different methods to calculate the average molecular weight of polymer. The two most common methods are number average molecular weight, M_n , and weight average molecular weight, M_w . The calculations for both of the methods is shown below.

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (1)$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (2)$$

In the equations above, N_i represents the number of molecules that have the molecular weight M_i . The number average molecular weight gives an equal value for all molecules. Nevertheless, the weight average molecular weight gives a bigger value for bigger molecules since they contribute more to the properties of the polymer. The ratio of the weight average molecular weight to the number average molecular weight is called the polydispersity index, PDI, which shows how uniform size of the chains is. PDI with a value of 1 indicates that all the chains have the same size, which is a very rare case.

2.1.2 Polystyrene

Polystyrene is a vinyl thermoplastic synthesized from the monomer styrene. Generally, polystyrene is considered an amorphous polymer, and therefore it has a relatively low melting point at approximately 200 C. This also allows it to be extruded easily making it one of the most widely used polymers. It is used in food packaging, foam packaging, electronics, and insulation. Figure 5 shows the mer structure of polystyrene (Yikrazuul, 2008).

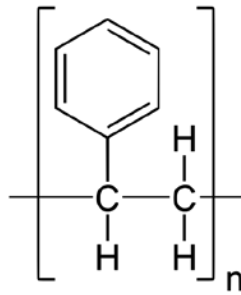


Figure 5: Mer structure of polystyrene (Yikrazuul, 2008).

2.2 Pyrolysis of Polystyrene

Pyrolysis is the process of rapidly heating a polymer in the absence of oxygen to break the polymer chains into lighter hydrocarbons. There are three main products that can be formed, styrene monomer, styrene dimer, and oligomers. Styrene monomer and dimer constitute the majority of the product. Nonetheless, further cracking of those two products will also result in gases and secondary products such as benzene, toluene, alpha- Methylstyrene, and ethylbenzene. Oligomers (waxes) typically break to form trimers, dimers, and monomers. Arabiourrutia et al. proposed an overall mechanism for the degradation of polymers in a sprouted bed reactor, which is shown in Figure 6.

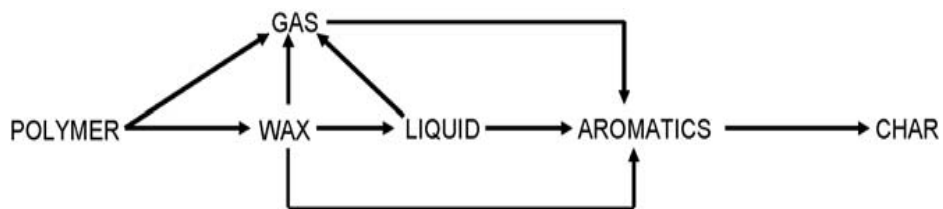


Figure 6: General mechanism of polymer degradation (Onwudili et al., 2009).

The pyrolysis of polystyrene is largely a temperature dependent process. The molecular weight of the polymer starts to decrease at temperatures higher than its melting point, which is about 200°C (Grassie et al., 1957). A typical molecular weight as function of time at a given pyrolysis temperature is shown in Figure 7. The graph is a theoretical model developed by Kruse et al. in 2001 to predict the change in the number average and weight average molecular weight of polystyrene over time at a given temperature. Initially, the change in the molecular weight of the polymer is rapid, but it starts to level toward the end when polymer has lost the majority of the mers.

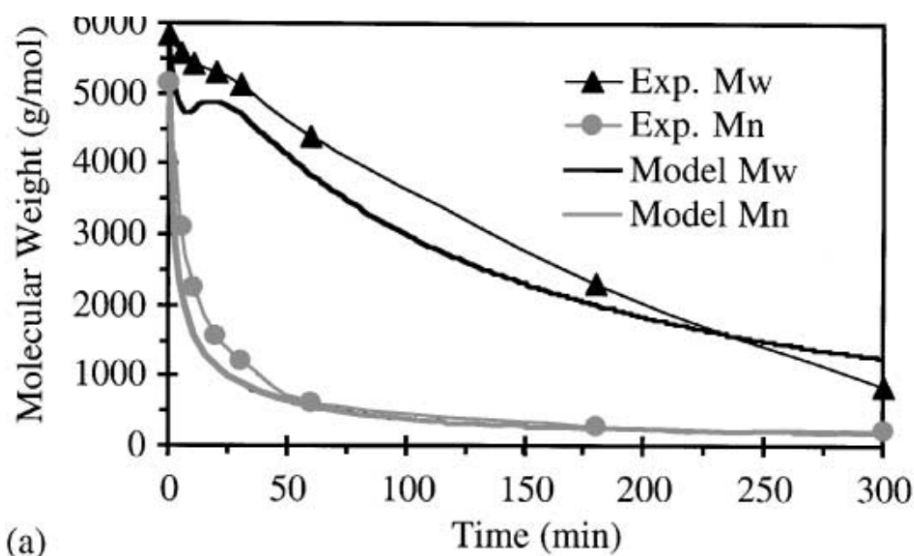


Figure 7: Theoretical model to predict the behavior of molecular weight over time at 623 K (Kruse et al., 2001).

Liquid yields of pyrolysis of polystyrene as high as 97% were obtained by Yirong and colleagues at 450°C in a fluidized bed reactor shown in Figure 8. Yirong and colleagues observed that the main components of the liquid product were styrene monomer, dimer and trimer as well as some secondary components such as benzene, toluene, ethylbenzene, and alpha-Methyl styrene. They also observed that the monomer yield increases with temperature until it reaches its maximum at 600°C, where it starts to decline. The yield of the dimer however stayed constant while the yield of trimer decreased as the temperature increased as shown in Figure 9. Overall, the liquid yield increased with temperature until it reached its maximum at 450°C after which it starts to decline, while both the cracking gas and the coke increase with temperature (Yirong et al., 2000).

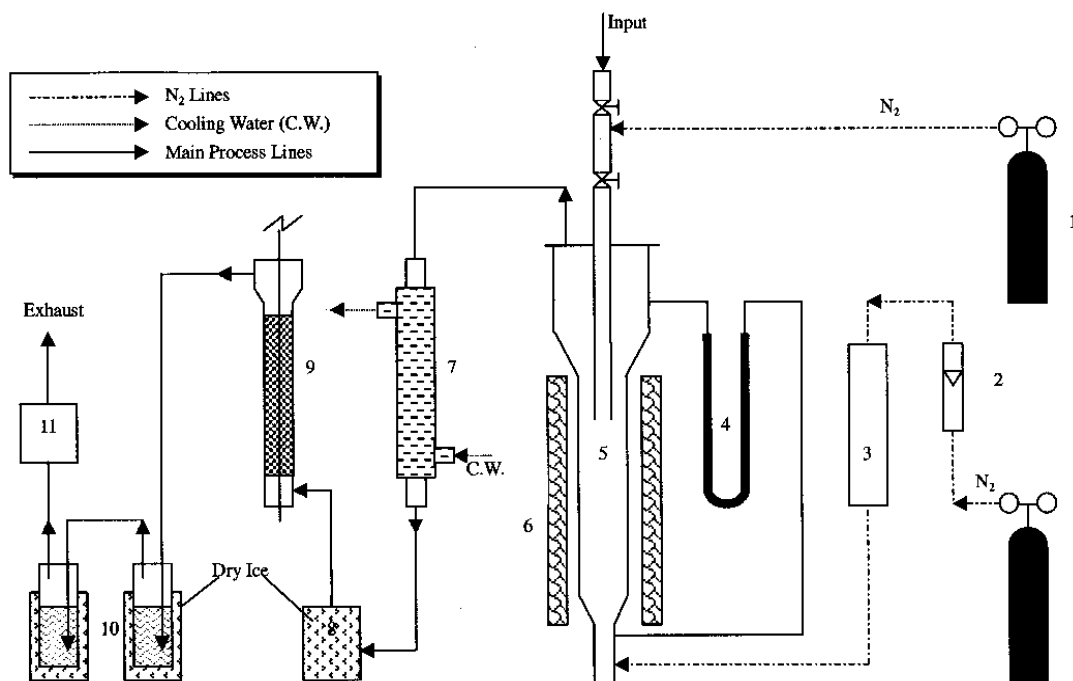


Figure 8: Fluidized-bed reactor apparatus for polystyrene pyrolysis (Yirong et al., 2000).

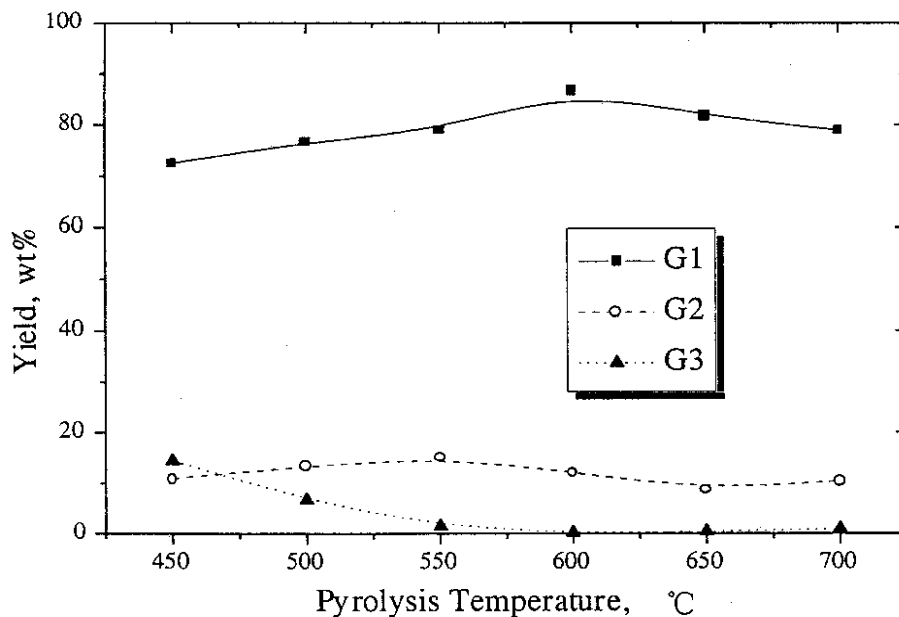


Figure 9: Liquid yield as function of temperature. G1: monomer, G2: dimer, G3: trimer (Yirong et al., 2000).

2.2.1 Mechanism of Reaction

The thermal depolymerization of polystyrene is a very complex process. There are many different mechanisms via which the polymer chain can break into lighter hydrocarbons. Generally, the first step in the reaction is called the initiation step. In this step, the polymer chain breaks at a random location to form a radical end as shown in Figure 10. This reaction is reversible, so it is possible for the chains to recombine and possibly form a branched chain.

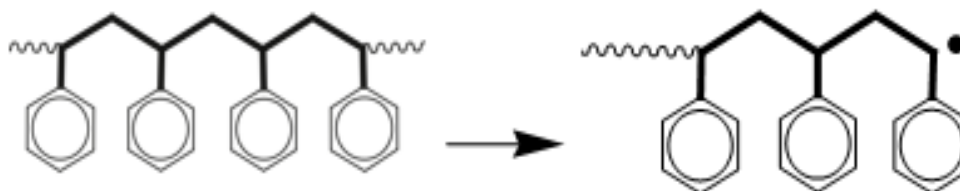


Figure 10: Initiation step (Levine et al., 2008).

The reaction could then proceed via many different mechanisms. One of these is the so-called chain unzipping or end-chain beta-scission in which the mers at the end of the chain break

to from monomers as shown in Figure 11 below. This mechanism is considered by many to be the dominating mechanism for the thermal decomposition of polystyrene and explains the high styrene monomer yield (Kruse et al., 2001).

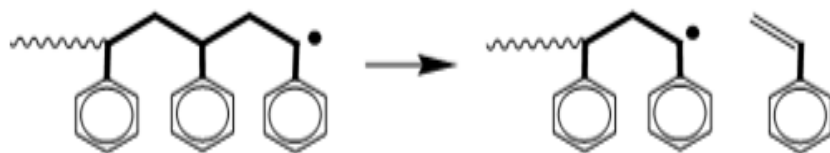


Figure 11: End-chain beta-scission (Levine et al., 2008).

Another common mechanism is intermolecular or intramolecular head radical transfer followed by mid-chain beta-scission. When the scission occurs at the third position, styrene dimer is formed and when it occurs at the fifth position, a trimer is formed as shown in Figure 12 (Levine et al., 2008).

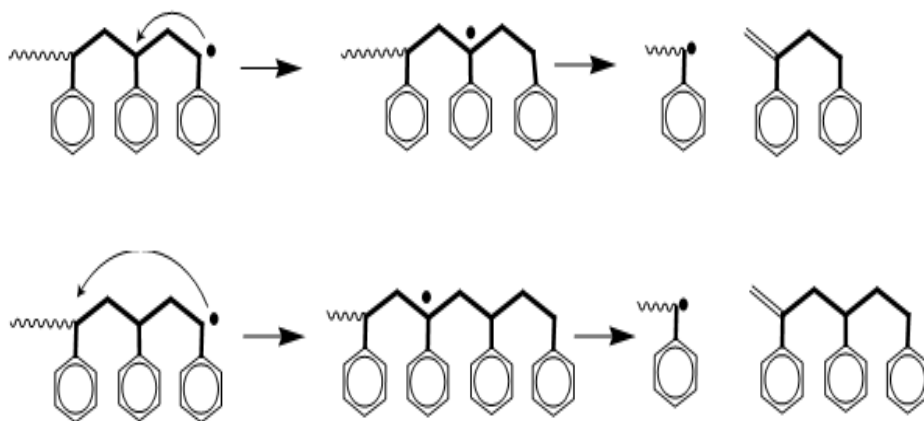


Figure 12: Mid-chain beta-scission (Levine et al., 2008).

Another common mechanism, which has a great importance in this study of molten salt pyrolysis, is the carbon-hydrogen bond fission, or hydrogen abstraction, which is also considered

as an initiation step. In this reaction, hydrogen is removed from a random location on the chain to form a proton and a radical as shown in Figure 13 below (Kruse et al., 2001).

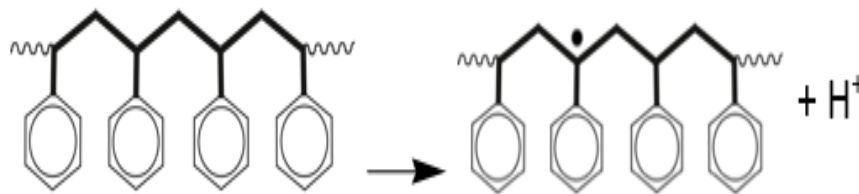


Figure 13: Hydrogen Abstraction (Levine et al., 2008).

2.2.2 Catalytic Pyrolysis of Polystyrene

The use of catalysts for thermal degradation of polymers can also provide many benefits. One of the greatest benefits is improving the kinetics of the reaction without the need of using high reaction temperatures (Ohkita et al., 1993). The use of catalysts can also improve the selectivity of the desired product. Lee and colleagues have found that by using zeolites, the selectivity of aromatic compounds can be increased to 99% (Lee et al., 2002).

Many have studied the use of acidic catalyst in the pyrolysis of polymers, and it showed to have a great potential in improving the yield of the pyrolysis. A study that was done in 1995 by Zhang et al. on the pyrolysis of polystyrene over solid acids showed that it is indeed possible to increase the cracking of polystyrene by using solid acids. They proposed a mechanism that explained how the acid catalyst affects the catalyst, which is shown in Figure 14 below. Essentially, the acids add protons to chains that have not formed a radical end, which will disrupt the C-C bond, making the fission easier. Nevertheless, Zhang et al. concluded that solid acids reduce the yield of liquid product, but increase the yield of gases and char due to severe cracking of styrene (Zhang et al, 1995).

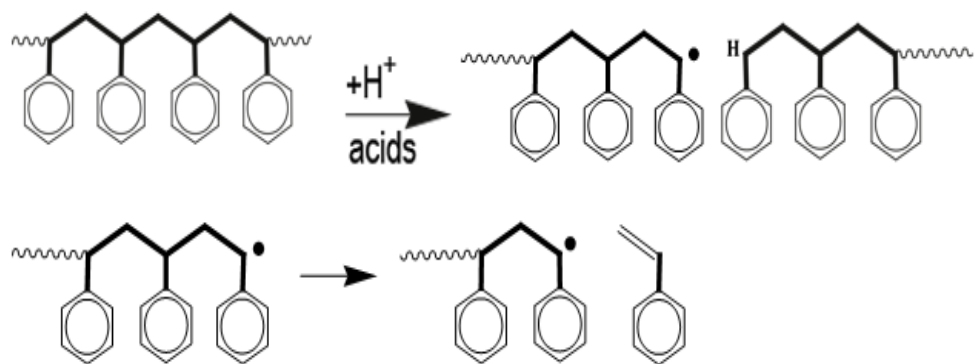


Figure 14: Solid acid catalysis mechanism (Levine et al., 2008).

Some of the common acid catalysts used by Zhang et al. are zeolites, which are a three-dimensional crystalline aluminosilicate with uniform pores that act as a molecular sized sieve. Zeolites also have ions exchange properties, which make them very attractive for a wide range of applications (Čejka, 2007). Zeolites consist of tetrahedral SiO_4 and AlO_4^- which give the zeolite a -1 charge. By controlling the ratio of aluminum to silicon, the number and size of the Brønsted acid sites, which have proton donating properties (Davis, 1991). One of the most popular types of zeolites is ZSM-5. Zeolites have been studied extensively as catalysts in the pyrolysis of polymers due to their Brønsted acid properties combined with large surface area. Nonetheless, it is usually found that zeolites results in decreasing the liquid yield and increasing the gas and char yield when used in polystyrene pyrolysis due to sever cracking caused by the acidic properties (Williams et al., 2004). Other types of acid catalysts that could prove useful in the pyrolysis of polystyrene are heteropoly acids, such as phosphotungstic acid. Heteropoly acids are strong Brønsted acids. They have been studied as catalysts for Friedel–Crafts reactions, but not for thermal pyrolysis of polymers. The main advantage of heteropoly acids over zeolites is the fact that they do not become deactivated during the reaction. Zeolites on the other hand, could get deactivated due to blockage of their acid sites (Kaur et al., 2002).

In 1995, Zhang et al. also studied the effect of using solid bases catalysts in the pyrolysis of polystyrene. They concluded that solid bases work even better than solid acids. The reaction time was reduced from 90 minutes with solid acids to only 20 minutes with solid bases. They proposed a similar mechanism that explained how base catalysts affect the reaction. In this mechanism, the base catalysts promote the hydrogen abstraction by absorbing a proton into the base site as shown in Figure 15 (Zhang et al., 1995).

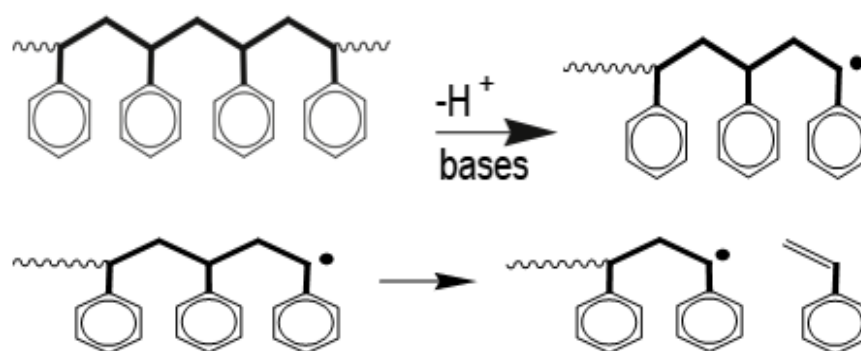


Figure 15: Solid Base Catalysts Mechanism (Levine et al., 2008).

2.3 Molten Salts

Molten salts are salts that are heated above their melting temperature. One of the biggest challenges associated with thermal pyrolysis of polystyrene is the high viscosity of the melt, and the poor heat transfer (Madras et al., 1997). Molten salts, such as metal chlorides, have low viscosity and they also have catalytic properties similar to those of solid acid catalysts. Thus, the use of molten salts for polystyrene pyrolysis provide an excellent heat transfer medium with low viscosity, and reactive ionic properties with the capabilities of solid Lewis acid catalysts. In addition, Brønsted acids, such as heteropoly acids, and bases such as, $Ni(OH)_2$, can be easily be dissolved in molten salts. With these properties, molten salts are expected to promote initiation. This phenomenon was analyzed in polymer waste pyrolysis in molten salt studied done by

Chambers et al. in 1984. The feed consisted of rubber-rich polymers from automobile shredders. Seven different metal chloride salts were studied, LiCl, KCl, CuCl, ZnCl₂, NaCl, SnCl₂, and AlCl₃ at temperatures ranging from 380°C to 570°C in a Semi-Batch reactor. Chambers et al. concluded that rate of reaction was greater than that of thermal pyrolysis, even when performed in a fluidized bed. The liquid yield was also increased, with the highest percent conversion in the presence of ZnCl₂ (Chambers et al., 1984).

Another study regarding the use of molten salt pyrolysis was done in 1987 by Bertolini et al. The salts that were used in this study were NaOH and Na₂CO₃ at 450°C to 480°C. The liquid yield from the molten salt pyrolysis of polystyrene was 98% with styrene composting 71.4% (Bertolini et al., 1987). Also, previous research at WPI on the use of molten salts in pyrolysis of biomass showed that molten salts do in fact improve the selective production of the desired products. Overall, the use of molten salts for polymer pyrolysis looks promising.

2.3.1 Eutectic Molten Salt

Since individual salts have very high melting points, it is important to utilize eutectic systems in order to lower the melting point of the salts. Through the use of a phase diagram, like the one shown in Figure 16, it is possible to choose the compositions of the salts that will result in a molten-salt at a reaction temperature lower than the melting point of the individual salts.

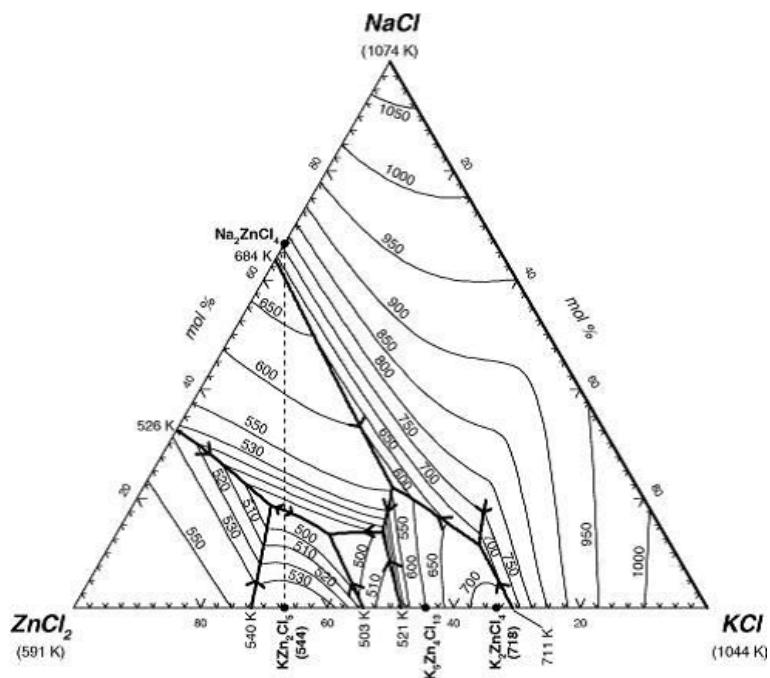


Figure 16: Ternary phase diagram of chloride salts (Nitta et al., 2009).

The chloride molten salts were chosen for this study since previous studies at WPI showed that in biomass pyrolysis, metal chloride melts were the most effective compositions. Furthermore, metal chlorides, such as ZnCl₂, are Lewis acid catalysts. In addition to studying the effect of chloride salts, the ideal reaction temperature and the effect of different additional catalysts were also studied in this project in order to produce high styrene yield.

CHAPTER 3. METHODOLOGY

3.1 Objectives

The objectives of this MQP project include:

- A study the effect of different chloride eutectics in the pyrolysis reaction of polystyrene, especially the yield of liquid and selectivity of monomer produced. These salts are:
 - Zinc Chloride (ZnCl_2)
 - Sodium Chloride (NaCl)
 - Potassium Chloride (KCl)
 - Lithium Chloride (LiCl)
- Determination of the ideal temperature for pyrolysis reaction of polystyrene.
- Determination of the best chloride eutectics which would produce the highest liquid yield.
- Determination the best chloride eutectic which would maximize monomer recovery and minimize secondary products.
- Testing the effect of different catalysts, namely:
 - Nickel (II) Hydroxide ($\text{Ni}(\text{OH})_2$)
 - Phosphotungstic Acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$)
 - Zeolite Socony Mobilie-5 (ZSM-5)

3.2 Reactor Layout

3.2.1 Reactor Setup

In this project, the molten salt polystyrene pyrolysis reactions were conducted in a Semi-Batch reactor, the setup is shown in Figure 17, which is located in WPI's Goddard Hall Reaction Engineering Lab 222. A compressed helium tank was used to provide inert gas flow to the reactor tube, which was placed inside a furnace as shown in Figure 18. The helium gas removed volatile compounds as well as gases produced, and it was used due to its properties as an inert gas.

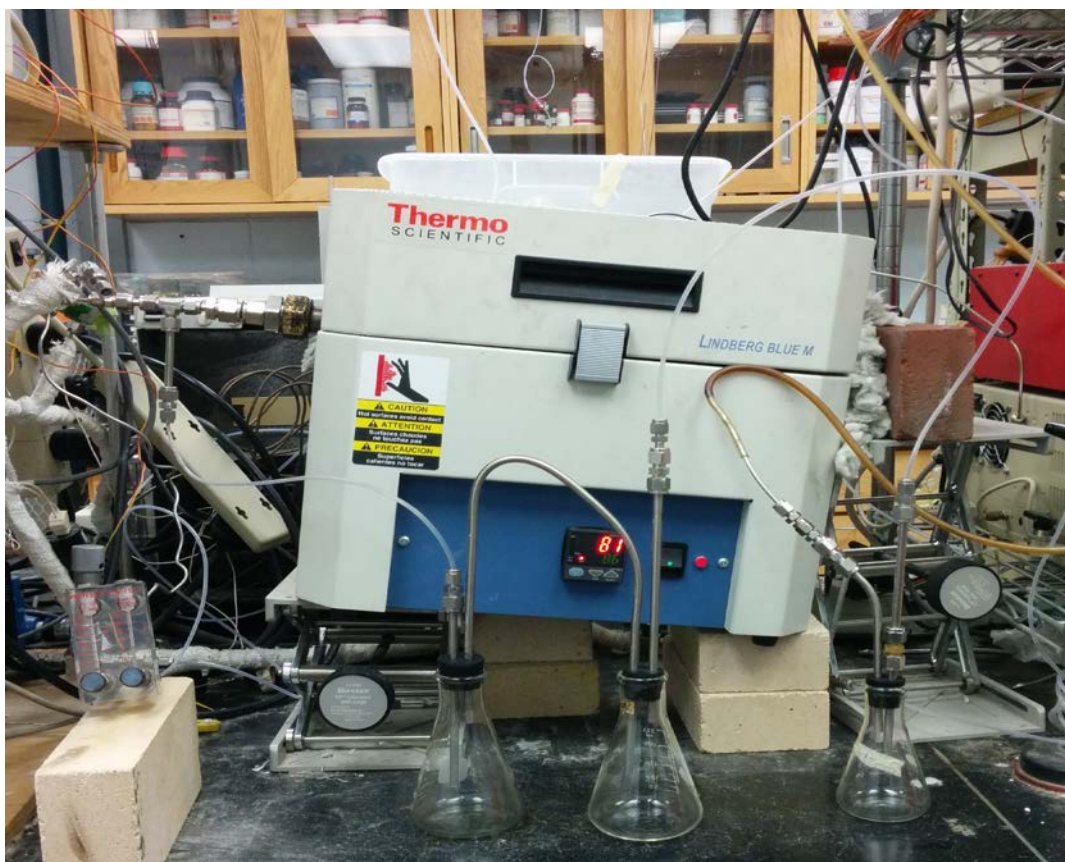


Figure 17: Semi-Batch reactor setup



Figure 18: Reactor tube inside the furnace

The helium flow was controlled using two needle valves, and the products removed by helium gas were condensed using three cold traps that were immersed in an ice bath. The condensed liquid were collected using a graduate pipette while any permanent gases produced were ventilated. Also, a J-type thermocouple was installed inside the reactor to accurately measure temperature inside the reactor. Figure 19 below shows a schematic of the apparatus used in this project.

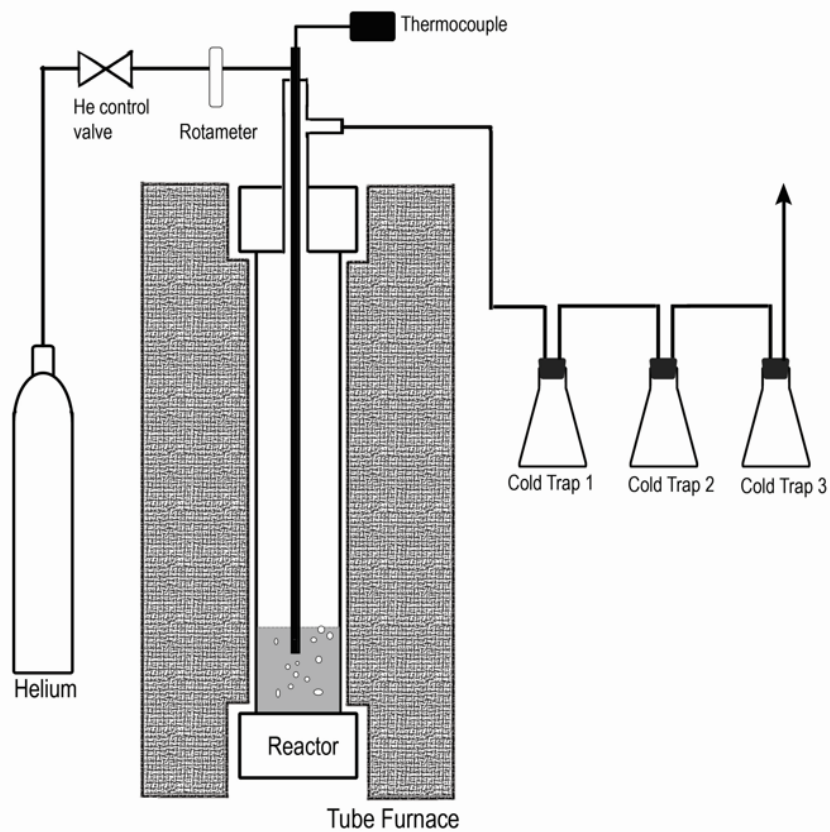


Figure 19: Schematic of the apparatus

3.2.2 Reactor Design

The reactor tube that was used in this project was a 14 inches long stainless steel tube with a $\frac{3}{4}$ inch diameter. The top of the reactor connected to a $\frac{3}{4}$ - $\frac{1}{4}$ of an inch diameter Swagelok reducing union with a heat exchanger tee, while the bottom of the reactor was sealed by a $\frac{3}{4}$ of an inch ferrule cap shown in Figure 20. The top of the reactor was attached to the helium inlet line, which delivered gas into the reactor, through a 15 inch long stainless steel tube with a $\frac{1}{8}$ inch diameter. This was done in order to ensure that the vapors produced were directly carried out of the reactor.

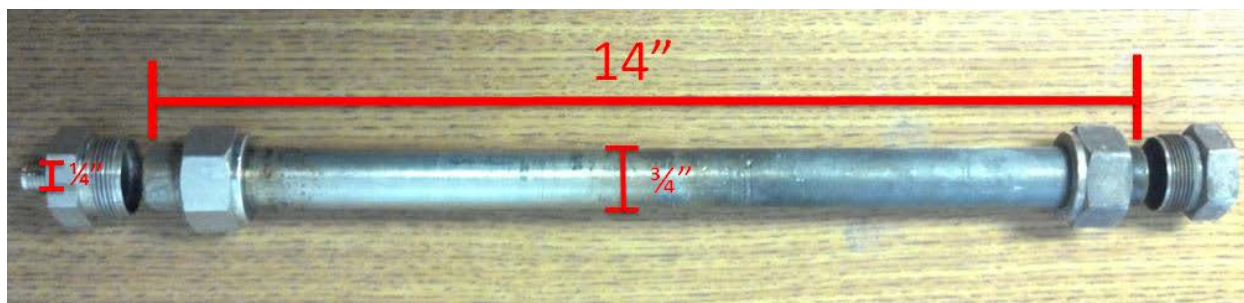


Figure 20: Reactor Tube

3.2.3 Furnace

The furnace used to heat the reactor is a Lindburg/Blue Mini-Miite TF55030A Tubular Heater shown in Figure 21. The furnace uses PID controller to control the set point temperature and the heating rate. It has a maximum temperature of 1100°C, with a heating rate up to 60°C /min. The heating tube inside the furnace is well insulated to reduce heat losses to the surrounding. The furnace could be oriented vertically or horizontally; however, in this project it was utilized in a horizontal configuration at a 30 degree angle.



Figure 21: Lindburg/Blue tubular heater

3.3 Procedure

In this project, we developed and followed a specific and consistent procedure during each experiment. The procedure steps are highlighted below:

1. A specific amount of chloride salts and polystyrene were measured and mixed using a mortar and a pestle.
2. The mixture was added to the reactor tube, and the reactor ends and the threads of the cap and reducing union were lubricated then sealed using a wrench.
3. Then, the helium inlet was attached to the reactor and sealed. The reactor was then placed at an angle of 30 degree inside the inclined furnace.
4. After the system was completely sealed, it was flushed with helium for roughly 20 minutes to ensure no oxygen was present.
5. Then, the furnace was turned on to the temperature of 150°C for 30 minutes in order to dry off water.
6. Once the water was dried, the temperature was then raised at 60°C /min to the desired temperature, typically 400°C, for an hour and a half.
7. After an hour and a half, the furnace was turned off and the produced liquid was collected from the flasks into vials and weighed.
8. Once the reactor cooled down, the reactor was cleaned and any solid product remaining in the reactor was weighed.
9. Finally, the reactor was reassembled and used for the next experiment.

3.4 Types of Different Experiment Conducted

To achieve the objectives of this project listed above, different experiments were conducted. These experiments are: 1) Polystyrene baseline tests, 2) Molten salt pyrolysis

temperature tests, 3) Varying chloride eutectic tests and 4) Effects of different catalysts. A description of each of these set of experiments is presented below.

3.4.1 Polystyrene Baseline Tests

In order to study the effect of temperature on polystyrene without any salt or catalyst, it was necessary to test polystyrene by itself at different temperatures. Two grams of polystyrene were charged into the reactor and allowed to undergo thermal pyrolysis for almost two hours. Five different experiments were conducted at the same heating rate of 60°C/min with final temperatures of 250°C, 300°C, 350°C, 400°C and 450°C.

3.4.2 Molten Salt Pyrolysis Temperature Tests

To determine the effect of final temperature of the molten salt pyrolysis before testing different chloride eutectics, it was necessary to test the same chloride eutectics with the same end temperatures as the baseline tests. A 10:1 eutectic to polystyrene molar ratio was used, because it is the minimum amount of salt that would cover the two grams of polystyrene. The chloride eutectic consisted of 60% mole of zinc chloride, 20% mole of sodium chloride, and 20% mole of potassium chloride. This specific combination of chloride eutectic was chosen since it has a melting temperature of 237°C, which is lower than the lowest temperature that was used in the baseline thermal tests.

3.4.3 Varying Chloride Eutectics Tests

Following the testing of the effect of molten salt pyrolysis final temperature, different chloride eutectics were tested to determine which chloride composition produce the highest liquid yield. To minimize operating cost, cheaper salts such as NaCl were tested and compared to the use of more expensive salts such as KCl and LiCl in order to see if they could be used interchangeably. The specific amount of each salt was selected in a way that the mixture would melt below operating

temperature i.e. 400°C. This selection was done using chloride binary and ternary diagrams shown in Figures 22 and 23. Each experiment in this test was run at the final temperature of 400°C for an hour and a half and at a constant helium flow rate of 90 ml/min.

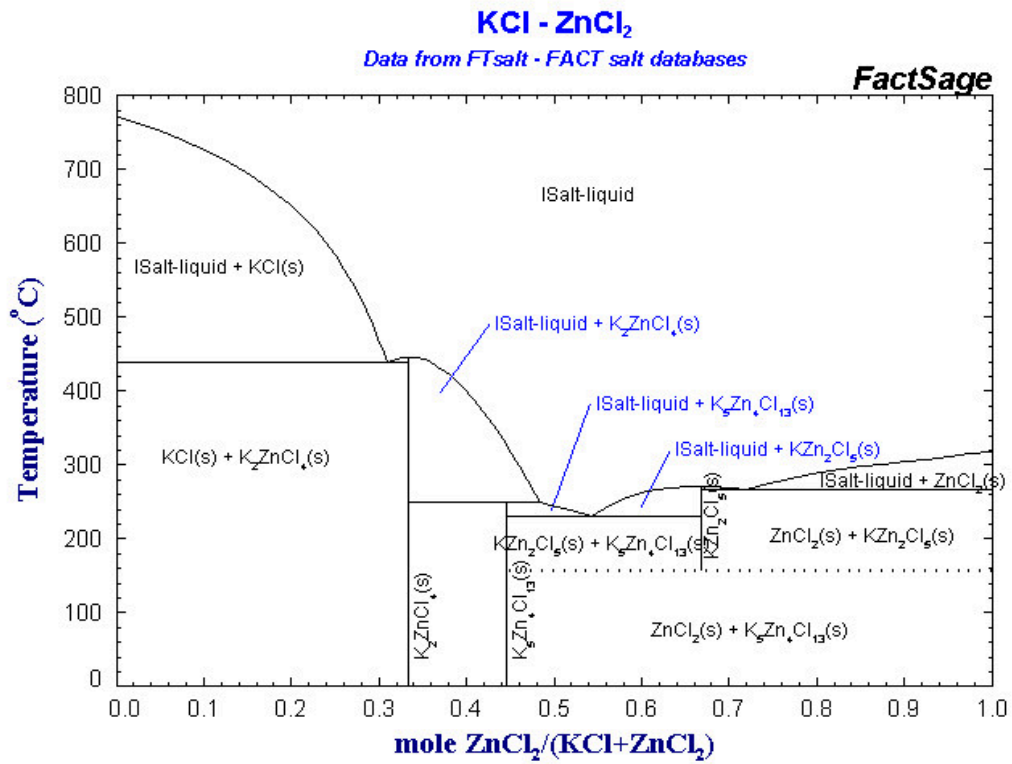


Figure 22: Binary phase diagram of chloride salts (FactSage, 2014).

SHIMADZU (model: 30 m \times 0.25 mm i.d., 0.25 mm film thickness). In this project, the GC/MS was set by the following temperature programming: initial oven temperature was 40 °C, held for 2 min; then the temperature was raised to 250°C at 5 °C/min, and held for 6 min. Helium was used as a carrier gas with a constant flow rate of 38.9 ml/min. The amount of injection was 0.5 μ l at split mode (split ratio, 20:1). The MS was operated in the electron impact mode, the ion source temperature was 230°C and electron energy was 70 eV. The mass range from 35 m/z to 500 m/z was scanned. The obtained liquids were diluted in acetone before injection to ensure that the GC would not be overloaded with concentrated samples.



Figure 24: WPI's Godard Hall gas chromatography and mass spectrometry

3.6 Safety Procedure

During the course of this project, the MQP team had to deal with some hazardous chemicals and very high temperature. Latex gloves and safety goggles were worn all the time in the lab. Also, it was necessary to wear heat resistant gloves when handling any component which was heated by

the furnace. The chemical wastes were separated carefully into municipal and hazardous wastes to ensure proper disposal of chemicals. A fume hood was placed above the furnace, in order to ensure that no gas produced would escape to the lab.

CHAPTER 4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Effect of Final Temperature and Molten Salt

The first part of this project was to determine the desired final temperature of polystyrene pyrolysis, and study the effects of molten salt on the pyrolysis. This was done using the procedure, described in section 3.3. During the experiment, the final set temperature was varied from 250°C to 450°C, i.e., by increments of 50°C all with 60°C /min heating rate. The blue line in Figure 25 shows the mass percent liquid yield of polystyrene at different temperatures via thermal pyrolysis, while the red line indicates the mass percent liquid yield of polystyrene with molten salt pyrolysis at different final temperatures. For polystyrene baseline pyrolysis, the minimum percent liquid yield of 25% was obtained at 250°C and 300°C, while the maximum percent liquid yield of 80% was obtained at the temperature of 450°C.

As seen in Figure 25, there is an increase of the liquid yield from 25% to 60% when the temperature is increased from 300°C to 350°C. At 350°C, the liquid yield increases by 10% for every 50°C rise in temperature, reaching the maximum liquid yield of 80% at 450°C. For the molten salt pyrolysis, it is clearly seen that the salt increases the overall liquid yield at a given temperature relative to the case of pyrolysis without salt. At temperatures of 250°C and 300°C, the relative liquid yield increases by 5% to 30% liquid yield. The maximum relative increment of liquid yield is achieved at temperatures of 400°C and 450°C, where the yield increases by 10% reaching 80% and 90%, respectively. Nevertheless, the minimum increment of 5% is obtained at 350°C.

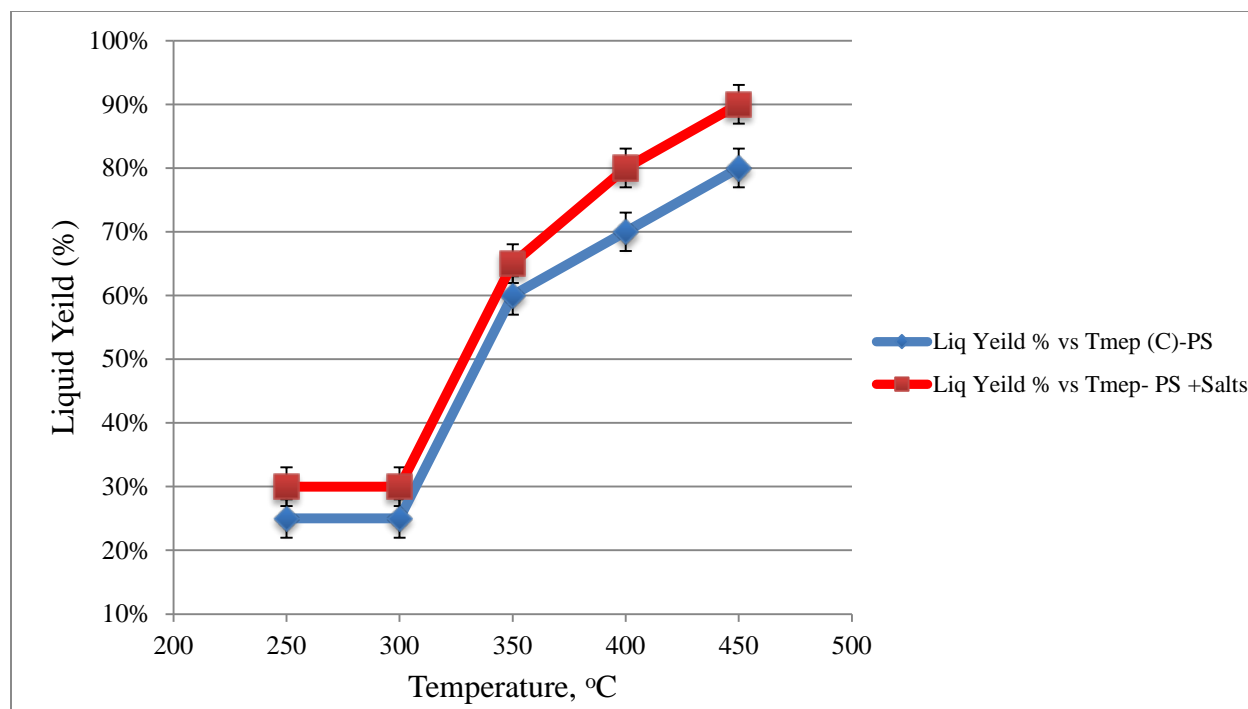


Figure 25: Percent gravimetric liquid yield vs. temperature

Using CMS, the obtained liquids from all the experiments were analyzed and their main product concentrations were determined. The main compounds identified by GC/MS are toluene, alpha-methyl styrene, styrene monomer, and styrene dimer. These four primary compounds make up about 85 wt. % of the obtained liquids on average. The other 15 wt. % consisted of xylene, ethylbenzene, bibenzyl, ethylene, and other unidentified compounds. Figure 26 shows the weight fraction of the four main compounds at different temperatures. It is clear from the graph that as temperature increases, the weight fraction of styrene, which is the primary product, increases. On the other hand, at 300°C, the weight fraction of styrene decreases and that of styrene dimer, another primary product, increases. At a temperature of 400°C, the primary products are maximized, whereas at 250°C the primary products are minimized and the secondary products reach the maximum.

Also, Figure 26 shows the effect of molten salt on the production of the primary and secondary products. In general, the molten salt increases the styrene monomer, alpha-methyl styrene, and toluene, but decreases dimer and other products. At a temperature of 400°C, all of the products are increased except for the alpha-methyl styrene. At 450°C, all of the products are almost constant with a big increment in styrene monomer compared to its weight fraction at 400°C. Overall, the effect of molten salt on styrene monomer production is minimized at high temperature, and the molten salt has the same effect on the styrene recovery as simply increasing the temperature.

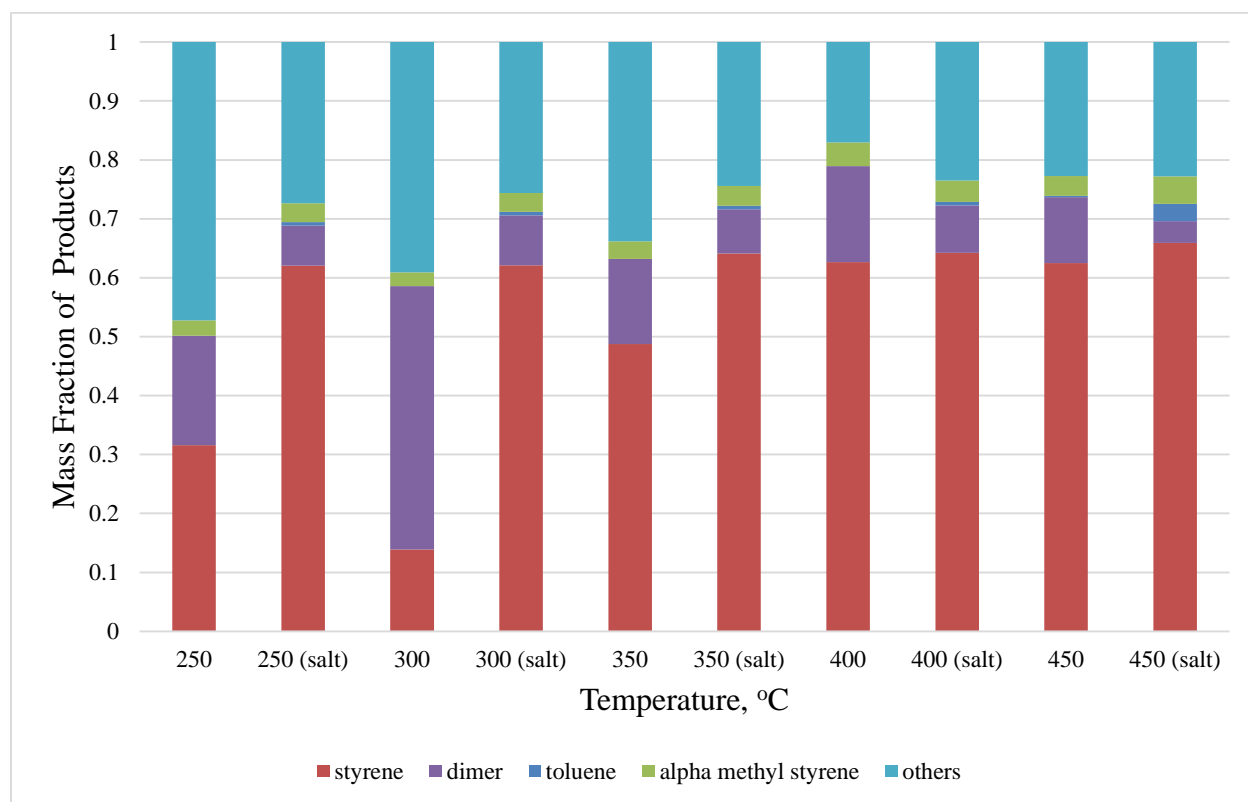


Figure 26: Mass fraction of products vs. temperature

Figure 27 shows the effect of temperature and molten salt on the selectivity of the two primary product of polystyrene pyrolysis, styrene monomer to styrene dimer. The blue squares represent the selectivity of styrene to dimer in dry pyrolysis of styrene, and the orange squares

represent the selectivity of styrene when molten salt is used at different temperatures. In general, the selectivity of styrene increases with increasing the temperature, and it reaches the highest selectivity value of almost six for thermal pyrolysis at the temperature of 450°C. Also, the molten salt has a strong effect of increasing selectivity of styrene, especially at 450°C where the selectivity reaches the highest value of eighteen. This indicates that the styrene monomer is favorable over the styrene dimer at high temperature, and it is more favorable when molten salt is used. It is possible that dimer is converted further into monomer at higher temperatures and in the presence of molten salts, i.e., it is an intermediate (rather than parallel) product of polystyrene pyrolysis.

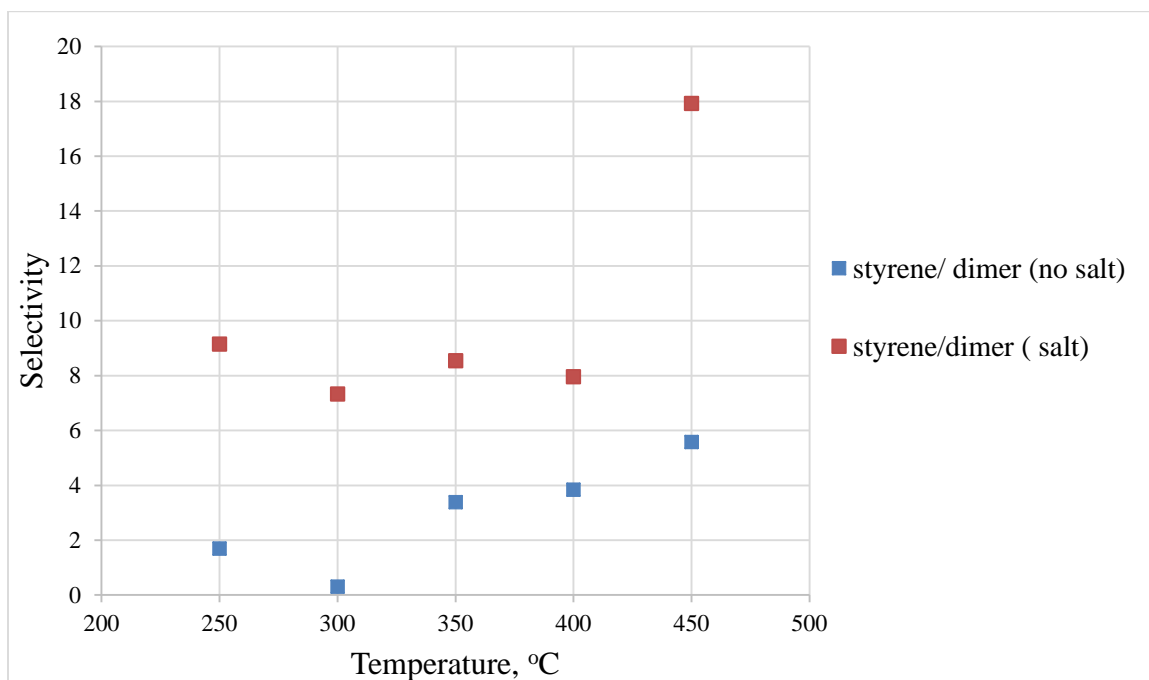


Figure 27: Selectivity of styrene to dimer vs. temperature

The graph in Figure 28 shows the selectivity of primary to secondary products, styrene dimer to alpha-methyl styrene. The graph shows two sets of data for dimer selectivity, the blue squares represent the selectivity without using molten salt, and the orange squares represent the selectivity with adding molten salt. The blue squares pattern indicates that the selectivity of dimer

decreases as temperature increases; however, at 300°C, the selectivity inexplicably increases sharply reaching the highest value of nineteen. Furthermore, the orange squares for molten salt pyrolysis show that the dimer selectivity follows the same trend as the one observed for the blue squares, reaching the highest selectivity value of 2.6 at temperature of 300°C. This demonstrates that the molten salt decreases the selectivity of dimer to alpha-methyl styrene, which means the salt helps the dimer to crack further and produce secondary product, alpha-methyl styrene. In other words, the dimer is an intermediate product in the production of alpha-methyl styrene as well.

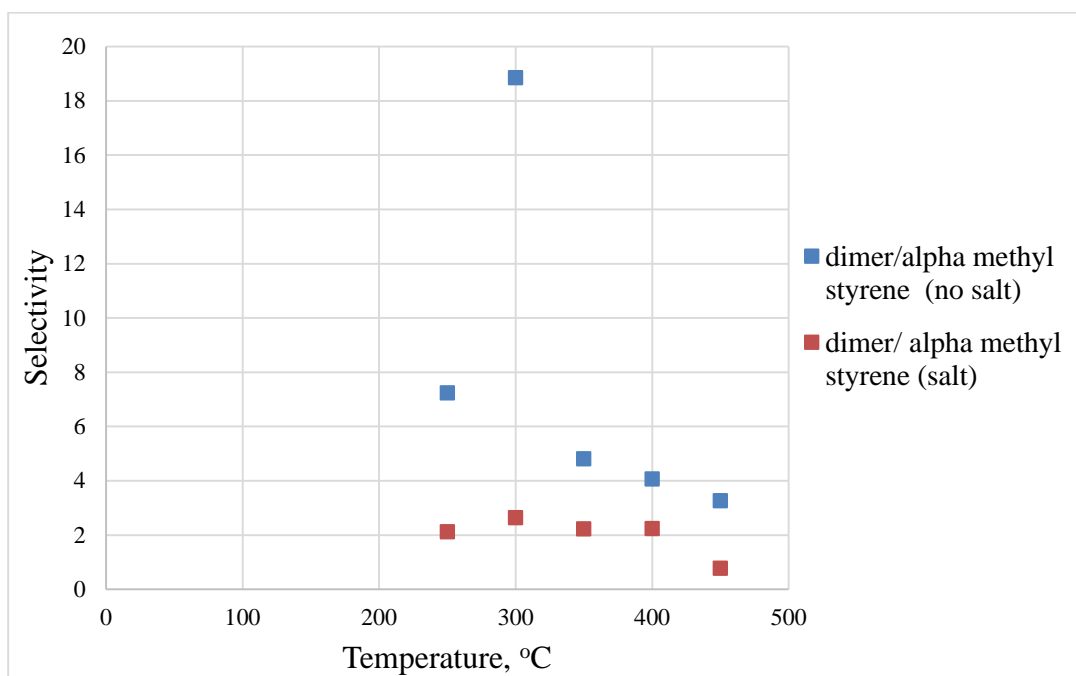


Figure 28: Selectivity of styrene dimer to alpha-methyl styrene

The selectivity of styrene to alpha-methyl styrene for polystyrene pyrolysis thermal and molten salt pyrolysis of polystyrene is shown in Figure 29. The blue squares represent the styrene selectivity for thermal pyrolysis, and the orange squares represent the selectivity for the molten salt pyrolysis. The blue squares show that the selectivity of styrene to alpha-methyl styrene increases with increasing temperature except at 300°C, where the selectivity drops reaching the

lowest value of 5.9. Moreover, the orange squares illustrate that adding molten salt increases the selectivity of styrene compared to its selectivity without molten salt. On the other hand, the overall selectivity of styrene in the molten salt pyrolysis decreases as the temperature increases, reaching the lowest value of fourteen at 450°C. This implies that at higher temperatures the monomer is converted into further products.

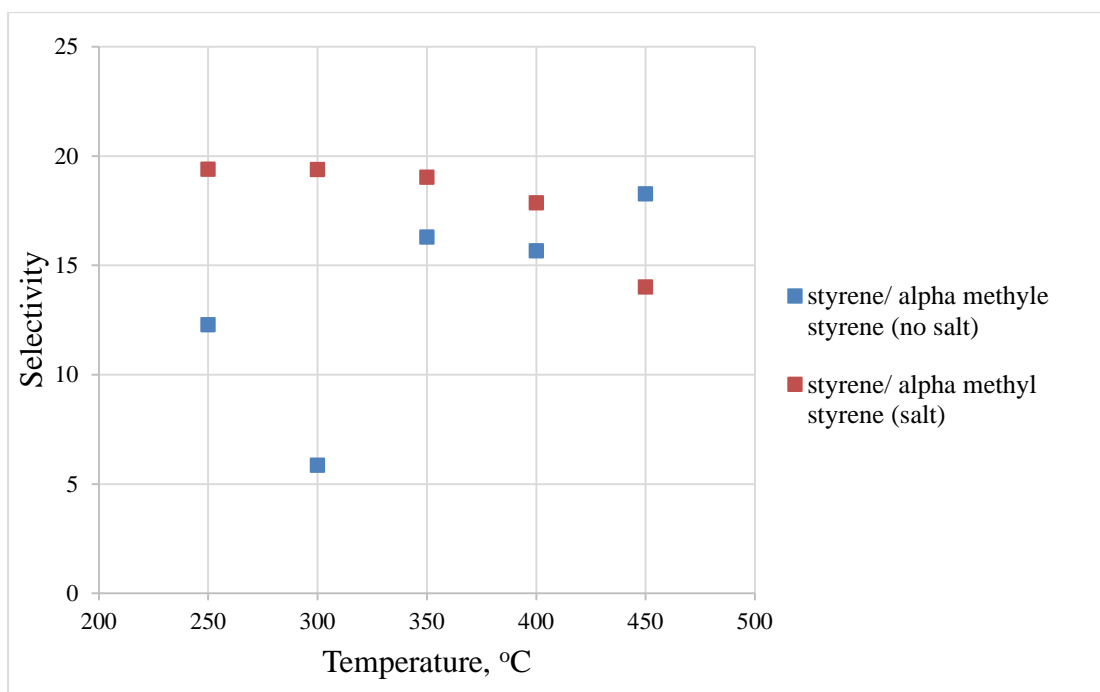


Figure 29: Selectivity of styrene to alpha-methyl styrene

4.2 Effect of Varying Chloride Eutectic

For the study of varying eutectic compositions, the temperature of choice was 400°C for two reasons. First, it allowed the team to study any eutectic with melting temperature below 400°C. Second, the difference in liquid yield between thermal pyrolysis and molten salt pyrolysis at 400°C was bigger than that of any temperature below that, which means that the effect of molten salt will be more desirable at that temperature. ZnCl₂ was used in most of the eutectics because it had the lowest melting point of any of the salts, so it helped bring down the melting temperature of the eutectic. Furthermore, it is a Lewis acid, which could be enhancing effectiveness of the molten salt. The results for varying the salt compositions are shown in Figure 30.

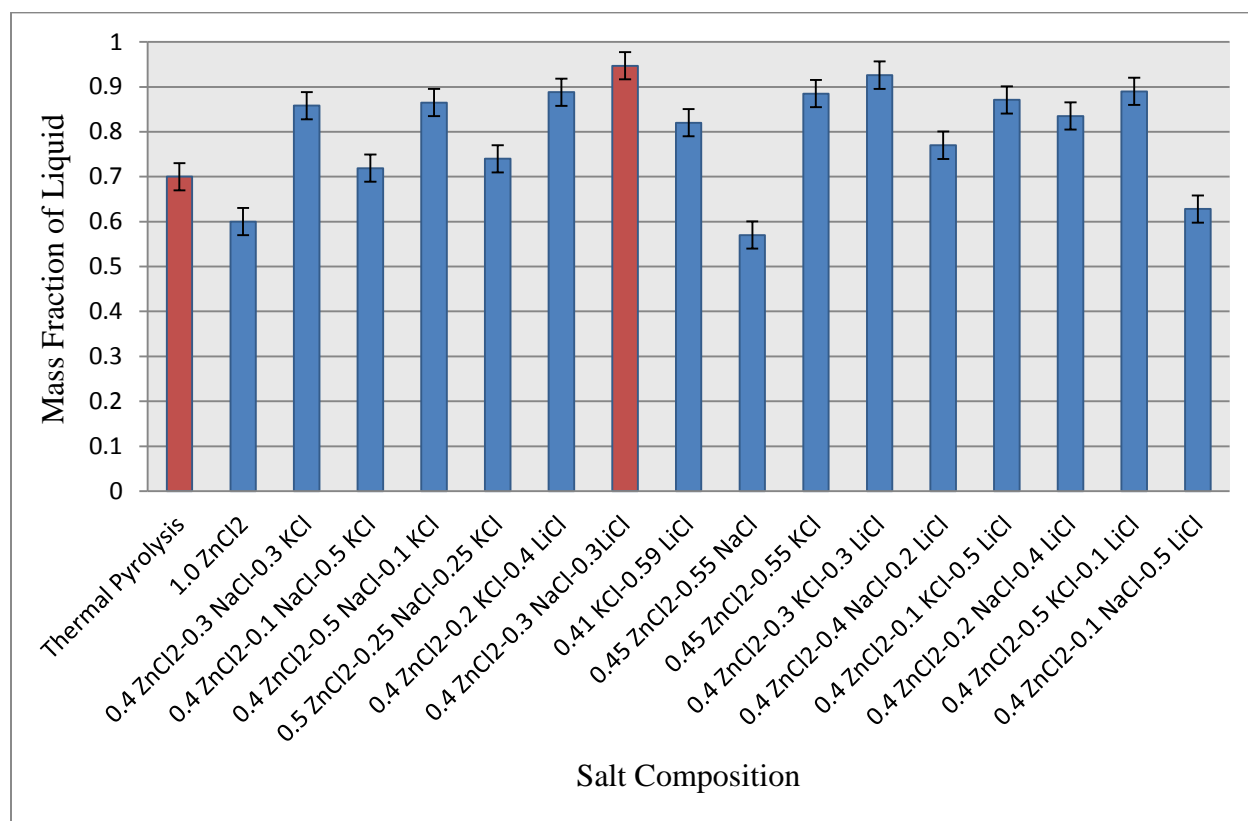


Figure 30: Mass fraction of liquid yield with different salts at 400°C

All the experiments were conducted under the same conditions; the temperature was 400°C, the helium flow rate was roughly 90 mL/min, the mole ratio of the salt to the polystyrene mer units was 10 to 1, and two identical stainless steel reactors were used. The uncertainty in the procedure, 0.0303, was calculated by repeating one of the runs 4 times and obtaining the standard deviation of the five data points. The highest liquid yield obtained was 94.7 ± 3.03 wt % by using 40 mol% ZnCl₂, 30 mol% NaCl, and 30 mol% LiCl. The second highest liquid yield was 92.6 ± 3.03 wt %, which was obtained by using 40 mol% ZnCl₂, 30 mol% KCl and 30 mol% LiCl. By visually inspecting the quality of products it was observed that when all the samples that used eutectic that contained NaCl were darker in color than the rest of the samples, especially when used with LiCl. Also, eutectics containing NaCl provided inconsistent yields. Eutectics containing a combination of LiCl and KCl provided excellent yields with good visual quality of product overall. The salt composition of 40% ZnCl₂, 10% KCl, and 50% LiCl had the liquid product with the best visual quality with an acceptable yield, 87.1 ± 3.03 wt%, and therefore, this eutectic was chosen for the subsequent catalyst study.

The data was analyzed using GC/MS in order to obtain the mass fraction of the major components in each of the samples. The results are shown in Figure 31. Overall, the styrene monomer accounts for the majority product, with lowest being 58.6 wt% with the salt combination 40 mol% ZnCl₂, 10 mol% NaCl, and 50 mol% LiCl, while the eutectic, 40 mol% ZnCl₂, 30 mol% NaCl, and 30 mol% LiCl, provided the highest monomer percent at 77.6 wt%. The highest monomer yield was 73.5 ± 2.35 wt% as shown in Figure 32. This figure also shows an interesting pattern which is, when keeping ZnCl₂ constant at 40 mol% and varying the other two salts, the monomer recovery approaches the highest value when the ratio of two salts is closest to 1.

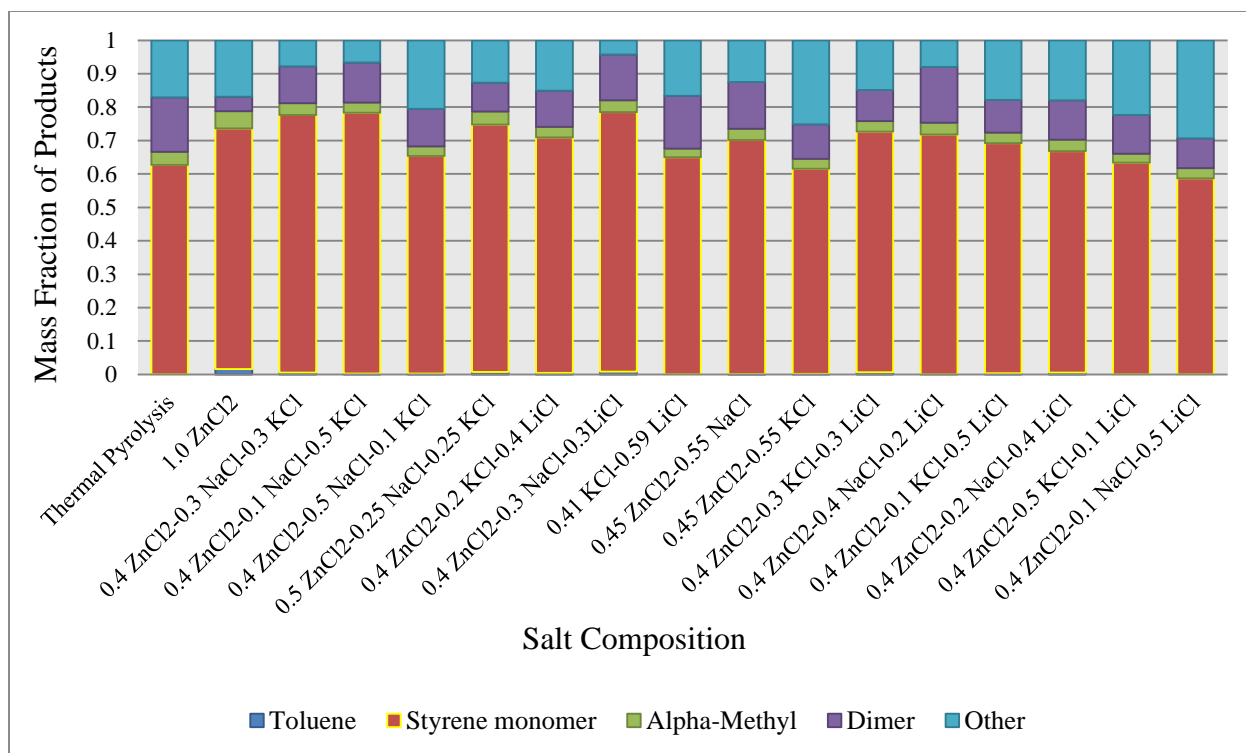


Figure 31: Mass fraction of products with different salts at 400°C

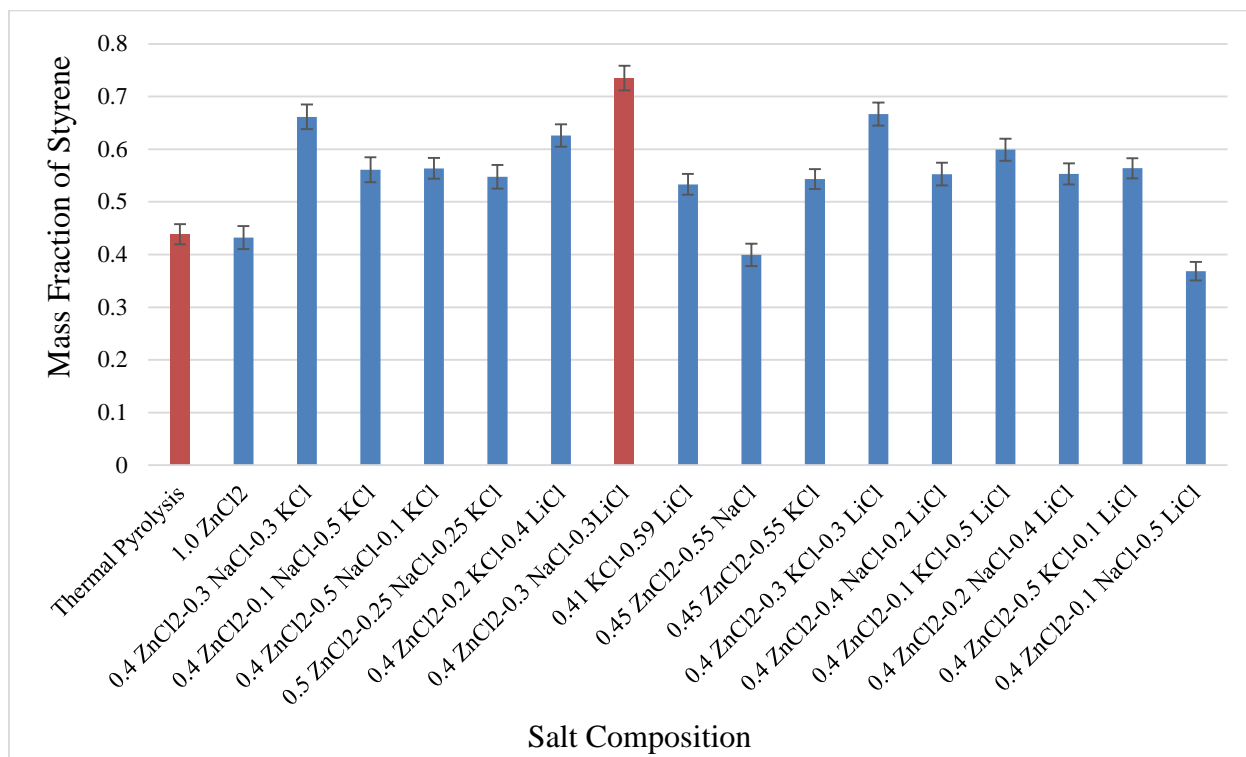


Figure 32: Styrene monomer yield with different salts at 400°C

In order to see which of the salts has the biggest effect on the mechanism of the reaction, the selectivity of styrene monomer to dimer was plotted as a function of mole fraction for each of the four salts that were tested. Figure 33 shows the selectivity of styrene monomer to dimer as a function of mol fraction of ZnCl_2 .

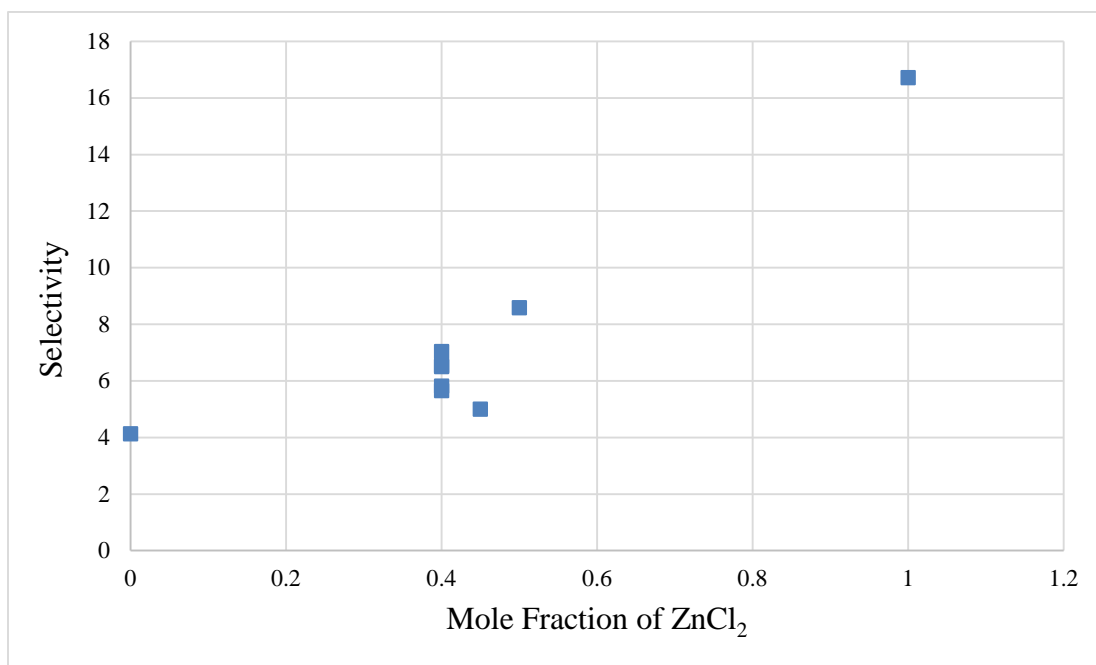


Figure 33: Selectivity of styrene monomer to dimer as a function of the mol fraction of ZnCl_2

The graph above shows a strong positive trend. The selectivity of styrene increases as the amount of ZnCl_2 in the salt mixture increases. This means that production of styrene monomer is more becomes more favorable in the presence ZnCl_2 . Figure 34 below shows the selectivity of styrene monomer to dimer as a function of the mol fraction of NaCl .

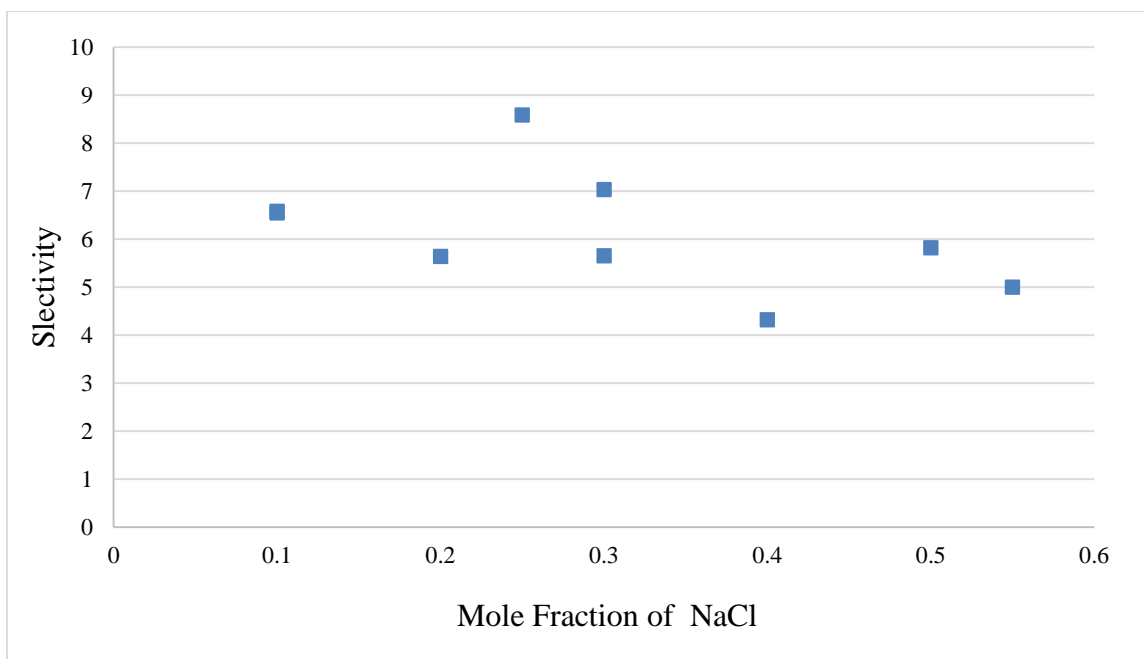


Figure 34: Selectivity of styrene monomer to dimer as a function of the mol fraction of NaCl

The effect of NaCl on the selectivity is uncertain. It seems that the selectivity fluctuates as the mol fraction of NaCl increases, but overall it has an almost constant trend. Nonetheless, this could be because the behavior changes depending on the nature of the other two salts. Figure 35 and Figure 36 represent the selectivity of styrene as a function of the mole ratio KCl and LiCl, respectively. Both data sets behave similarly to that of NaCl, with selectivity fluctuating but have an overall constant trend.

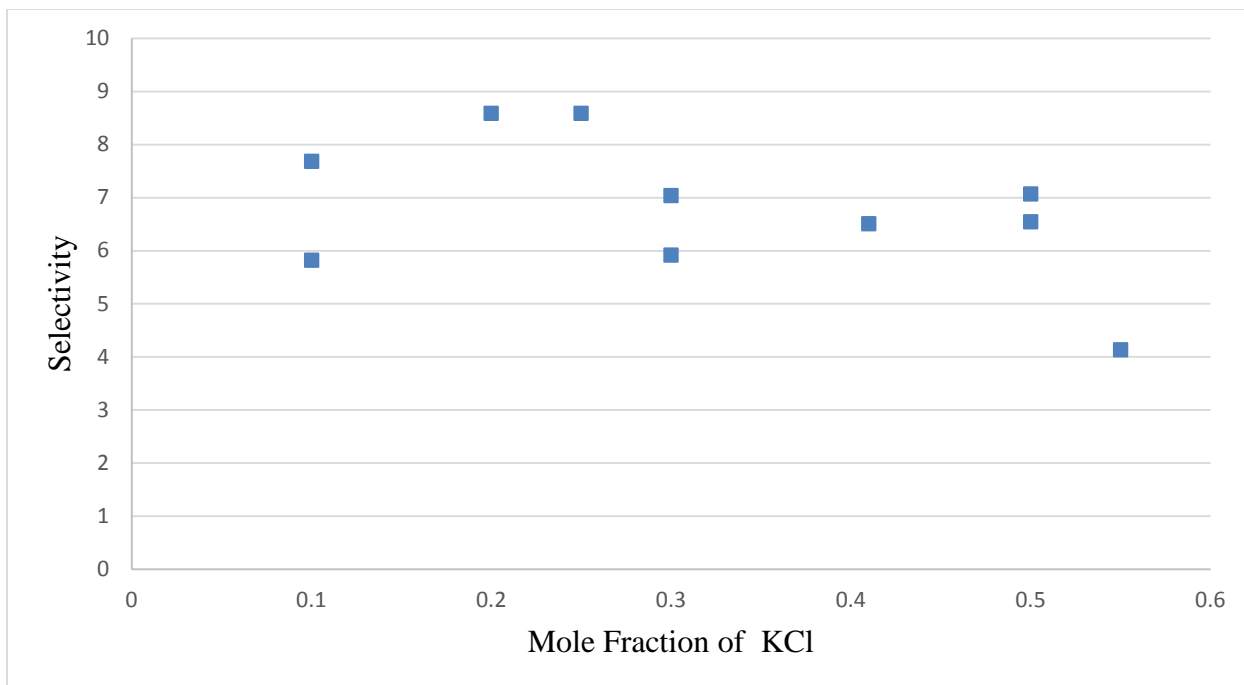


Figure 35: Selectivity of styrene monomer to dimer as a function of the mol fraction of KCl

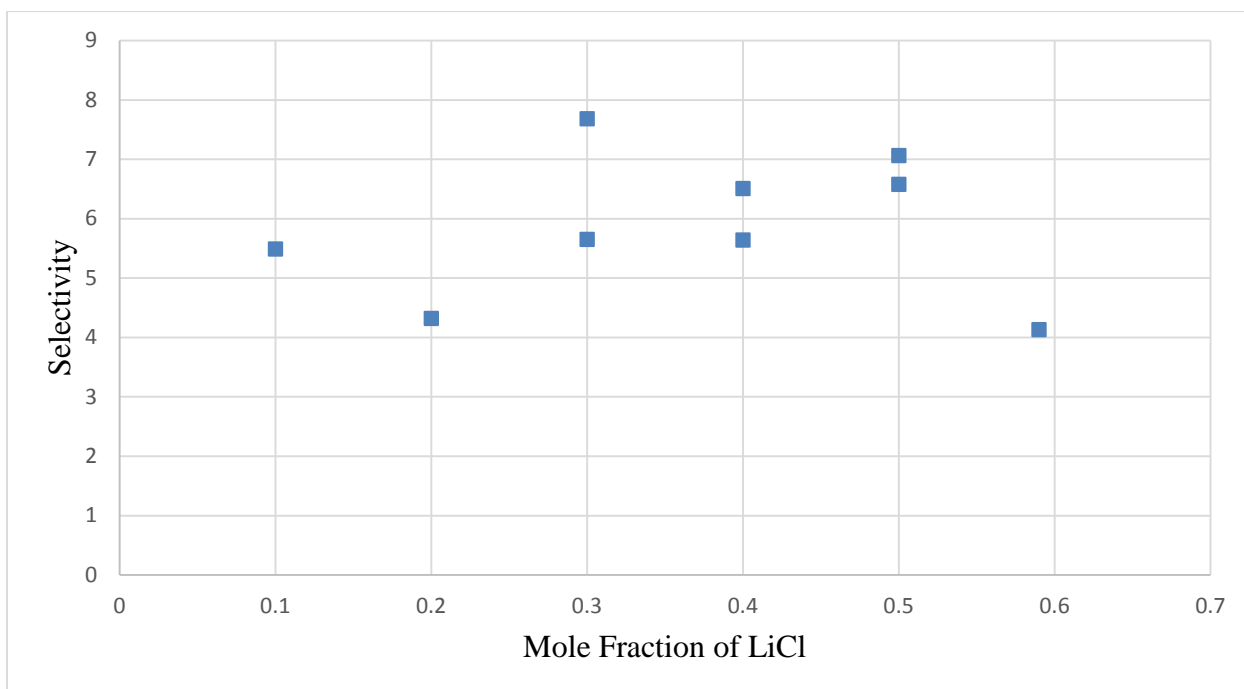


Figure 36: Selectivity of styrene monomer to dimer as a function of the mol fraction of LiCl

In order to obtain a more clear understanding of how a combination of salt affect the behavior of the selectivity of styrene monomer to dimer, Figure 37 was plotted. In this figure, selectivity is a represented as a function of the mole ratio LiCl to NaCl. From the graph it can be seen that the selectivity can in fact increase with increasing LiCl/NaCl ratio.

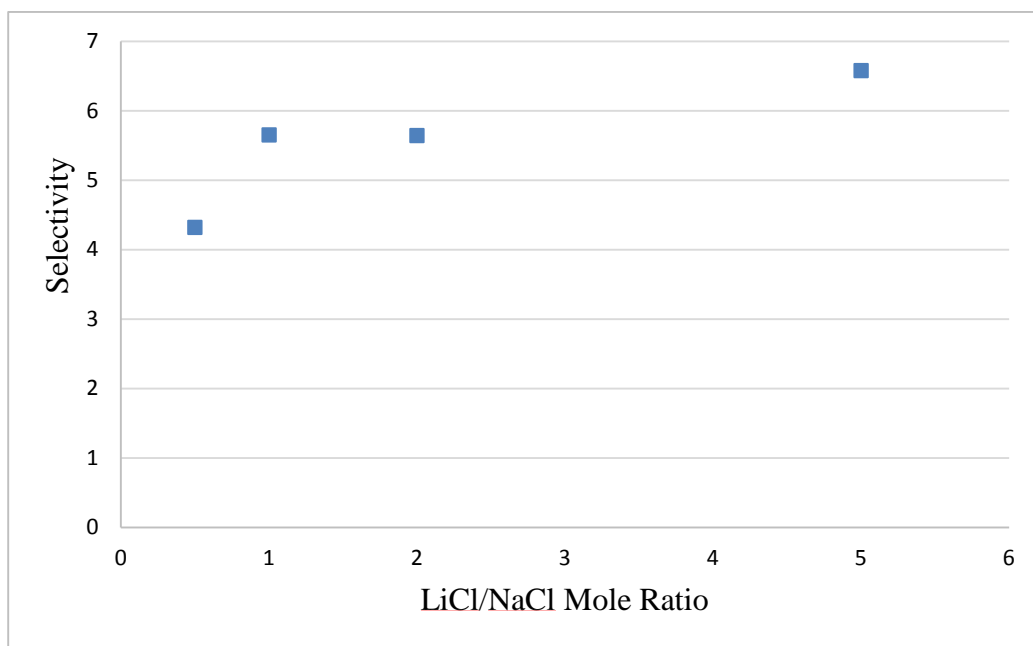


Figure 37: Selectivity of styrene monomer to dimer as a function of the mol ratio of LiCl to NaCl

Among the salts that were studied, ZnCl_2 had the strongest effect on the liquid yield and selectivity of styrene. This could be caused by its Lewis acidic nature which promote hydrogen transfer and electrophilic aromatic substitution. The nature of the other salts appear to matter less, although the visual quality of the product decline when NaCl is used, so a eutectic of 40 mol% ZnCl_2 , 30 mol% LiCl, and KCl mol%, should be used since it gave the second highest yield at 92.6 ± 3.03 wt%, with 66.7 ± 2.31 wt% monomer yield.

4.3 Effect of Catalyst

The composition chosen for the catalysts study is 40 mol% ZnCl_2 , 50 mol% LiCl , and 10 mol% KCl , because it provided a liquid yield with good visual quality and acceptable quantity. The temperature chosen was 350°C , and the catalysts that were studied are $\text{Ni}(\text{OH})_2$, ZSM-5, and phosphotungstic acid. The results for the liquid yield, product composition, and styrene yield are shown below in Figure 38-40.

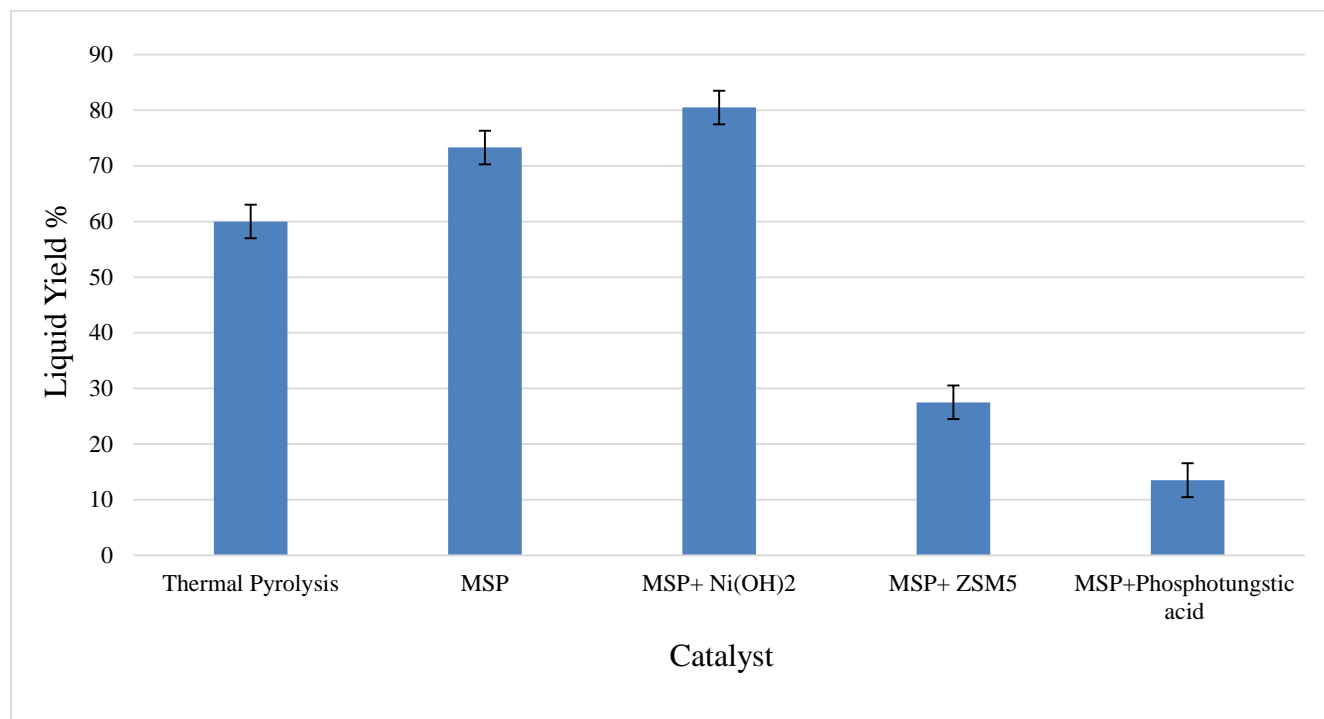


Figure 38: Mass percent liquid yield with different catalysts at 350°C

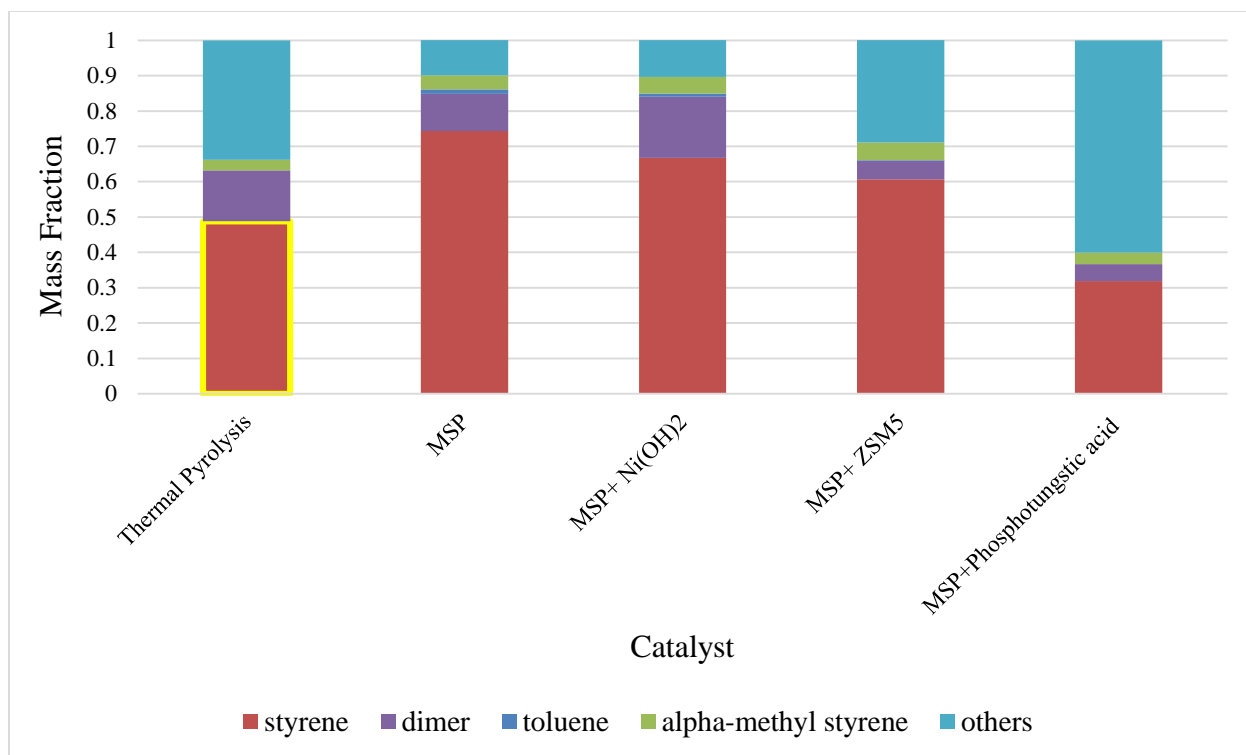


Figure 39: Mass fraction of compounds with different catalysts at 350°C

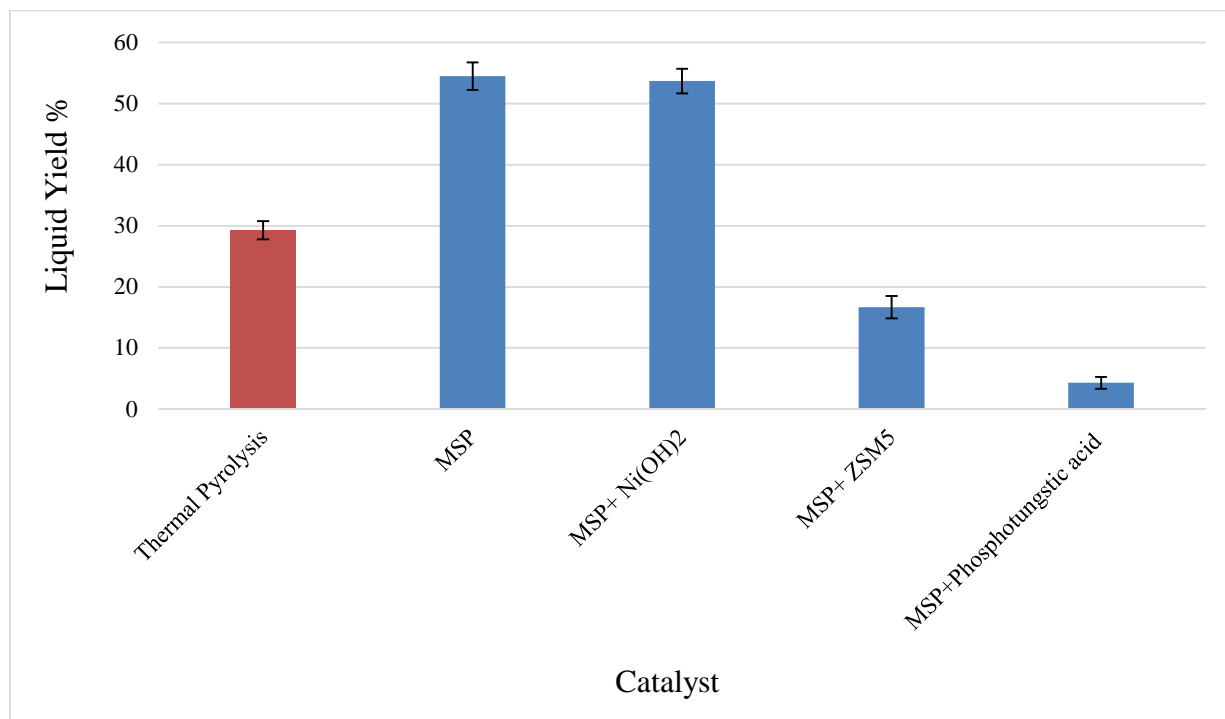


Figure 40: Styrene monomer yield with different catalysts at 350°C

From the figures above, it can be seen that the acidic catalyst, ZSM-5 and phosphotungstic acid, reduced the liquid yield significantly, but resulted in the formation of char. This was caused by the severe cracking due to the strong Brønsted acidic properties of those two catalysts, which agrees with many of the literature studies. On the other hand, Ni(OH)₂ increased the liquid yield to 80.5±3.03% compared to 73.3±3.03% for the molten salt pyrolysis of polystyrene, and 60 ±3.03% for the thermal pyrolysis. As a base, Ni(OH)₂ had a different effect than the acid catalyst. This could be explained by the mechanism proposed in 1995 by Zhang et al., which means that Ni(OH)₂ enhanced the hydrogen abstraction mechanism that resulted in increasing the rate of the reaction (Zhang et al., 1995).

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

After the analysis and discussion of all experimental results above, several conclusions can be made regarding the temperature of the reaction, the effect of molten salts, and the effect of catalysts on the pyrolysis of polystyrene. First, it can be concluded that 400°C provide the highest monomer recovery for the thermal pyrolysis of polystyrene, so it could be considered the ideal reaction temperature at least in the absence of salts. Nonetheless, this temperature was also used for molten salt pyrolysis.

Second, 40 mol percent zinc chloride, 30 mol percent sodium chloride, and 30 mol percent lithium chloride provided both the highest liquid yield, at 94.7 mass percent, and the highest styrene monomer recovery at, 77.6 mass percent, compared to 70 mass percent liquid yield and 62.6 mass percent styrene monomer recovery for the thermal pyrolysis of polystyrene. This translates into a styrene yield of 73.5% for best molten salt pyrolysis result as compared with 43.8% for best thermal pyrolysis results, which is a significant increase. The percent of secondary products was greatly reduced from 21.3 mass percent to only 8.63 mass percent using the same salt composition.

Third, zinc chloride had the strongest effect on the selectivity of styrene monomer to dimer, which could be attributed to its Lewis acid nature, which promotes hydrogen transfer and electrophilic aromatic substitution. Fourth, the acid catalysts, ZSM-5 and phosphotungstic acid, reduced the liquid yield due to their strong cracking capabilities when used in combination with the molten salts, which resulted in higher char, secondary liquid products and gases. Nickel (II) hydroxide, on the other hand, increased the liquid yield by 7 percent, but reduced the monomer recovery and the selectivity of styrene monomer to dimer. In summary, it is possible to produce

styrene monomer at high yields through molten salt pyrolysis of polystyrene, and these results show that the monomer yield can be significantly enhanced via molten salt pyrolysis as compared to thermal pyrolysis. Clearly, this process warrants further investigation and optimization.

5.2 Recommendations for Future Work

The results of using molten salts to aid the process of polystyrene pyrolysis look promising. However, more studies and further optimization should be performed before this process can be used commercially.

5.2.1 Effect of Residence Time/Flow Rate

Inert gas flow rate study should be done in the molten salt pyrolysis process in order to understand how the residence time affects the formation and selectivity of different products. At high flow rates and short residence time, the expected product would be mostly composed of heavier hydrocarbons, while at low flow rate and long residence time, the product is expected to be composed of gases, lighter hydrocarbons, and char. The flow rate should be optimized to maximize the styrene monomer selective production, and minimize styrene from further cracking into secondary products and gases.

5.2.2 Gas Analysis

Although the reaction of gas product was relatively small, the gas produced from polystyrene pyrolysis should be captured and analyzed. This might help perform a more accurate mass balance around the entire system, which will also help future teams to further understand the mechanism of the process. Also, it would be beneficial to know the composition of the gas product in order to see if any of the gases can be recycled and used in the process or used in a different process.

5.2.3 Different Types of Salts

Different types of salts should be studied in order to have a better understanding of the effect molten salts have on pyrolysis. In particular, basic salts should be studied as they might have a more positive effect on pyrolysis of polystyrene than chloride, due to their behavior as base catalysts which was explained in chapter 2, Section 2.2.2. An example is NaOH-KOH eutectic, which has a low melting point.

5.2.4 Different Types of Polymer/Commercial Plastic

Ideally, this process should be suitable to treat a mixture of different types of commercial plastics, it is not always possible to separate the waste into different categories. In order to use this process commercially, a study should be performed to understand which types of polymers can be treated together in this way, and how the behavior of molten salts changes with the type of polymer being treated and the additives in the polymer.

REFERENCES

- Abdel-Bary, Elsayed, ed. *Handbook of plastic films*. iSmithers Rapra Publishing, 2003.
- Al-Salem, S. M., P. Lettieri, and J. Baeyens. "Recycling and recovery routes of plastic solid waste (PSW): A review." *Waste Management* 29, no. 10 (2009): 2625-2643.
- Arabiourrutia, M., G. Lopez, G. Elordi, M. Olazar, R. Aguado, and J. Bilbao. "Product distribution obtained in the pyrolysis of tyres in a conical spouted bed reactor." *Chemical Engineering Science* 62, no. 18 (2007): 5271-5275.
- Aznar, María P., Miguel A. Caballero, Jesús A. Sancho, and E. Francés. "Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant." *Fuel Processing Technology* 87, no. 5 (2006): 409-420.
- Bagri, Ranbir, and Paul T. Williams. "Catalytic pyrolysis of polyethylene." *Journal of Analytical and Applied Pyrolysis* 63, no. 1 (2002): 29-41.
- Bertolini, Gerard E., and Jacques Fontaine. "Value recovery from plastics waste by pyrolysis in molten salts." *Conservation & recycling* 10, no. 4 (1987): 331-343.
- Čejka, Jiří. *Introduction to zeolite science and practice*. 3rd rev. ed. Amsterdam: Elsevier, 2007.
- Chambers, Carey, John W. Larsen, Walter Li, and Bob Wiesen. "Polymer waste reclamation by pyrolysis in molten salts." *Industrial & Engineering Chemistry Process Design and Development* 23, no. 4 (1984): 648-654.
- Chambers, Carey, John W. Larsen, Walter Li, and Bob Wiesen. "Polymer waste reclamation by pyrolysis in molten salts." *Industrial & Engineering Chemistry Process Design and Development* 23, no. 4 (1984): 648-654.

CRCT, École Polytechnique de Montréal. "FACT salt database - list of systems and phases."

Accessed April 30, 2014.

http://www.crct.polymtl.ca/fact/documentation/FTsalt/FTsalt_list.htm.

Davis, Mark E. "Zeolites and molecular sieves: not just ordinary catalysts." *Industrial & engineering chemistry research* 30, no. 8 (1991): 1675-1683.

Grassie, N., and W. W. Kerr. "The thermal depolymerization of polystyrene. Part 1.—The reaction mechanism." *Transactions of the Faraday Society* 53 (1957): 234-239.

Kaur, Jaspalne, K. Griffin, B. Harrison, and I. V. Kozhevnikov. "Friedel–Crafts acylation catalysed by heteropoly acids." *Journal of Catalysis* 208, no. 2 (2002): 448-455.

Kruse M., Todd, Oh Sang Woo, and Linda J Broadbelt. "Detailed mechanistic modeling of polymer degradation: application to polystyrene." *Chemical engineering science* 56, no. 3 (2001): 971-979.

Lee, Seung-Yup, Jik-Hyun Yoon, Jong-Ryeul Kim, and Dae-Won Park. "Degradation of polystyrene using clinoptilolite catalysts." *Journal of analytical and applied pyrolysis* 64, no. 1 (2002): 71-83.

Levine, Seth E., and Linda J. Broadbelt. "Reaction pathways to dimer in polystyrene pyrolysis: a mechanistic modeling study." *Polymer Degradation and Stability* 93, no. 5 (2008): 941-951.

Liu, Yirong, Jialin Qian, and Jianqiu Wang. "Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction." *Fuel Processing Technology* 63, no. 1 (2000): 45-55.

Madras, Giridhar, J. M. Smith, and Benjamin J. McCoy. "Thermal degradation kinetics of polystyrene in solution." *Polymer degradation and stability* 58, no. 1 (1997): 131-138.

Unknown. *Mer structure of nylon 6,6*. Digital image. Wikipedia. N.p., 13 Dec. 2005. Web.

Unknown. *Mer structure of polyethylene*. Digital image. Wikipedia. N.p., n.d. Web.

Nitta, Koji, Toshiyuki Nohira, Rika Hagiwara, Masatoshi Majima, and Shinji Inazawa.

"Physicochemical properties of ZnCl₂-NaCl-KCl eutectic melt." *Electrochimica Acta* 54, no. 21 (2009): 4898-4902

Ohkita, Hironobu, Ryuji Nishiyama, Yoshihisa Tochihara, Takanori Mizushima, Noriyoshi Kakuta, Yoshio Morioka, Akifumi Ueno, Yukihiro Namiki, and Susumu Tanifuji. "Acid properties of silica-alumina catalysts and catalytic degradation of polyethylene." *Industrial & engineering chemistry research* 32, no. 12 (1993): 3112-3116.

Onwudili, Jude A., Nagi Insura, and Paul T. Williams. "Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time." *Journal of Analytical and Applied Pyrolysis* 86, no. 2 (2009): 293-303.

Sperling, L. H.. *Introduction to physical polymer science*. 4th ed. Hoboken, N.J.: Wiley, 2006.

US Environmental Protection Agency. "*Municipal Solid Waste in the United States: Facts and Figures* | Municipal Solid Waste | Wastes | US EPA." Accessed April 30, 2014.
<http://www.epa.gov/waste/nonhaz/municipal/msw99.htm>.

Williams, Paul T., and Ranbir Bagri. "Hydrocarbon gases and oils from the recycling of polystyrene waste by catalytic pyrolysis." *international journal of energy research* 28, no. 1 (2004): 31-44.

Yikrazuul. *Polystyrene*. Digital image. Wikipedia. N.p., 21 May 2008. Web.

Zhang, Zhibo, Tamaki Hirose, Suehiro Nishio, Yoshio Morioka, Naoto Azuma, Akifumi Ueno, Hironobu Ohkita, and Mitsunori Okada. "Chemical recycling of waste polystyrene into styrene over solid acids and bases." *Industrial & engineering chemistry research* 34, no. 12 (1995): 4514-4519.

APPENDICES

A.1 Experimental Raw Data

Table 2: Experiments table with temperatures and liquid yield

EXP	PS	He flow	Temp	Liquid Yield	liquid yield %
20	2.0 g	94.3 mL/m	400 C	1.4 g	70%
21	2.0 g	95.2 mL/m	350 C	1.2 g	60%
22	2.0 g	95.2 mL/m	250 C	0.5 g	25%
23	2.0 g	95.2 mL/m	300 C	0.5 g	25%
24	2.0 g	88.3 mL/m	450 c	1.6 g	80%
25	2.0 g	95.2 mL/m	250 C	0.6 g	30%
26	2.0 g	95.2 mL/m	300 C	0.6 g	30%
27	2.0 g	89.4 mL/m	350 C	1.3 g	65%
28	2.0 g	95.2 mL/m	400 C	1.6 g	80%
29	2.0 g	88.4 mL/m	450 C	1.8 g	90%
30	2.0 g	95.2 mL/m	400 C	1.199 g	60.0%
31	2.0 g	92.4 mL/m	400 C	1.715 g	85.8%
32	2.0 g	95.2 mL/m	400 C	1.437 g	71.9%
33	2.0 g	92.1 mL/m	400 C	1.73 g	86.5%
34	2.0 g	95.1 mL/m	400 C	1.48 g	74.0%
35	2.0 g	95.2 mL/m	400 C	1.776 g	88.8%
36	2.0 g	95.2 mL/m	400 C	1.894 g	94.7%
37	2.0 g	95.2 mL/m	400 C	1.639 g	82.0%
38	2.0 g	95.2 mL/m	400 C	1.14 g	57.0%
39	2.0 g	95.2 mL/m	400 C	1.77 g	88.5%
43	2.0 g	90.2 mL/m	400 C	1.851 g	92.6%
44	2.0 g	95.2 mL/m	400 C	1.533 g	77.0%
45*	2.0 g	90.2 mL/m	400 C	1.741 g	87.1%
46	2.0 g	95.2 mL/m	400 C	1.669 g	83.5%
47	2.0 g	91.4 mL/m	400 C	1.78 g	89.0%
48	2.0 g	95.2 mL/m	400 C	1.255 g	62.8%
49*	2.0 g	90.2 mL/m	400 C	1.7173 g	85.9%
52*	2.0 g	90.6 mL/m	400 C	1.715 g	85.8%
53*	2.0 g	90.6 mL/m	400 C	1.647 g	82.4%
54*	2.0 g	90.1 mL/m	400 C	1.8306 g	91.5%
56	2.0 g	90.4 mL/m	350 C	1.466 g	73.3%
57	2.0 g	90.4 mL/m	350 C	1.609 g	80.5%
58	2.0 g	90.4 mL/m	350 C	0.549 g	27.5%
59	2.0 g	90.4 mL/m	350 C	0.269 g	13.5%
63	2.0 g	89.3 mL/m	400 C	0.9 g	45.0%

Table 3: Experiments table with salts mole fraction and additives

EXP	Salts Mol fractions			Additives
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0.6 ZnCl ₂	0.2 NaCl	0.2 KCl	0
26	0.6 ZnCl ₂	0.2 NaCl	0.2 KCl	0
27	0.6 ZnCl ₂	0.2 NaCl	0.2 KCl	0
28	0.6 ZnCl ₂	0.2 NaCl	0.2 KCl	0
29	0.6 ZnCl ₂	0.2 NaCl	0.2 KCl	0
30	1.0 ZnCl ₂			0
31	0.4 ZnCl ₂	0.3 NaCl	0.3 KCl	0
32	0.4 ZnCl ₂	0.1 NaCl	0.5 KCl	0
33	0.4 ZnCl ₂	0.5 NaCl	0.1 KCl	0
34	0.5 ZnCl ₂	0.25 NaCl	0.25 KCl	0
35	0.4 ZnCl ₂	0.4 LiCl	0.2 KCl	0
36	0.4 ZnCl ₂	0.3 LiCl	0.3 NaCl	0
37	0.41 KCl	0.59 LiCl		0
38	0.45 ZnCl ₂	0.55 NaCl		0
39	0.45 ZnCl ₂	0.55 KCl		0
43	0.4 ZnCl ₂	0.3 LiCl	0.3 KCl	0
44	0.4 ZnCl ₂	0.2 LiCl	0.4 NaCl	0
45*	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	0
46	0.4 ZnCl ₂	0.4 LiCl	0.2 NaCl	0
47	0.4 ZnCl ₂	0.1 LiCl	0.5 KCl	0
48	0.4 ZnCl ₂	0.5 LiCl	0.1 NaCl	0
49*	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	0
52*	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	0
53*	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	0
54*	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	0
56	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	0
57	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	1.00 g Ni(OH) ₂
58	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	1.00 g ZSM-5
59	0.4 ZnCl ₂	0.5 LiCl	0.1 KCl	1.00 g Phosphotungstic acid
63	0.4 ZnCl ₂	0.3 MgCl ₂	0.3 KCl	

Table 4: Mass fraction

Sample	Mass Fraction				
	toluene	styrene	alpha-methyle styrene	dimer	Others
20	0	0.62671934	0.04000640	0.16288460	0.17038967
21	0	0.48779242	0.02993711	0.14400066	0.33826980
22	0	0.31571644	0.02568793	0.18606850	0.47252712
23	0	0.13887808	0.02368994	0.44685421	0.39057776
24	0.00218707	0.62465849	0.03417369	0.11187844	0.22710231
25	0.00593981	0.62062571	0.03198035	0.06778279	0.27367133
26	0.00564323	0.62134613	0.03205573	0.08470036	0.25625455
27	0.00632200	0.64097628	0.03367270	0.07503850	0.24399053
28	0.00618411	0.64206626	0.03594832	0.08059220	0.23520910
29	0.02907662	0.65931516	0.04705674	0.03677163	0.22777985
30	0.0164364	0.7200822	0.0517608	0.0430712	0.1686494
31	0.0059126	0.7710305	0.0353878	0.1095518	0.0781173
32	0.0028724	0.7803802	0.0310126	0.1192058	0.0665291
33	0.0025664	0.6516678	0.0283418	0.1118872	0.2055367
34	0.0073305	0.7400932	0.039885	0.0861947	0.1264966
35	0.0049733	0.7048434	0.0314736	0.1082459	0.1504638
36	0.0088321	0.7764004	0.0352012	0.1372749	0.0422915
37	0	0.6502999	0.0260282	0.1573124	0.1663595
38	0.0010375	0.7009593	0.0335732	0.139959	0.1244711
39	0.0012323	0.6141044	0.0299156	0.1037864	0.2509613
43	0.0067957	0.7199082	0.0312204	0.0937053	0.1483705
44	0.0001679	0.7179118	0.0358025	0.1660867	0.080031
45	0.004064	0.6878963	0.0321998	0.0973334	0.1785065

46	0.0058448	0.6627297	0.0340951	0.1174393	0.179891
47	0	0.6336534	0.0271658	0.1153918	0.223789
48	0	0.5864856	0.0314974	0.0890928	0.2929242
56	0.0121097	0.7437306	0.0401015	0.1050354	0.0990227
57	0.0089728	0.6671153	0.0467599	0.1734192	0.1037328
58	0.001245	0.6068834	0.0503288	0.0526719	0.2888708
59	0	0.3189575	0.0329235	0.0476363	0.6004827

Table 5: Styrene yield

Sample	Styrene Yield	Error
20	0.438703538	0.0189896
21	0.292675452	0.0147801
22	0.078929110	0.0095662
23	0.034719520	0.0042080
24	0.499726792	0.0189272
25	0.186187713	0.0188050
26	0.186403839	0.0188268
27	0.416634582	0.0194216
28	0.513653008	0.0194546
29	0.593383644	0.0199772
30	0.43204935	0.0189896
31	0.66154418	0.023362
32	0.561093371	0.023646
33	0.563692687	0.019746
34	0.547668969	0.022425

35	0.625900948	0.021357
36	0.735251182	0.023525
37	0.533245903	0.019704
38	0.399546784	0.021239
39	0.543482378	0.018607
43	0.666634964	0.021813
44	0.552792083	0.021753
45	0.599157681	0.020843
46	0.553379286	0.020081
47	0.563951504	0.0192
48	0.36831297	0.017771
56	0.545154531	0.022535
57	0.537027791	0.020214
58	0.166892946	0.018389
59	0.04305926	0.009664

A.2 GC/MS Results

Peak Report TIC												
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name		
1	3.780	3.745	3.820	286444	1.04	210975	1.88	1.36		Toluene		
2	5.625	5.620	5.625	-217	-0.00	0	0.00	0.00	MI			
3	6.080	6.050	6.115	61407	0.22	36921	0.33	1.66		Ethylbenzene		
4	6.921	6.860	6.980	16279799	59.18	8209836	73.20	1.98		Styrene		
5	9.768	9.715	9.820	705285	2.56	336649	3.00	2.10		.alpha.-Methylstyrene		
6	25.565	25.535	25.630	64871	0.24	23895	0.21	2.71				
7	25.679	25.630	25.735	568325	2.07	214394	1.91	2.65	V	Bibenzyl		
8	26.533	26.480	26.595	300978	1.09	111676	1.00	2.70		1,2 diphenylpropane		
9	29.082	29.015	29.155	845091	3.07	259895	2.32	3.25		1,3 diphenylpropane		
10	29.856	29.805	29.930	197711	0.72	54396	0.49	3.63				
11	30.868	30.750	30.975	6869093	24.97	1554420	13.86	4.42		Dimer		
12	31.150	31.075	31.280	610969	2.22	87074	0.78	7.02				
13	33.073	32.985	33.200	717399	2.61	114774	1.02	6.25				
				27507155	100.00	11214905	100.00					

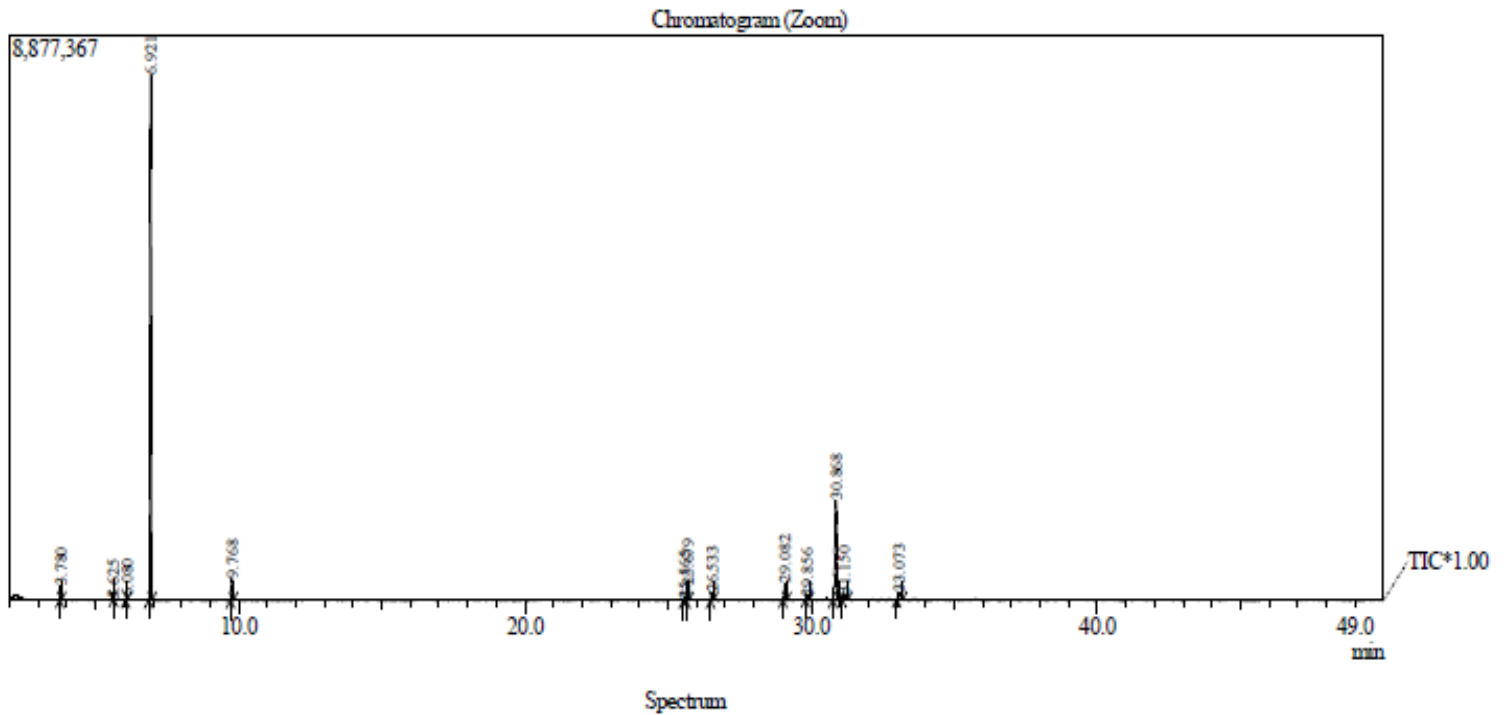


Figure 41: GC/MS spectrum for sample 20

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.789	3.755	3.835	308399	1.44	226107	2.54	1.36		Toluene
2	5.650	5.645	5.650	-358	-0.00	0	0.00	0.00	MI	
3	6.091	6.055	6.120	41976	0.20	24061	0.27	1.74	MI	Ethylbenzene
4	6.930	6.875	6.990	12449534	57.93	6489699	72.94	1.92		Styrene
5	9.779	9.735	9.830	366384	1.70	176898	1.99	2.07		.alpha.-Methylstyrene
6	25.686	25.620	25.745	501530	2.33	184690	2.08	2.72		Bibenzyl
7	26.540	26.485	26.595	262442	1.22	95451	1.07	2.75		1,2 diphenylpropane
8	29.085	29.025	29.160	584876	2.72	179787	2.02	3.25		1,3 diphenylpropane
9	30.870	30.755	30.965	6058623	28.19	1377969	15.49	4.40		Dimer
10	31.191	31.085	31.280	531161	2.47	75425	0.85	7.04		
11	33.085	33.010	33.200	386541	1.80	67200	0.76	5.75		
				21491108	100.00	8897287	100.00			

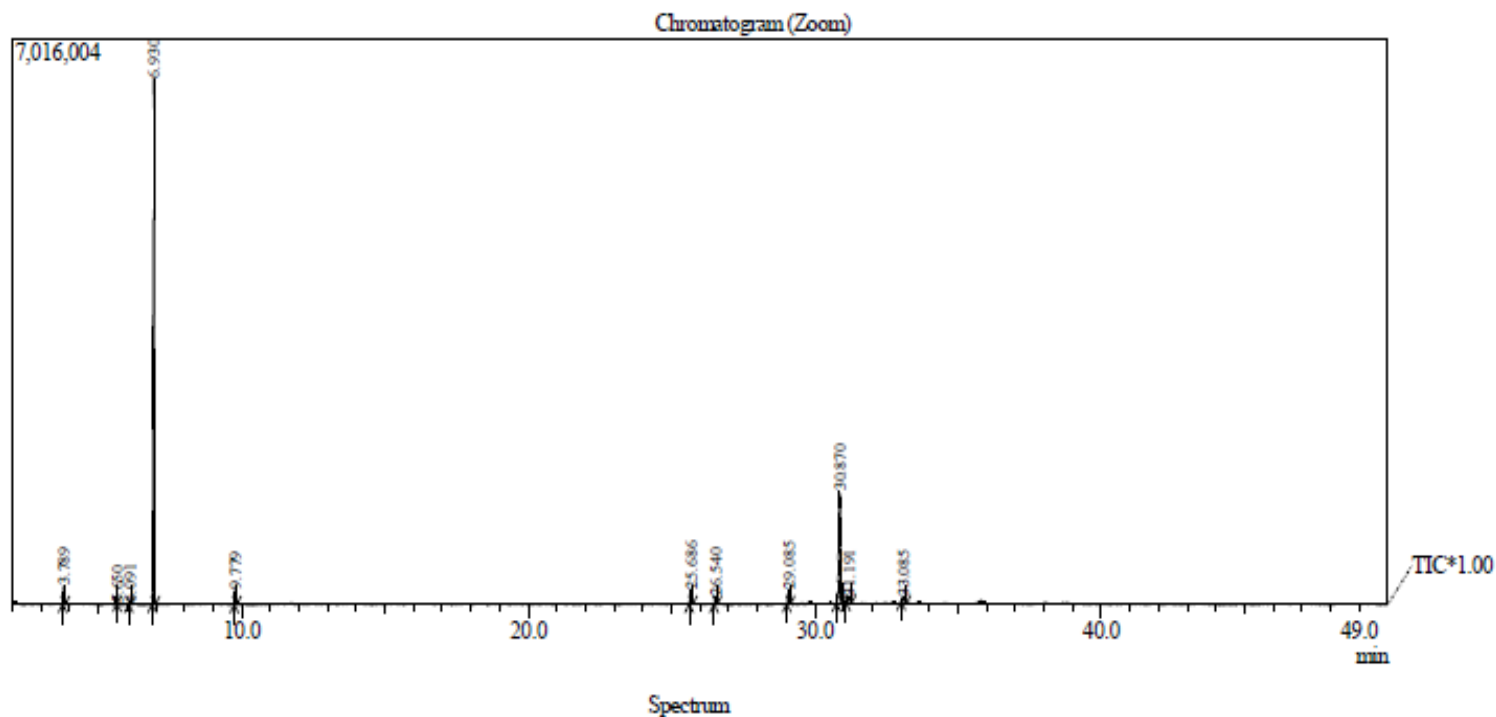


Figure 42: GC/MS spectrum for sample 21

Peak Report TIC												
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name		
1	3.790	3.760	3.835	194806	0.97	143377	2.01	1.36		Toluene		
2	5.655	5.650	5.655	-198	-0.00	0	0.00	0.00	MI			
3	6.094	6.070	6.120	12685	0.06	7901	0.11	1.61	MI	Ethylbenzene		
4	6.928	6.875	6.990	8003738	39.97	4183958	58.76	1.91		Styrene		
5	9.105	9.100	9.105	-114	-0.00	0	0.00	0.00	MI			
6	9.780	9.735	9.825	221753	1.11	105224	1.48	2.11		.alpha.-Methylstyrene		
7	25.684	25.630	25.745	508831	2.54	189204	2.66	2.69		Bibenzyl		
8	26.537	26.480	26.595	362675	1.81	133544	1.88	2.72		1,2 diphenylpropane		
9	29.086	29.015	29.160	968774	4.84	287106	4.03	3.37		1,3 diphenylpropane		
10	29.857	29.795	29.930	311937	1.56	86358	1.21	3.61				
11	30.873	30.755	30.975	7596015	37.93	1718801	24.14	4.42		Dimer		
12	31.167	31.070	31.290	856606	4.28	114397	1.61	7.49				
13	33.092	32.975	33.210	988420	4.94	150096	2.11	6.59				
				20025928	100.00	7119966	100.00					

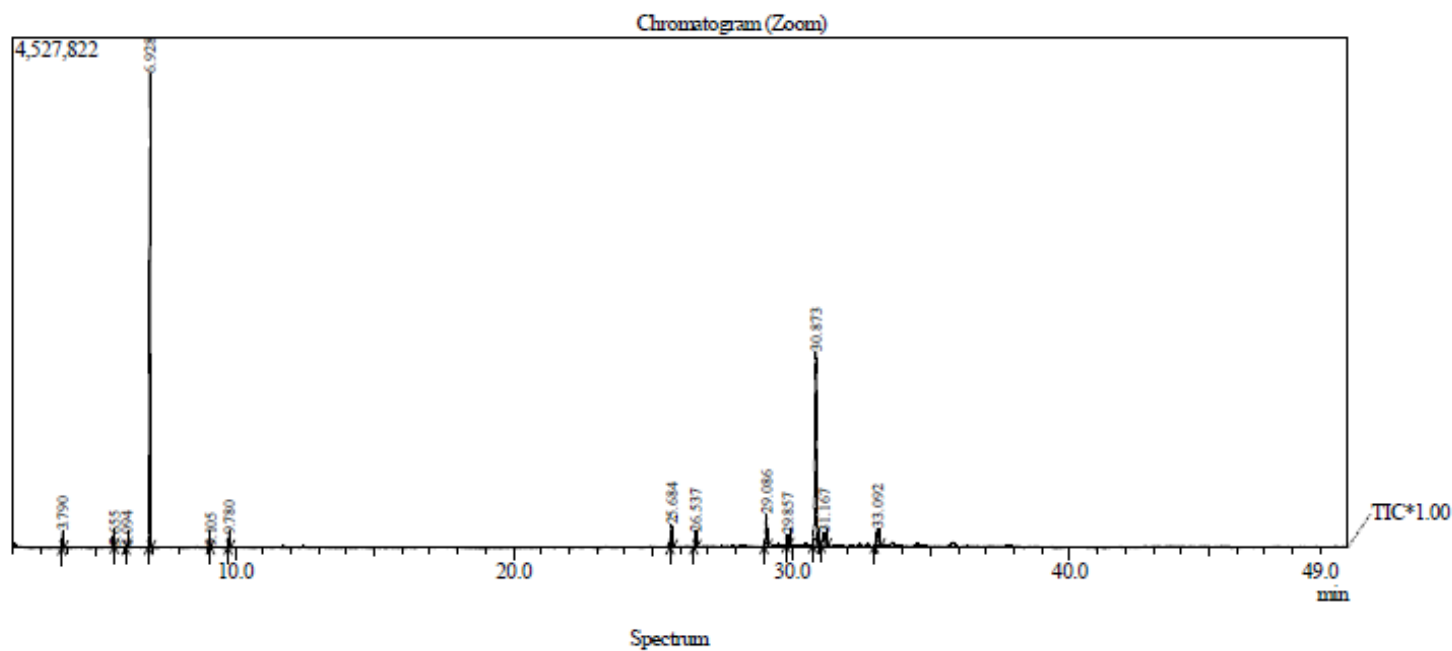


Figure 43: GC/MS spectrum for sample 22

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.789	3.760	3.825	133775	0.50	99968	1.46	1.34		Toluene
2	5.655	5.650	5.655	-325	-0.00	0	0.00	0.00	MI	
3	6.924	6.875	6.985	3295161	12.23	1783945	26.02	1.85		Styrene
4	9.780	9.735	9.815	151702	0.56	74292	1.08	2.04		.alpha.-Methylstyrene
5	25.592	25.550	25.635	131831	0.49	51692	0.75	2.55		
6	25.702	25.635	25.760	665197	2.47	249909	3.65	2.66	V	Bibenzyl
7	26.558	26.500	26.620	416557	1.55	150005	2.19	2.78		1,2 diphenylpropane
8	29.119	29.045	29.200	1565400	5.81	455692	6.65	3.44		1,3 diphenylpropane
9	29.899	29.850	29.970	159374	0.59	46021	0.67	3.46		
10	30.952	30.795	31.040	18423830	68.37	3656235	53.33	5.04		Dimer
11	31.196	31.110	31.345	1315453	4.88	178405	2.60	7.37		
12	33.160	33.070	33.280	690209	2.56	109303	1.59	6.31		
				26948164	100.00	6855467	100.00			

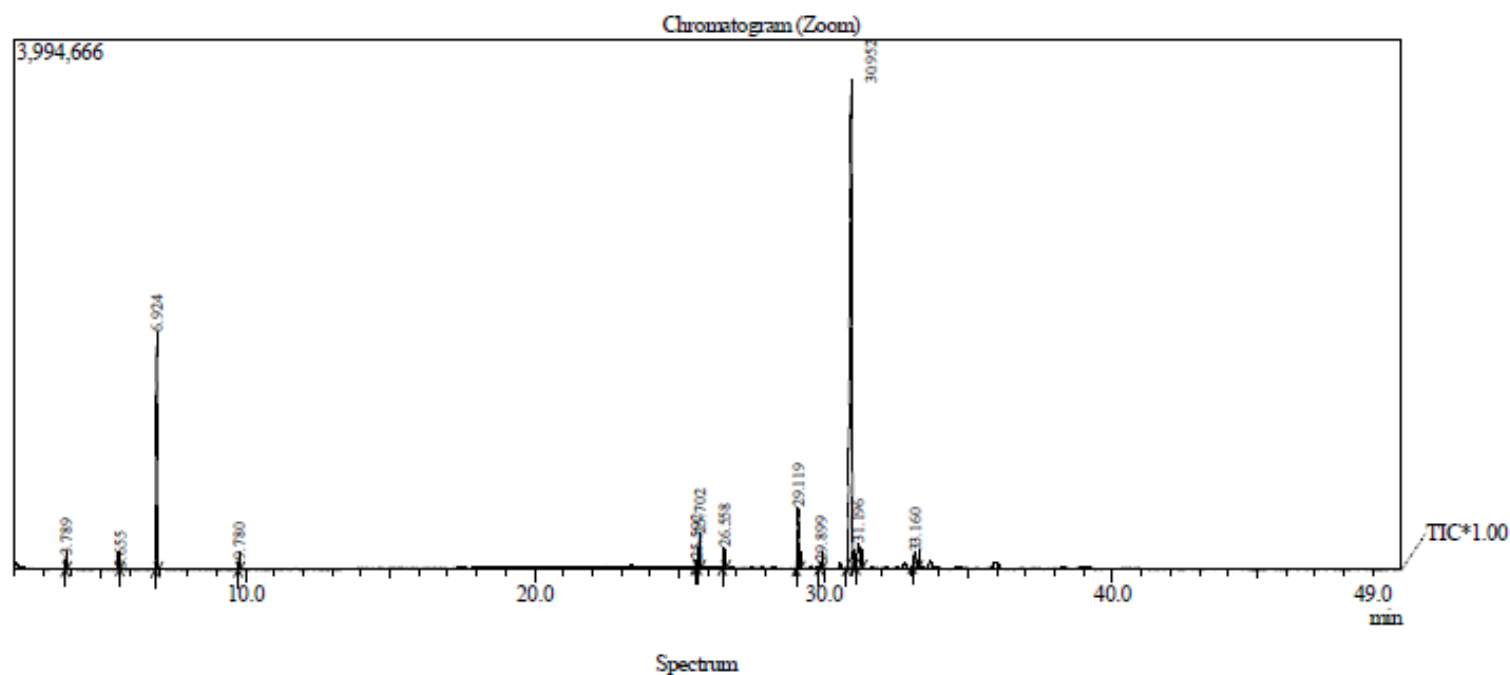


Figure 44: GC/MS spectrum for sample 23

Peak Report TIC											
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name	
1	3.789	3.755	3.830	379860	1.61	282435	2.73	1.34		Toluene	
2	5.650	5.645	5.650	-122	-0.00	0	0.00	0.00	MI		
3	6.093	6.060	6.130	64279	0.27	38331	0.37	1.68		Ethylbenzene	
4	6.935	6.870	6.990	16100679	68.10	8205205	79.36	1.96		Styrene	
5	9.781	9.730	9.835	514708	2.18	249570	2.41	2.06		.alpha.-Methylstyrene	
6	25.576	25.550	25.605	22496	0.10	11731	0.11	1.92	MI		
7	25.686	25.635	25.745	313464	1.33	117571	1.14	2.67		Bibenzyl	
8	26.539	26.495	26.595	166623	0.70	64503	0.62	2.58		1,2 diphenylpropane	
9	29.088	29.020	29.160	511100	2.16	151886	1.47	3.37		1,3 diphenylpropane	
10	30.864	30.760	30.960	4701888	19.89	1079827	10.44	4.35		Dimer	
11	31.156	31.080	31.275	459714	1.94	64347	0.62	7.14			
12	33.090	33.010	33.190	408241	1.73	74454	0.72	5.48			
				23642930	100.00	10339860	100.00				

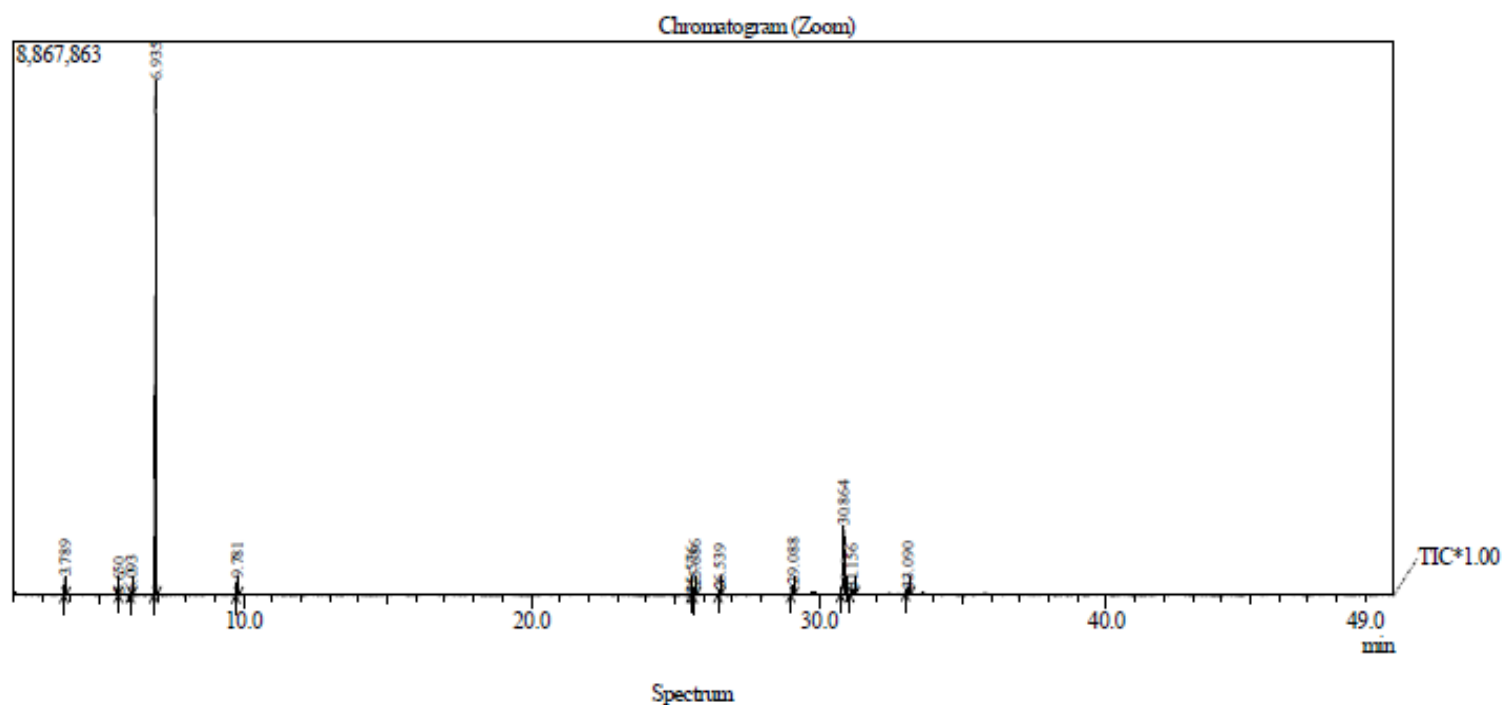


Figure 45: GC/MS spectrum for sample 24

Peak Report TIC												
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name		
1	3.790	3.760	3.830	464379	2.21	343503	3.52	1.35		Toluene		
2	5.660	5.655	5.660	-30	-0.00	0	0.00	0.00	MI			
3	6.092	6.055	6.135	132516	0.63	71016	0.73	1.87		Ethylbenzene		
4	6.936	6.870	6.990	15982026	76.21	8181558	83.81	1.95		Styrene		
5	9.783	9.740	9.835	437682	2.09	209506	2.15	2.09		.alpha.-Methylstyrene		
6	25.581	25.550	25.600	12107	0.06	6079	0.06	1.99	MI			
7	25.684	25.650	25.735	94026	0.45	40033	0.41	2.35		Bibenzyl		
8	26.543	26.510	26.585	64246	0.31	25336	0.26	2.54	MI	1,2 diphenylpropane		
9	29.086	29.030	29.150	313103	1.49	97583	1.00	3.21		1,3 diphenylpropane		
10	29.759	29.715	29.800	87849	0.42	33264	0.34	2.64	MI			
11	29.864	29.820	29.915	98676	0.47	30942	0.32	3.19	MI			
12	30.859	30.760	30.955	2821026	13.45	644796	6.61	4.38		Dimer		
13	33.094	33.005	33.205	463715	2.21	78191	0.80	5.93				
				20971321	100.00	9761807	100.00					

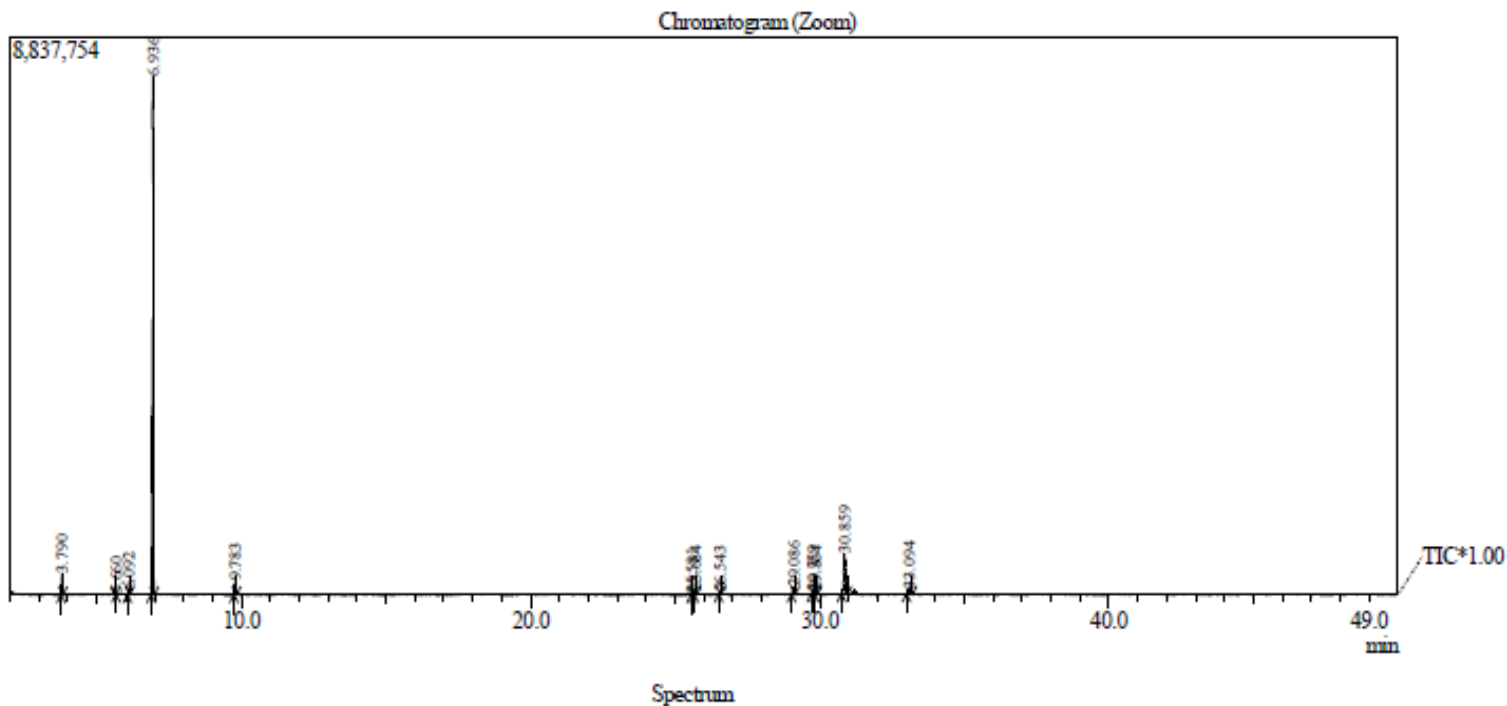


Figure 46: GC/MS spectrum for sample 25

Peak Report TIC											
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name	
1	3.790	3.750	3.835	456198	2.04	336485	3.27	1.36		Toluene	
2	4.490	4.470	4.525	43567	0.19	30137	0.29	1.45			
3	5.562	5.540	5.645	266857	1.19	138497	1.34	1.93			
4	6.091	6.055	6.130	128381	0.57	71823	0.70	1.79		Ethylbenzene	
5	6.935	6.870	6.995	16169479	72.27	8341413	80.99	1.94		Styrene	
6	9.781	9.735	9.830	454441	2.03	221040	2.15	2.06		.alpha.-Methylstyrene	
7	25.681	25.635	25.735	132488	0.59	50798	0.49	2.61		Bibenzyl	
8	29.080	29.025	29.150	366242	1.64	114241	1.11	3.21		1,3 diphenylpropane	
9	29.749	29.705	29.800	125886	0.56	39869	0.39	3.16			
10	29.860	29.800	29.915	133809	0.60	40726	0.40	3.29	V		
11	30.853	30.755	30.955	3472409	15.52	814386	7.91	4.26		Dimer	
12	33.062	32.975	33.185	624002	2.79	99536	0.97	6.27			
				22373759	100.00	10298951	100.00				

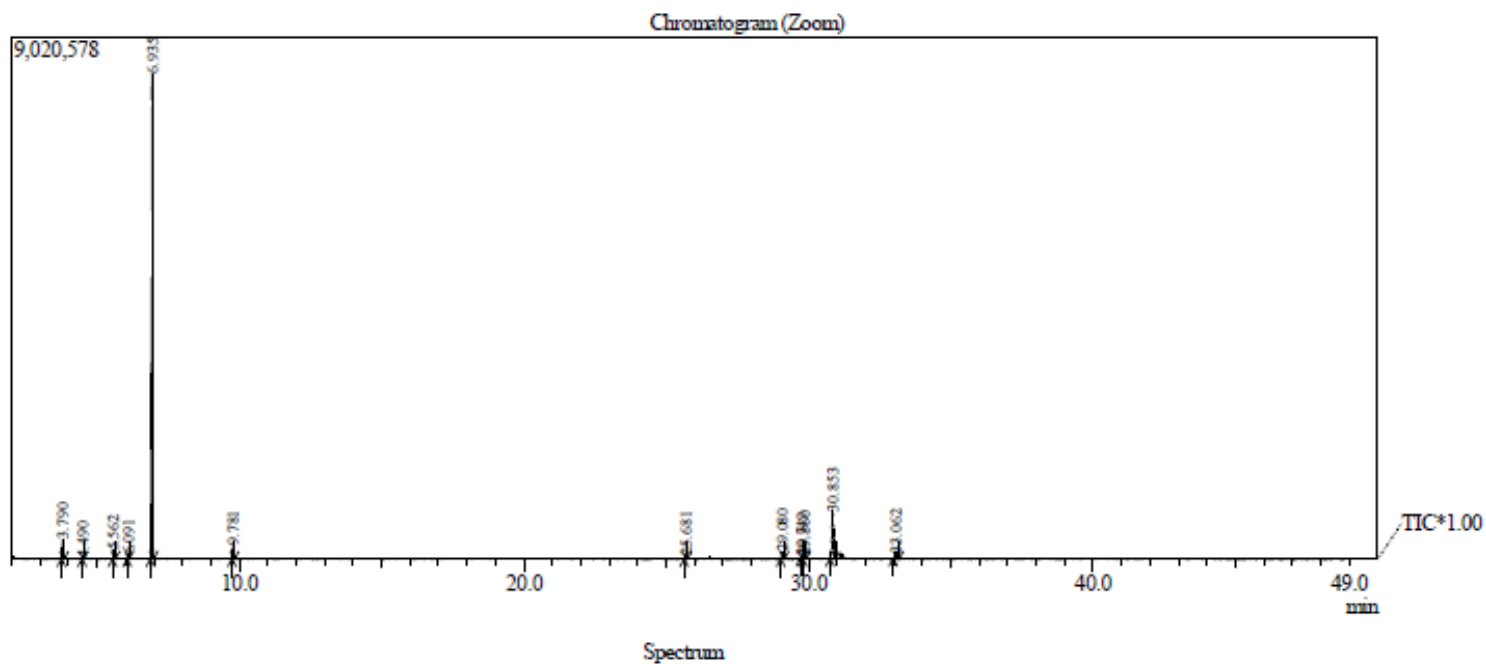


Figure 47: GC/MS spectrum for sample 26

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.755	3.725	3.795	463970	1.86	353283	3.31	1.31		Toluene
2	5.525	5.505	5.600	164255	0.66	84363	0.79	1.95		
3	6.046	6.005	6.090	140854	0.57	76361	0.72	1.84		Ethylbenzene
4	6.890	6.830	6.950	16808057	67.46	8459553	79.32	1.99		Styrene
5	9.727	9.685	9.780	477973	1.92	232378	2.18	2.06		.alpha.-Methylstyrene
6	24.623	24.480	24.770	2728211	10.95	360255	3.38	7.57		
7	25.616	25.565	25.675	472495	1.90	176136	1.65	2.68		Bibenzyl
8	26.472	26.425	26.530	239311	0.96	88775	0.83	2.70		1,2 diphenylpropane
9	29.012	28.960	29.080	300602	1.21	96604	0.91	3.11		1,3 diphenylpropane
10	30.784	30.690	30.885	3118667	12.52	737228	6.91	4.23		Dimer
				24914395	100.00	10664936	100.00			

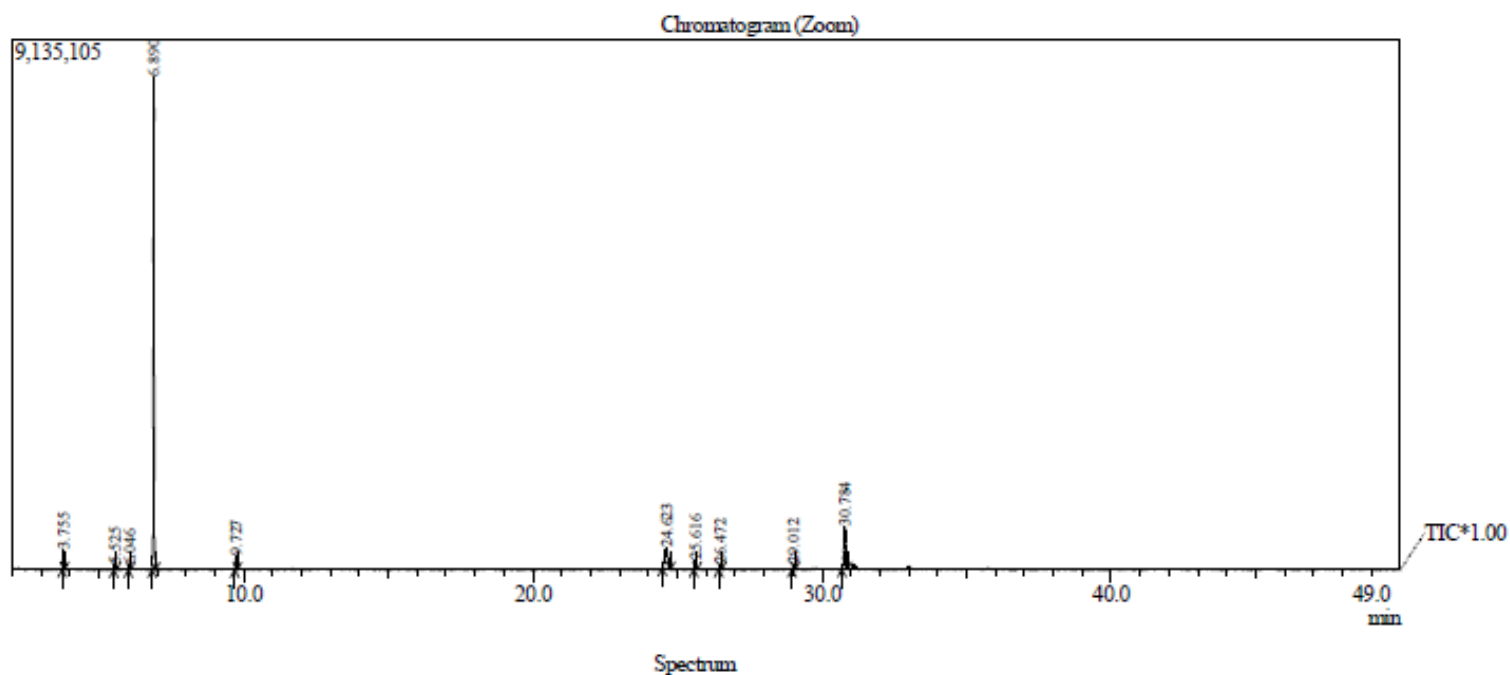


Figure 48: GC/MS spectrum for sample 27

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.801	3.765	3.840	464846	1.79	342807	3.00	1.36		Toluene
2	5.573	5.560	5.650	258703	1.00	131393	1.15	1.97		
3	6.105	6.065	6.145	187703	0.72	106720	0.93	1.76		Ethylbenzene
4	6.949	6.890	7.010	16736839	64.55	8632078	75.43	1.94		Styrene
5	9.793	9.745	9.845	574520	2.22	273495	2.39	2.10		.alpha.-Methylstyrene
6	25.689	25.635	25.750	589813	2.27	224373	1.96	2.63		Bibenzyl
7	26.545	26.485	26.605	455157	1.76	165071	1.44	2.76		1,2 diphenylpropane
8	29.085	29.025	29.165	478988	1.85	143933	1.26	3.33		1,3 diphenylpropane
9	29.752	29.685	29.810	447418	1.73	122469	1.07	3.65		
10	29.859	29.810	29.910	352486	1.36	94495	0.83	3.73	V	
11	29.961	29.910	30.030	421372	1.63	117975	1.03	3.57	V	
12	30.359	30.305	30.425	311558	1.20	93425	0.82	3.33		
13	30.857	30.755	30.955	3312745	12.78	775396	6.78	4.27		Dimer
14	31.197	31.095	31.285	545777	2.11	93001	0.81	5.87		
15	33.071	32.985	33.195	788654	3.04	126978	1.11	6.21		
				25926579	100.00	11443609	100.00			

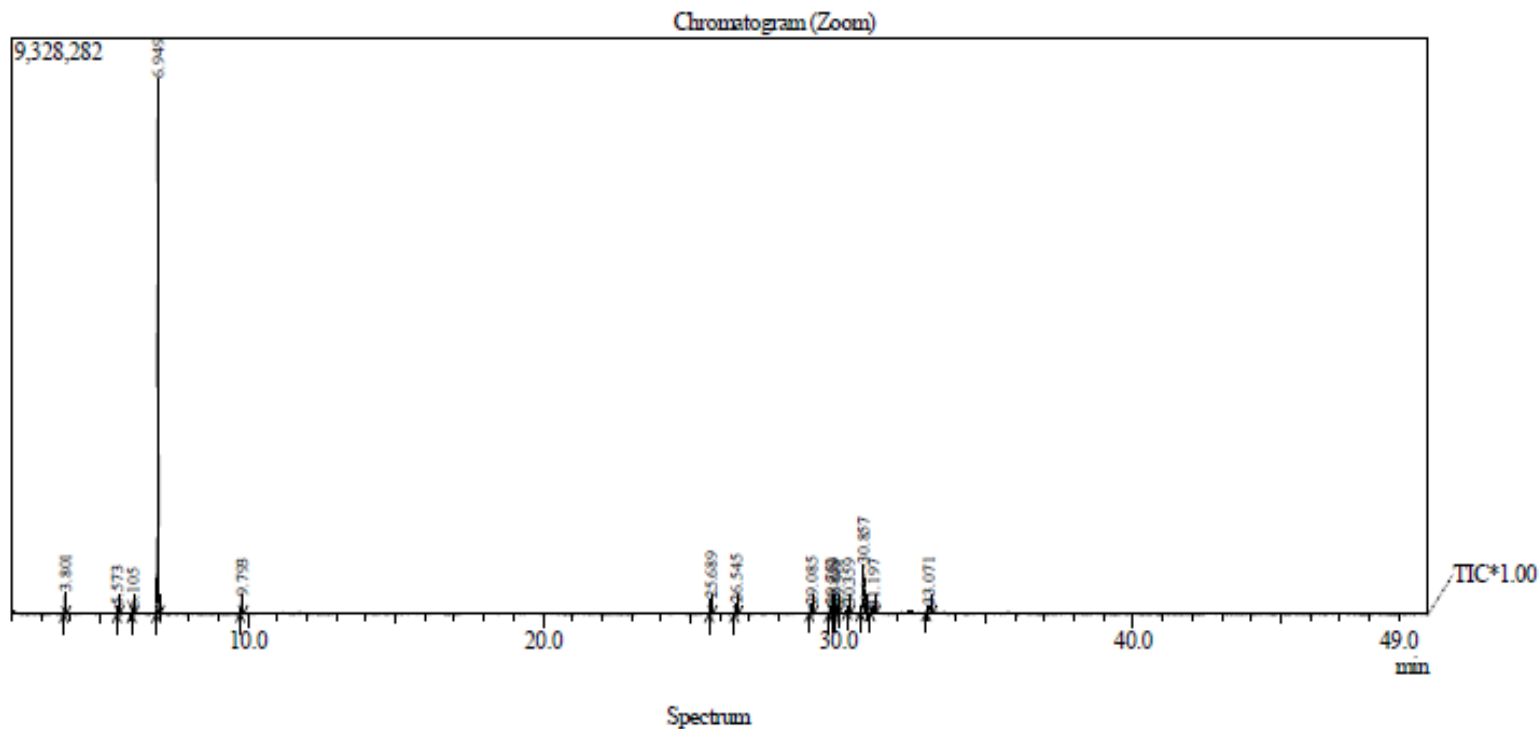


Figure 49: GC/MS spectrum for sample 28

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	2.238	2.225	2.265	26648	0.11	30652	0.26	0.87		
2	3.801	3.765	3.845	961477	3.79	700249	5.89	1.37		Toluene
3	5.577	5.565	5.665	244397	0.96	124370	1.05	1.97		
4	6.106	6.060	6.160	574069	2.26	324845	2.73	1.77		Ethylbenzene
5	6.951	6.890	7.015	17096385	67.45	8744429	73.50	1.96		Styrene
6	8.645	8.615	8.680	55187	0.22	30690	0.26	1.80		
7	9.795	9.750	9.845	942816	3.72	469497	3.95	2.01		.alpha.-Methylstyrene
8	11.192	11.160	11.230	66000	0.26	33228	0.28	1.99		
9	11.752	11.720	11.805	98184	0.39	46522	0.39	2.11		
10	25.693	25.640	25.750	519515	2.05	192589	1.62	2.70		Bibenzyl
11	26.545	26.490	26.610	525403	2.07	190151	1.60	2.76		1,2 diphenylpropane
12	29.089	29.030	29.155	449722	1.77	142051	1.19	3.17		1,3 diphenylpropane
13	29.760	29.700	29.805	280964	1.11	84293	0.71	3.33		
14	29.867	29.805	29.920	385671	1.52	98986	0.83	3.90	V	
15	29.968	29.920	30.020	185038	0.73	57110	0.48	3.24	V	
16	30.364	30.320	30.430	127832	0.50	41331	0.35	3.09		
17	30.855	30.765	30.955	1475940	5.82	350921	2.95	4.21		Dimer
18	31.205	31.140	31.290	354769	1.40	88427	0.74	4.01		
19	33.085	32.975	33.220	977329	3.86	147600	1.24	6.62		
				25347346	100.00	11897941	100.00			

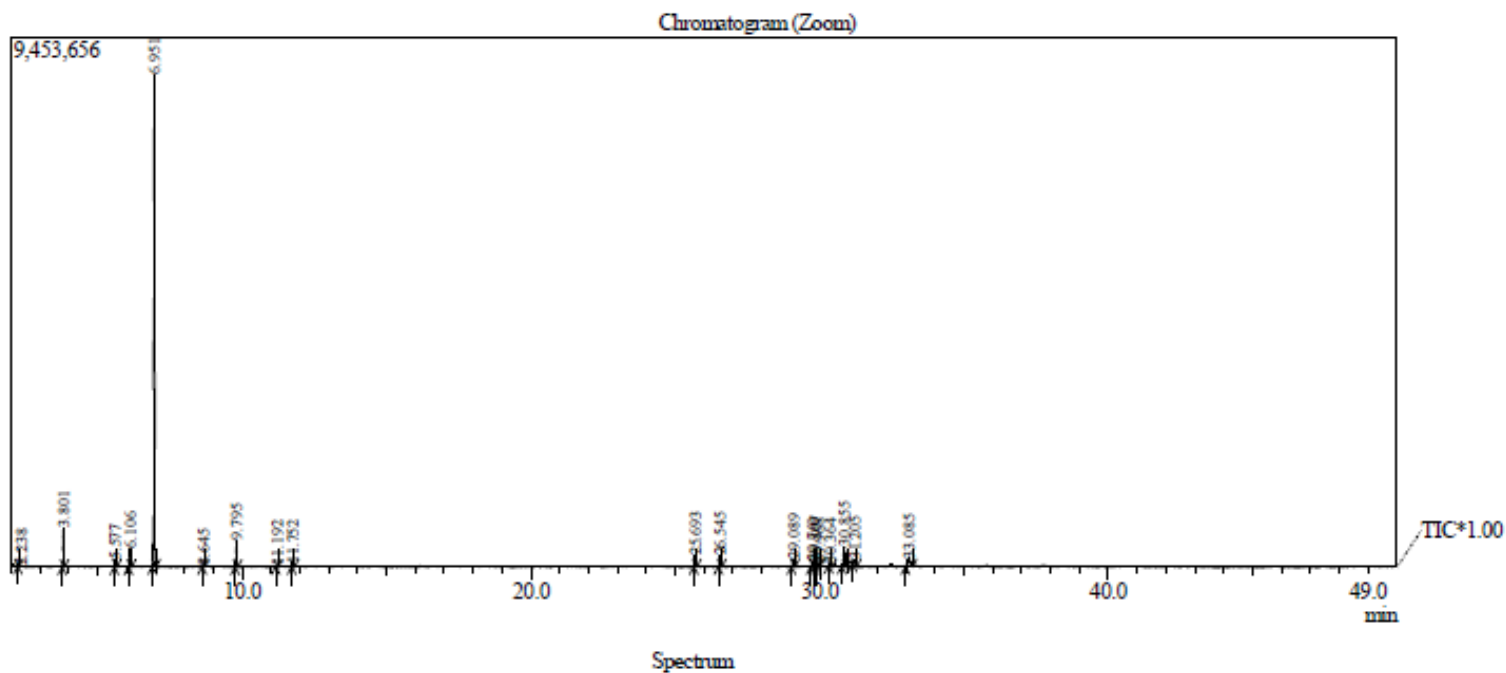


Figure 50: GC/MS spectrum for sample 29

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	2.239	2.215	2.265	48326	0.17	52568	0.42	0.92		
2	3.803	3.770	3.845	689095	2.47	505764	4.00	1.36		Toluene
3	5.577	5.565	5.650	227196	0.81	115809	0.92	1.96		
4	6.107	6.065	6.150	650091	2.33	362266	2.86	1.79		Ethylbenzene
5	6.954	6.890	7.005	18675062	66.94	9423063	74.51	1.98		Styrene
6	7.981	7.945	8.020	108409	0.39	55910	0.44	1.94		
7	9.796	9.745	9.850	1115556	4.00	534128	4.22	2.09		.alpha.-Methylstyrene
8	25.695	25.645	25.755	271207	0.97	103509	0.82	2.62		Bibenzyl
9	26.547	26.495	26.605	273097	0.98	102832	0.81	2.66		1,2 diphenylpropane
10	29.091	29.025	29.165	844859	3.03	253108	2.00	3.34		1,3 diphenylpropane
11	29.764	29.695	29.815	505796	1.81	143466	1.13	3.53		
12	29.867	29.815	29.915	323990	1.16	82579	0.65	3.92	V	
13	29.967	29.915	30.040	418224	1.50	116496	0.92	3.59	V	
14	30.363	30.310	30.445	299203	1.07	88586	0.70	3.38		
15	30.859	30.765	30.950	1760758	6.31	415092	3.28	4.24		Dimer
16	31.208	31.095	31.290	877795	3.15	166212	1.31	5.28		
17	33.083	32.985	33.215	809623	2.90	124621	0.99	6.50		
				27898287	100.00	12646009	100.00			

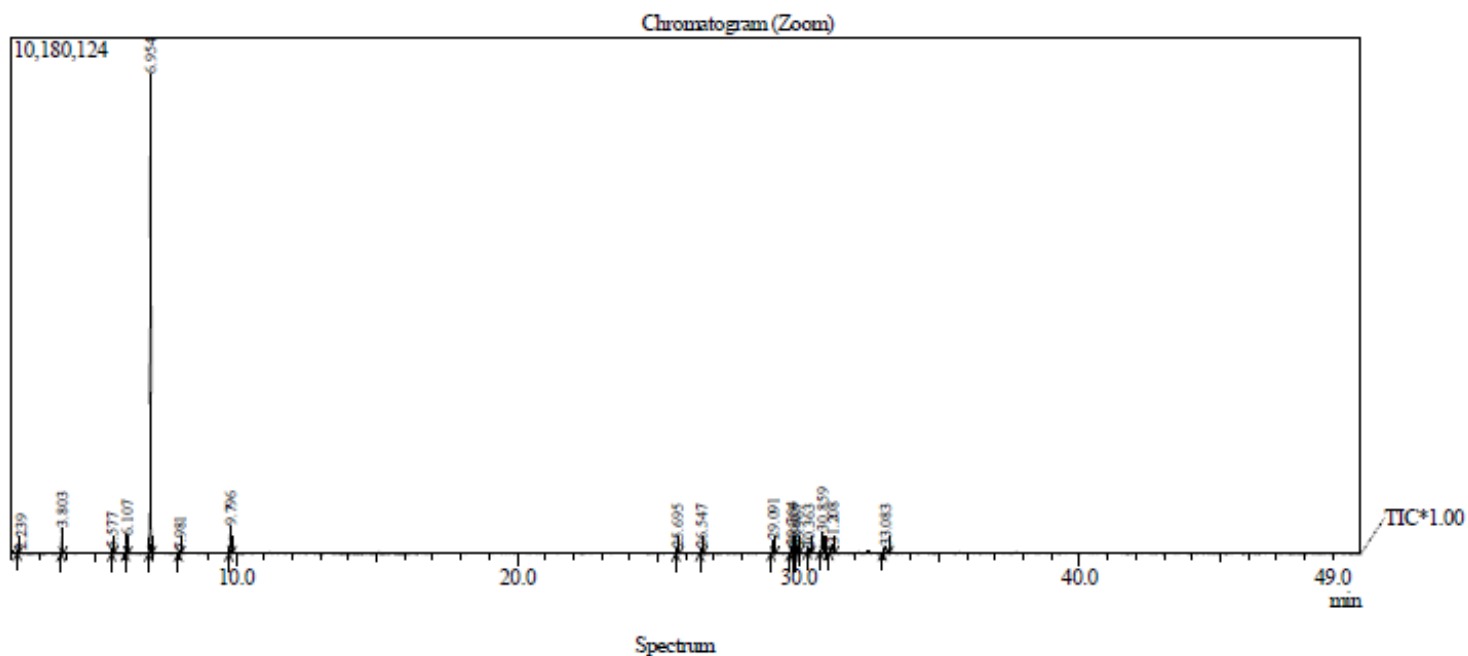


Figure 51: GC/MS spectrum for sample 30

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.803	3.770	3.845	470311	1.61	337078	2.66	1.40		Toluene
2	5.577	5.555	5.670	248360	0.85	122773	0.97	2.02		
3	6.108	6.080	6.150	99191	0.34	57883	0.46	1.71		Ethylbenzene
4	6.955	6.885	7.015	20048516	68.52	10001762	79.02	2.00		Styrene
5	9.797	9.750	9.855	541687	1.85	252520	2.00	2.15		.alpha.-Methylstyrene
6	25.695	25.635	25.750	321969	1.10	121151	0.96	2.66		Bibenzyl
7	26.546	26.495	26.600	232887	0.80	83851	0.66	2.78		1,2 diphenylpropane
8	29.091	29.025	29.165	662603	2.26	198475	1.57	3.34		1,3 diphenylpropane
9	29.765	29.705	29.810	311298	1.06	95149	0.75	3.27		
10	29.869	29.810	29.925	190688	0.65	55803	0.44	3.42	V	
11	30.868	30.755	30.965	4673891	15.97	1090776	8.62	4.28		Dimer
12	31.202	31.090	31.300	680744	2.33	112695	0.89	6.04		
13	33.090	32.990	33.205	778639	2.66	127195	1.00	6.12		
				29260784	100.00	12657111	100.00			

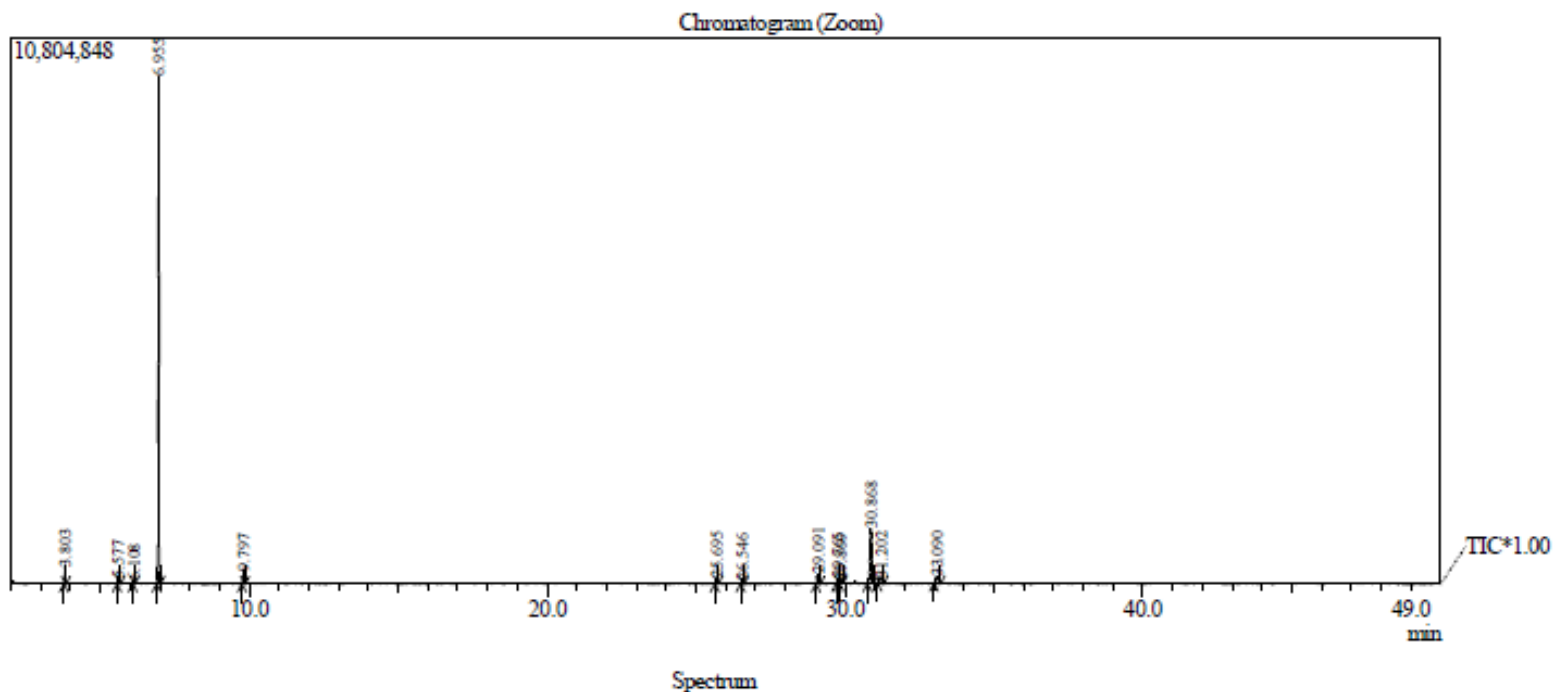


Figure 52: GC/MS spectrum for sample 31

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.803	3.765	3.845	396949	1.44	288012	2.34	1.38		Toluene
2	5.581	5.565	5.660	187181	0.68	98214	0.80	1.91		
3	6.109	6.075	6.145	48162	0.17	28431	0.23	1.69		Ethylbenzene
4	6.955	6.890	7.015	20202464	73.04	10127138	82.35	1.99		Styrene
5	9.797	9.750	9.855	414333	1.50	196243	1.60	2.11		.alpha.-Methylstyrene
6	25.696	25.640	25.755	405616	1.47	152837	1.24	2.65		Bibenzyl
7	26.549	26.495	26.600	220618	0.80	80959	0.66	2.73		1,2 diphenylpropane
8	29.091	29.035	29.160	292518	1.06	91697	0.75	3.19		1,3 diphenylpropane
9	30.869	30.765	30.975	5077713	18.36	1176357	9.57	4.32		Dimer
10	31.175	31.085	31.295	412534	1.49	57408	0.47	7.19		
				27658088	100.00	12297296	100.00			

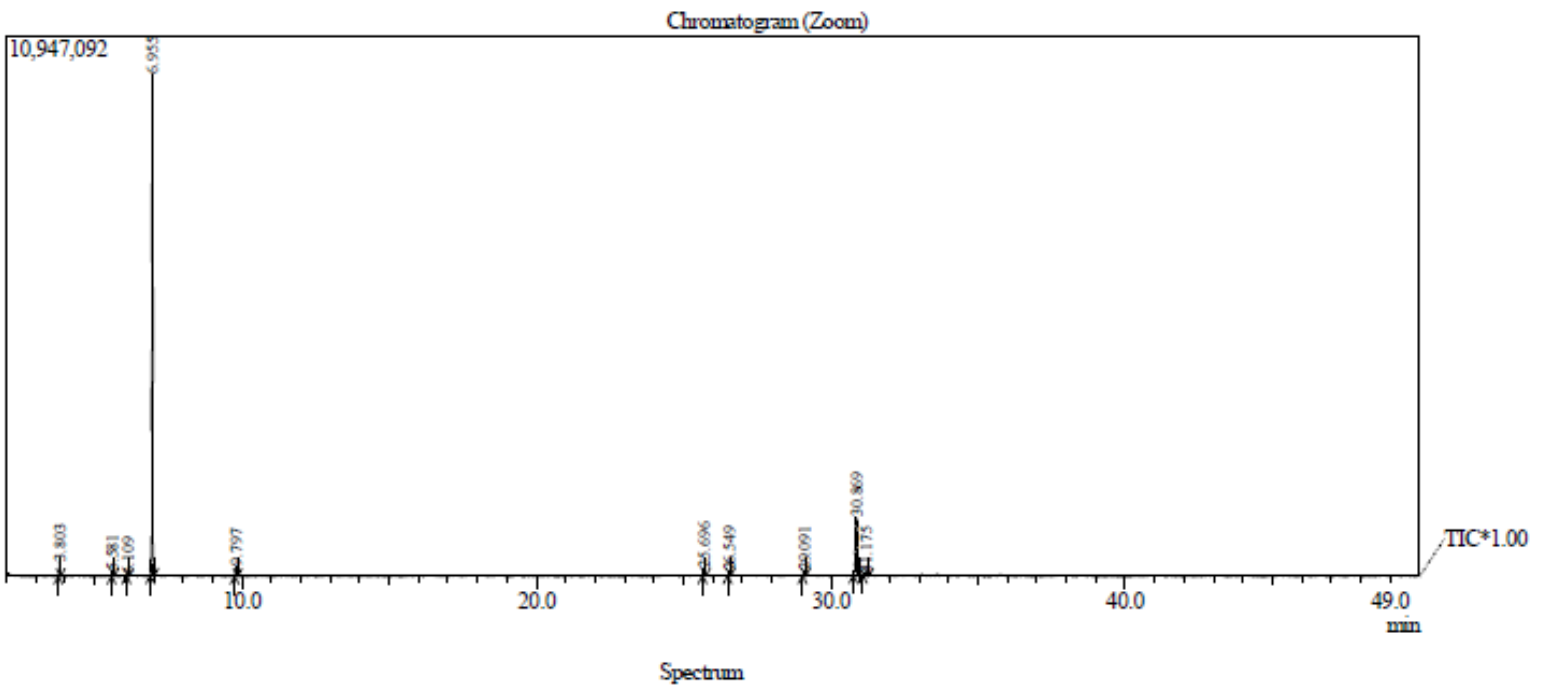


Figure 53: GC/MS spectrum for sample 32

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.803	3.770	3.840	385507	1.64	278036	2.66	1.39		Toluene
2	5.582	5.560	5.660	189542	0.81	96723	0.92	1.96		
3	6.108	6.080	6.140	48699	0.21	29030	0.28	1.68		Ethylbenzene
4	6.952	6.885	7.010	16749362	71.15	8499319	81.21	1.97		Styrene
5	9.796	9.750	9.845	316266	1.34	149283	1.43	2.12		.alpha.-Methylstyrene
6	25.694	25.645	25.750	254636	1.08	96159	0.92	2.65		Bibenzyl
7	26.545	26.505	26.600	122529	0.52	46749	0.45	2.62		1,2 diphenylpropane
8	29.088	29.035	29.165	315936	1.34	94294	0.90	3.35		1,3 diphenylpropane
9	30.866	30.760	30.965	4811653	20.44	1123291	10.73	4.28		Dimer
10	31.190	31.095	31.280	345165	1.47	53517	0.51	6.45		
				23539295	100.00	10466401	100.00			

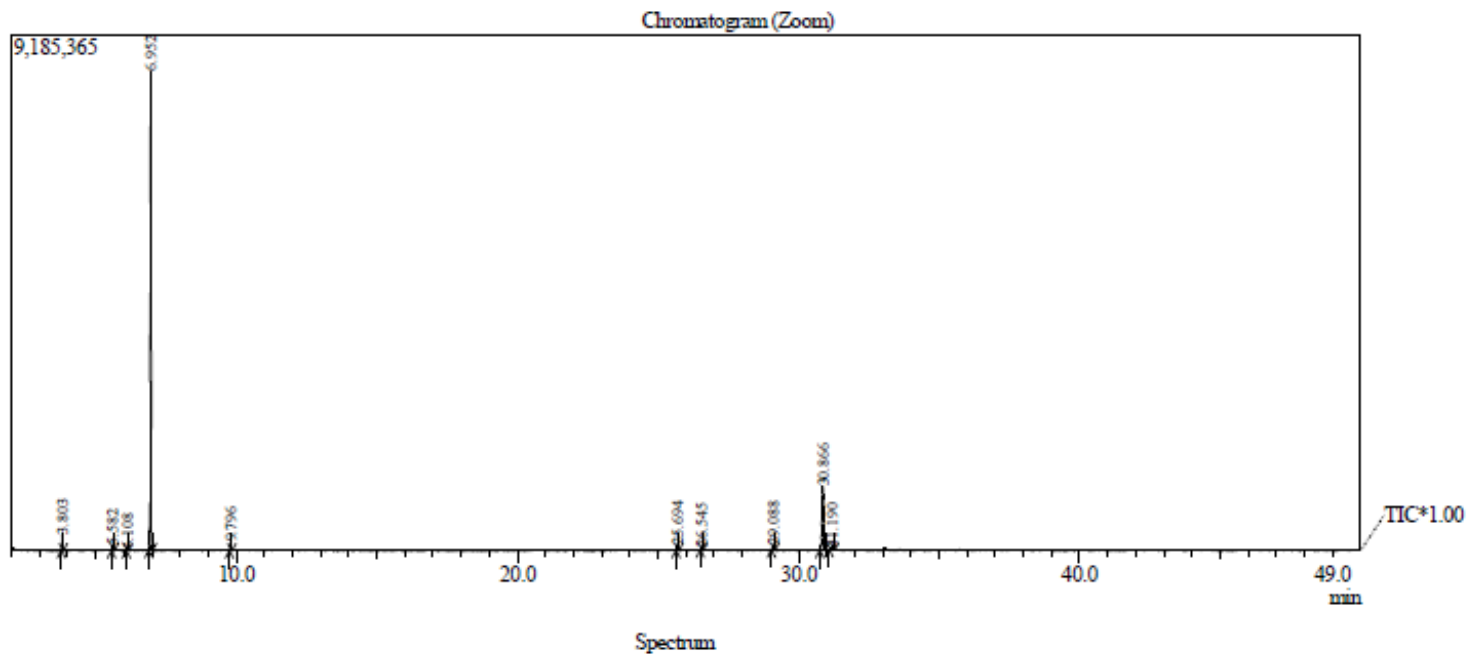


Figure 54: GC/MS spectrum for sample 33

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.802	3.765	3.845	503127	1.91	347801	2.95	1.45		Toluene
2	5.577	5.565	5.655	229531	0.87	121000	1.03	1.90		
3	6.108	6.070	6.145	180369	0.69	98770	0.84	1.83		Ethylbenzene
4	6.953	6.890	7.010	19168370	72.86	9463124	80.22	2.03		Styrene
5	9.796	9.750	9.850	696903	2.65	337905	2.86	2.06		.alpha.-Methylstyrene
6	11.753	11.715	11.795	88466	0.34	40539	0.34	2.18		
7	25.695	25.640	25.755	591653	2.25	219307	1.86	2.70		Bibenzyl
8	26.549	26.495	26.615	387823	1.47	144140	1.22	2.69		1,2 diphenylpropane
9	29.091	29.035	29.165	299744	1.14	92886	0.79	3.23		1,3 diphenylpropane
10	30.864	30.765	30.965	3695555	14.05	859271	7.28	4.30		Dimer
11	31.200	31.095	31.290	466892	1.77	71588	0.61	6.52		
				26308433	100.00	11796331	100.00			

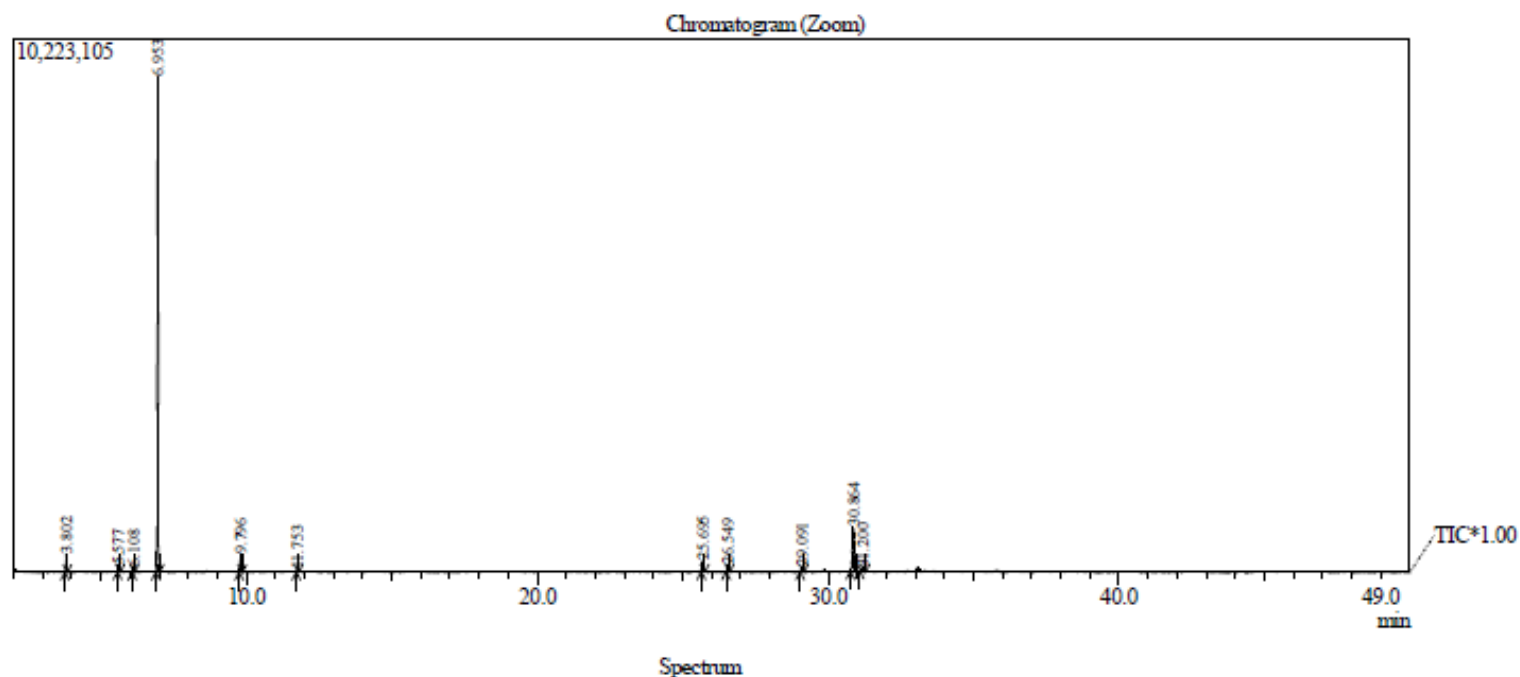


Figure 55: GC/MS spectrum for sample 34

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.782	3.745	3.820	438121	1.70	315330	2.77	1.39		Toluene
2	5.552	5.535	5.615	210246	0.82	115947	1.02	1.81		
3	6.082	6.050	6.120	75198	0.29	43768	0.38	1.72		Ethylbenzene
4	6.926	6.860	6.980	18374097	71.36	9196175	80.72	2.00		Styrene
5	9.767	9.720	9.820	429008	1.67	205434	1.80	2.09		.alpha.-Methylstyrene
6	25.666	25.620	25.725	315612	1.23	121737	1.07	2.59		Bibenzyl
7	26.521	26.470	26.575	216467	0.84	79886	0.70	2.71		1,2 diphenylpropane
8	29.065	29.010	29.130	325803	1.27	103994	0.91	3.13		1,3 diphenylpropane
9	30.843	30.745	30.945	4635943	18.01	1089489	9.56	4.26		Dimer
10	31.174	31.060	31.260	509356	1.98	75510	0.66	6.75		
11	33.058	33.000	33.160	216833	0.84	45414	0.40	4.77		
				25746684	100.00	11392684	100.00			

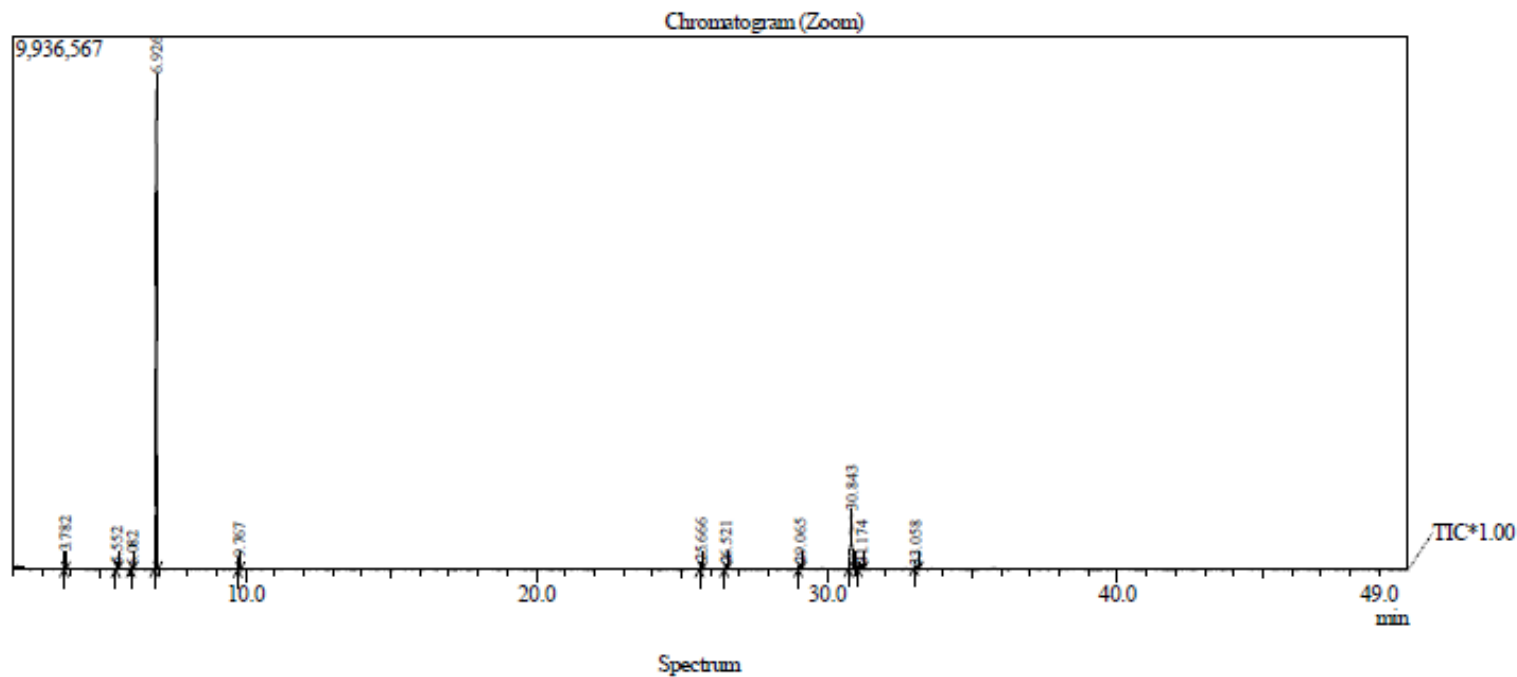


Figure 56: GC/MS spectrum for sample 35

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.791	3.760	3.825	526713	1.79	384006	3.03	1.37		Toluene
2	5.564	5.540	5.635	217399	0.74	109332	0.86	1.99		
3	6.093	6.060	6.135	101826	0.35	56028	0.44	1.82		Ethylbenzene
4	6.939	6.875	6.995	20122826	68.57	9992911	78.75	2.01		Styrene
5	9.780	9.730	9.830	534086	1.82	257480	2.03	2.07		.alpha.-Methylstyrene
6	25.675	25.625	25.735	401976	1.37	155481	1.23	2.59		Bibenzyl
7	26.526	26.480	26.580	245326	0.84	94371	0.74	2.60		1,2 diphenylpropane
8	29.069	29.005	29.145	499428	1.70	149893	1.18	3.33		1,3 diphenylpropane
9	30.847	30.740	30.955	5774203	19.68	1347606	10.62	4.28		Dimer
10	31.160	31.060	31.275	647379	2.21	90451	0.71	7.16		
11	33.049	32.990	33.160	273399	0.93	51879	0.41	5.27		
				29344561	100.00	12689438	100.00			

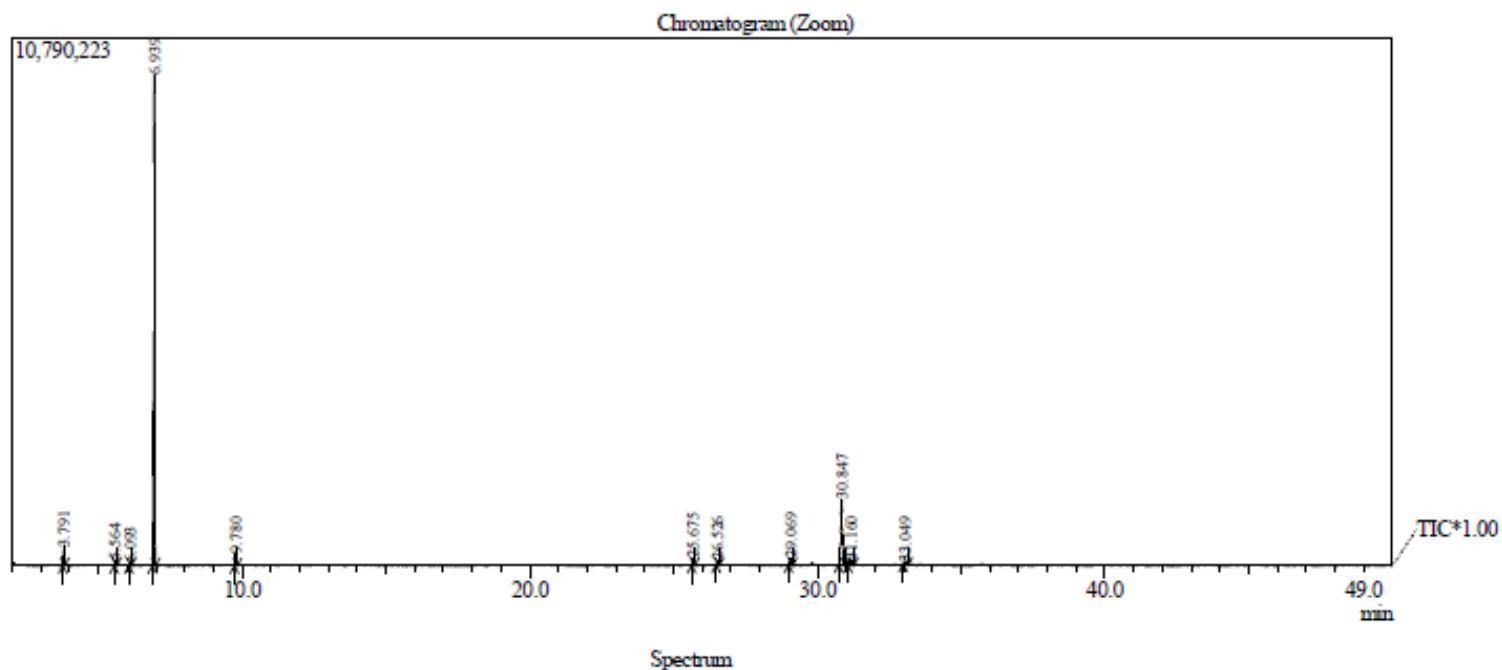


Figure 57: GC/MS spectrum for sample 36

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.793	3.760	3.835	317822	1.28	232175	2.16	1.37		Toluene
2	5.567	5.550	5.645	207775	0.84	106076	0.99	1.96		
3	6.939	6.875	7.000	16648748	66.96	8487816	79.04	1.96		Styrene
4	9.782	9.740	9.835	247480	1.00	115125	1.07	2.15		.alpha.-Methylstyrene
5	25.675	25.625	25.725	185961	0.75	71626	0.67	2.60		Bibenzyl
6	26.527	26.490	26.585	111917	0.45	44173	0.41	2.53		1,2 diphenylpropane
7	29.071	29.015	29.145	404555	1.63	126273	1.18	3.20		1,3 diphenylpropane
8	30.851	30.740	30.960	6737741	27.10	1555903	14.49	4.33		Dimer
				24861999	100.00	10739167	100.00			

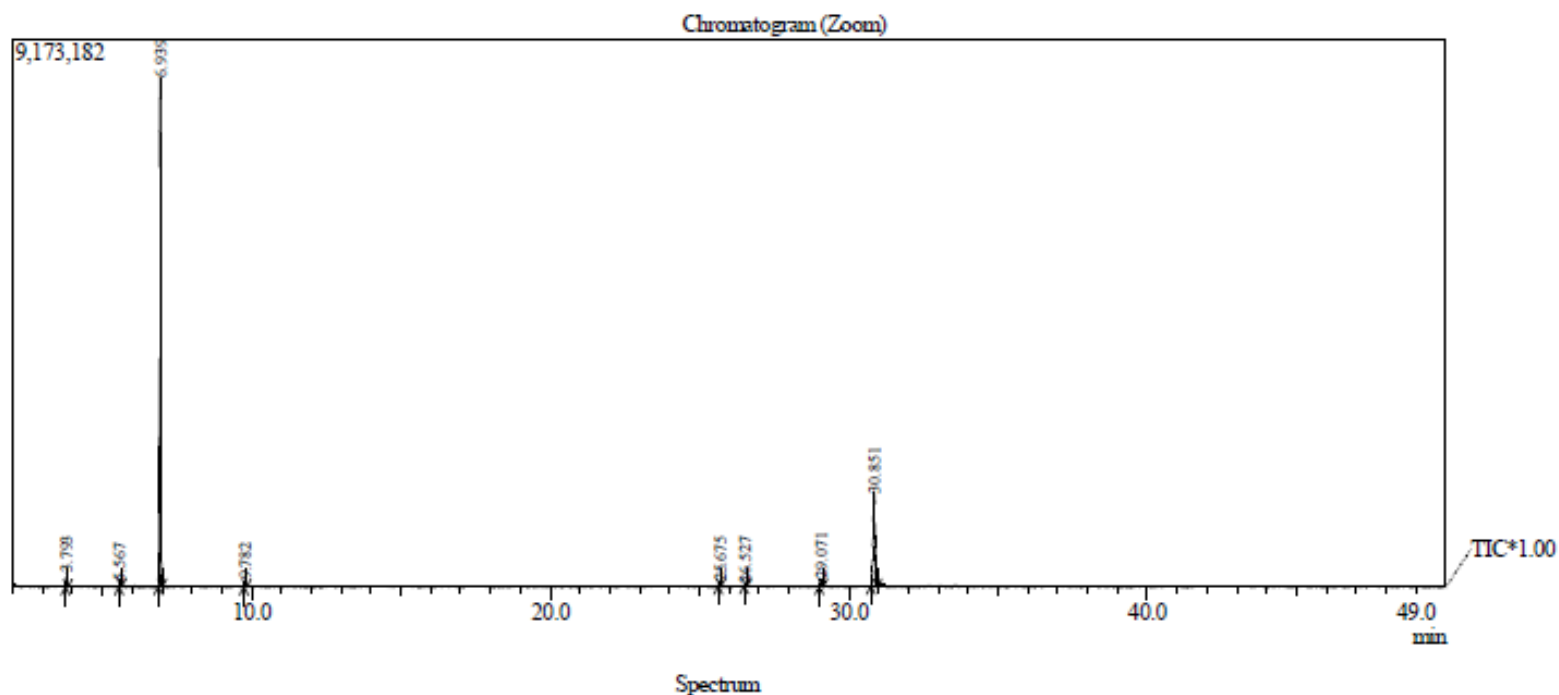


Figure 58: GC/MS spectrum for sample 37

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.795	3.760	3.830	358448	1.36	270305	2.37	1.33		Toluene
2	5.568	5.550	5.645	209706	0.80	107396	0.94	1.95		
3	6.097	6.060	6.135	131397	0.50	74111	0.65	1.77		Ethylbenzene
4	6.941	6.880	6.995	18010948	68.33	8992099	78.83	2.00		Styrene
5	9.785	9.740	9.835	493518	1.87	235329	2.06	2.10		.alpha.-Methylstyrene
6	25.680	25.625	25.740	303892	1.15	116269	1.02	2.61		Bibenzyl
7	26.534	26.480	26.585	183357	0.70	67760	0.59	2.71		1,2 diphenylpropane
8	29.078	29.015	29.150	393391	1.49	116696	1.02	3.37		1,3 diphenylpropane
9	30.852	30.745	30.955	5877161	22.30	1368863	12.00	4.29		Dimer
10	31.142	31.075	31.260	395053	1.50	57580	0.50	6.86		
				26356871	100.00	11406408	100.00			

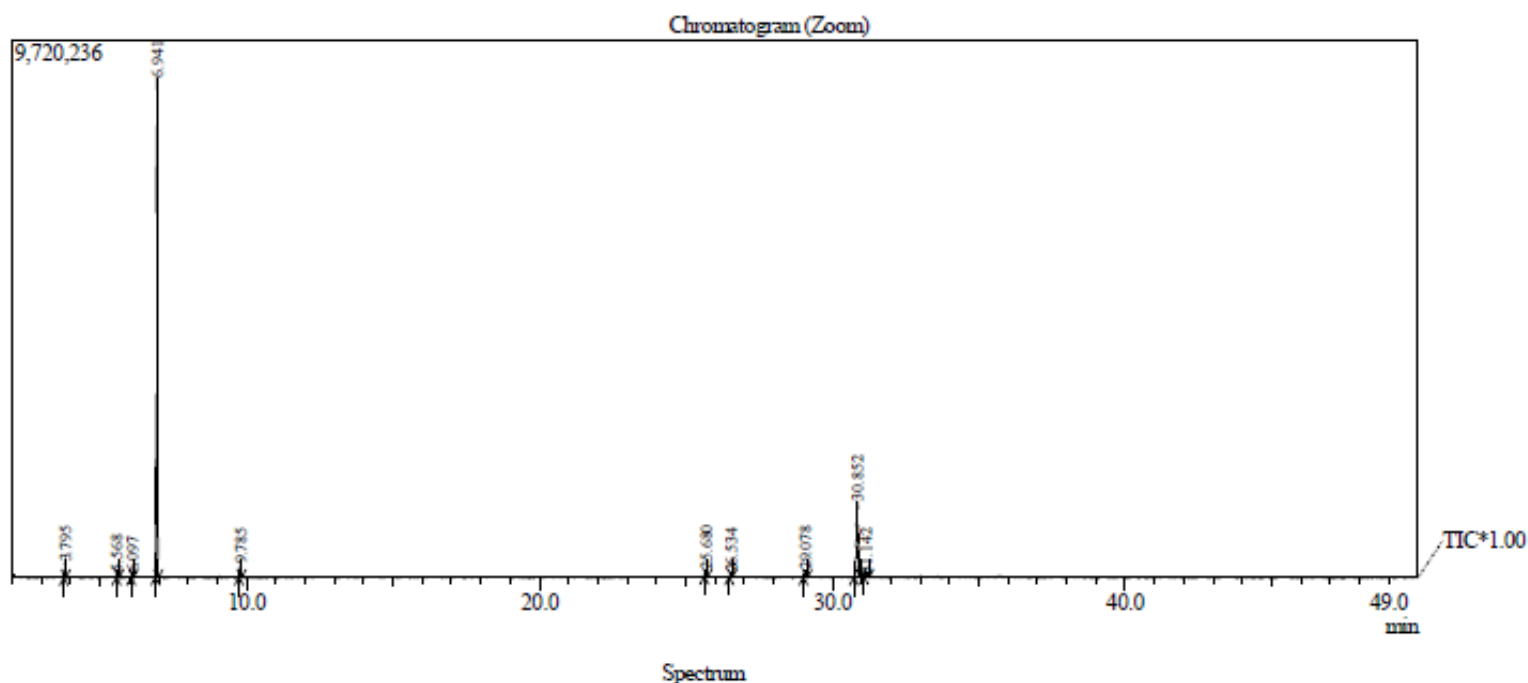


Figure 59: GC/MS spectrum for sample 38

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.796	3.765	3.835	360287	1.63	270585	2.72	1.33		Toluene
2	5.570	5.545	5.640	203438	0.92	106048	1.07	1.92		
3	6.099	6.065	6.145	71517	0.32	39577	0.40	1.81		Ethylbenzene
4	6.943	6.880	7.005	15674828	70.79	8010260	80.64	1.96		Styrene
5	9.787	9.740	9.840	368197	1.66	173218	1.74	2.13		.alpha.-Methylstyrene
6	25.679	25.630	25.740	258633	1.17	101074	1.02	2.56		Bibenzyl
7	26.530	26.490	26.585	151773	0.69	58218	0.59	2.61		1,2 diphenylpropane
8	29.076	29.020	29.140	319028	1.44	102870	1.04	3.10		1,3 diphenylpropane
9	30.849	30.745	30.960	4373077	19.75	1017224	10.24	4.30		Dimer
10	31.158	31.085	31.270	361663	1.63	53783	0.54	6.72		
				22142441	100.00	9932857	100.00			

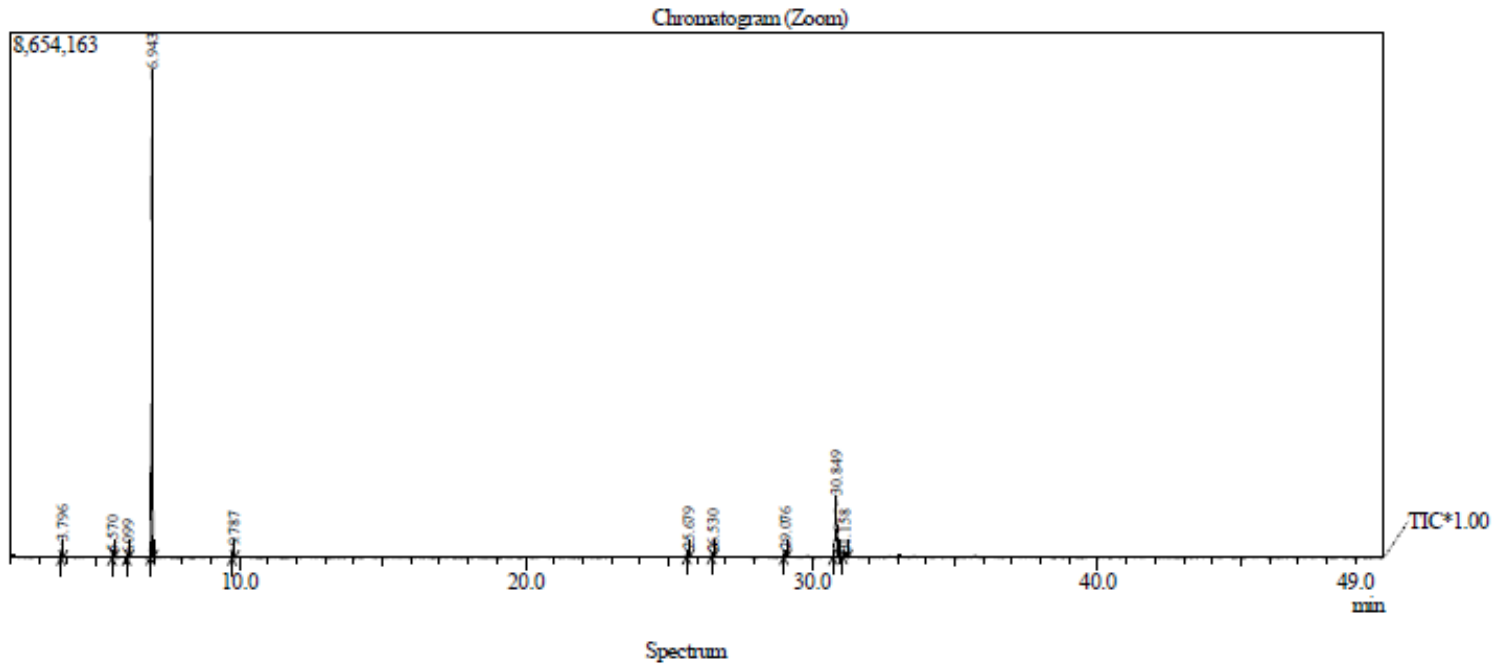


Figure 60: GC/MS spectrum for sample 39

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.796	3.765	3.835	481409	1.95	345731	3.08	1.39		Toluene
2	5.570	5.555	5.650	231846	0.94	117414	1.05	1.97		
3	6.100	6.070	6.140	79202	0.32	43513	0.39	1.82		Ethylbenzene
4	6.946	6.880	6.995	18650706	75.74	9326675	83.07	2.00		Styrene
5	9.788	9.745	9.830	408041	1.66	195175	1.74	2.09		.alpha.-Methylstyrene
6	25.681	25.630	25.740	253092	1.03	96163	0.86	2.63		Bibenzyl
7	26.532	26.480	26.590	164657	0.67	59609	0.53	2.76		1,2 diphenylpropane
8	29.077	29.020	29.135	265566	1.08	83465	0.74	3.18		1,3 diphenylpropane
9	30.850	30.745	30.950	4091515	16.61	959240	8.54	4.27		Dimer
				24626034	100.00	11226985	100.00			

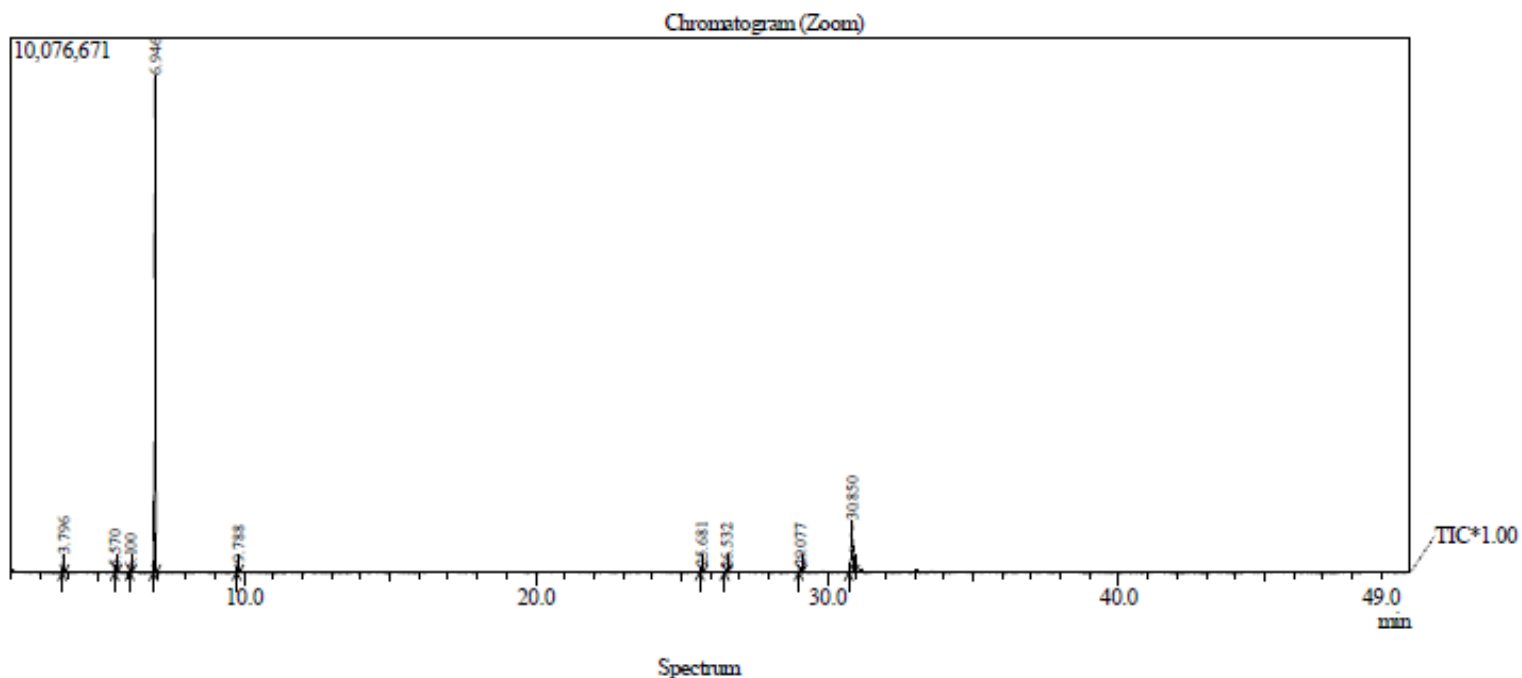


Figure 61: GC/MS spectrum for sample 43

Peak Report TIC												
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name		
1	3.816	3.785	3.855	338560	1.15	248480	2.02	1.36		Toluene		
2	5.589	5.570	5.660	262061	0.89	139822	1.14	1.87				
3	6.123	6.090	6.160	141759	0.48	81614	0.66	1.74		Ethylbenzene		
4	6.971	6.905	7.030	18568848	63.23	9326338	75.89	1.99		Styrene		
5	9.090	9.060	9.135	67086	0.23	34056	0.28	1.97				
6	9.816	9.770	9.870	562168	1.91	267922	2.18	2.10		.alpha.-Methylstyrene		
7	25.719	25.665	25.775	325207	1.11	124219	1.01	2.62		Bibenzyl		
8	26.572	26.525	26.635	232178	0.79	83883	0.68	2.77		1,2 diphenylpropane		
9	29.120	29.055	29.190	538683	1.83	166063	1.35	3.24		1,3 diphenylpropane		
10	29.894	29.850	29.945	118877	0.40	40162	0.33	2.96				
11	30.904	30.780	31.005	7142909	24.32	1613770	13.13	4.43		Dimer		
12	31.225	31.105	31.320	733343	2.50	102319	0.83	7.17				
13	33.111	33.040	33.220	336787	1.15	60232	0.49	5.59				
				29368466	100.00	12288880	100.00					

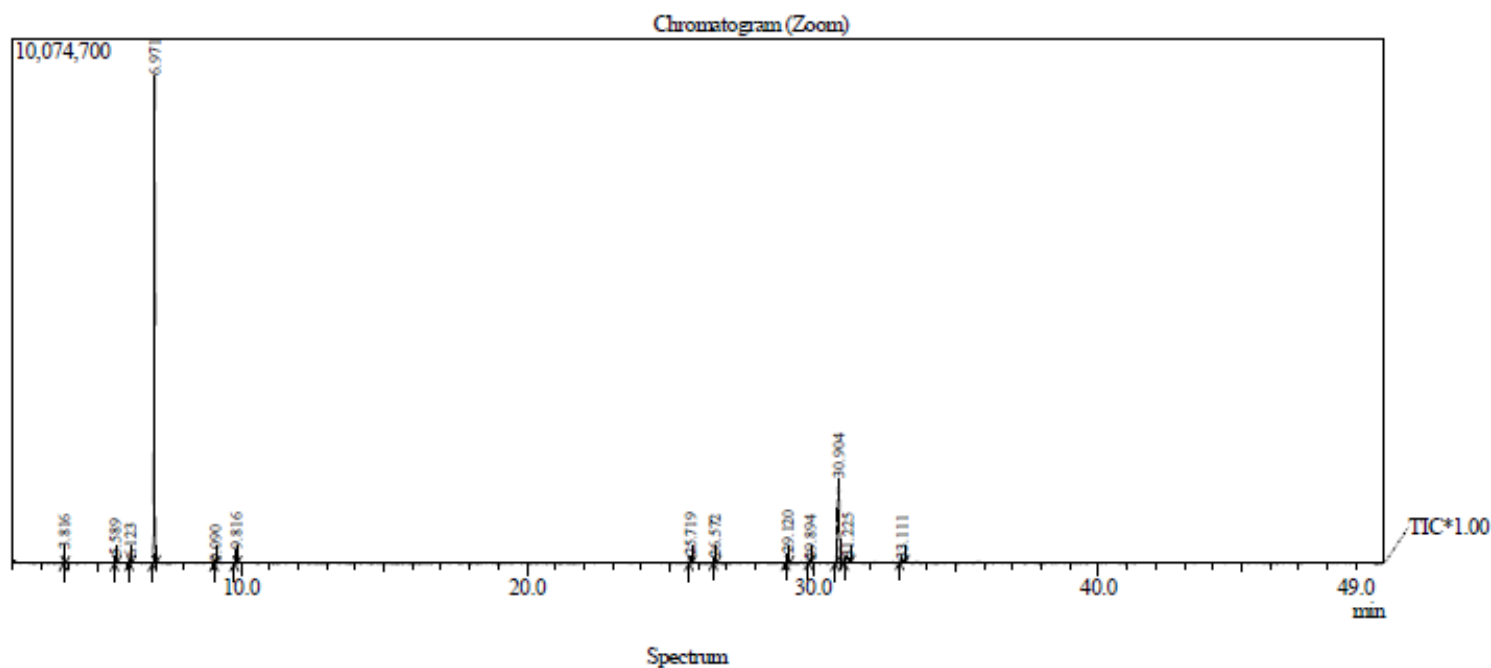


Figure 62: GC/MS spectrum for sample 44

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.797	3.765	3.830	421853	1.72	304733	2.77	1.38		Toluene
2	5.571	5.555	5.635	204611	0.84	108900	0.99	1.88		
3	6.101	6.065	6.140	80956	0.33	43917	0.40	1.84		Ethylbenzene
4	6.945	6.885	7.005	17738186	72.48	8952577	81.41	1.98		Styrene
5	9.789	9.740	9.840	433284	1.77	214115	1.95	2.02		alpha-Methylstyrene
6	25.684	25.630	25.745	311076	1.27	116097	1.06	2.68		Bibenzyl
7	26.537	26.485	26.590	192141	0.79	70282	0.64	2.73		1,2 diphenylpropane
8	29.081	29.015	29.150	384167	1.57	116603	1.06	3.29		1,3 diphenylpropane
9	30.854	30.755	30.950	4212098	17.21	996696	9.06	4.23		Dimer
10	31.190	31.075	31.275	493645	2.02	72392	0.66	6.82		
				24472017	100.00	10996312	100.00			

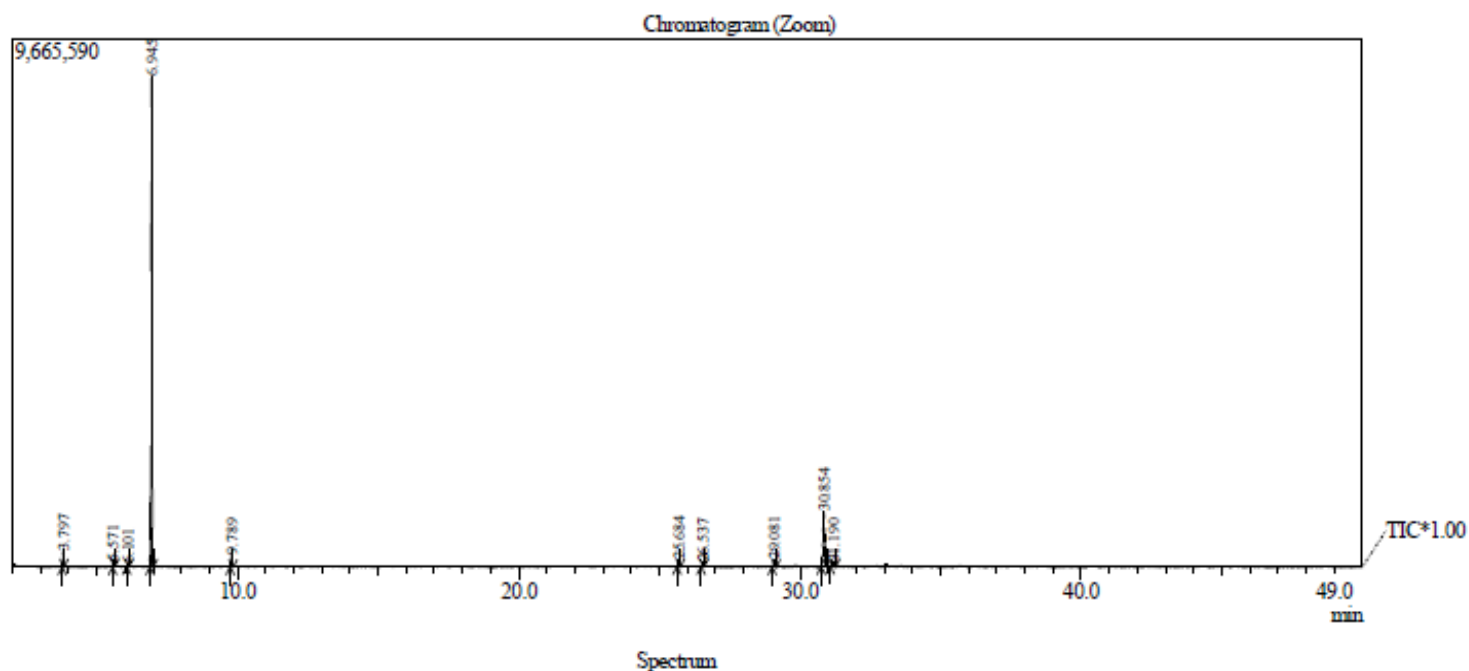


Figure 63: GC/MS spectrum for sample 45

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.799	3.760	3.835	461512	1.82	336964	3.07	1.37		Toluene
2	5.571	5.550	5.660	265170	1.04	131004	1.19	2.02		
3	6.103	6.065	6.135	120557	0.47	68045	0.62	1.77		Ethylbenzene
4	6.947	6.880	7.005	17093722	67.25	8549257	77.90	2.00		Styrene
5	9.791	9.745	9.840	510031	2.01	243456	2.22	2.09		.alpha.-Methylstyrene
6	25.686	25.635	25.745	329619	1.30	122028	1.11	2.70		Bibenzyl
7	26.537	26.490	26.605	224762	0.88	79815	0.73	2.82		1,2 diphenylpropane
8	29.083	29.025	29.150	405834	1.60	126194	1.15	3.22		1,3 diphenylpropane
9	30.860	30.750	30.960	4979393	19.59	1151549	10.49	4.32		Dimer
10	31.186	31.075	31.280	630103	2.48	94464	0.86	6.67		
11	33.060	32.980	33.175	399293	1.57	71425	0.65	5.59		
				25419996	100.00	10974201	100.00			

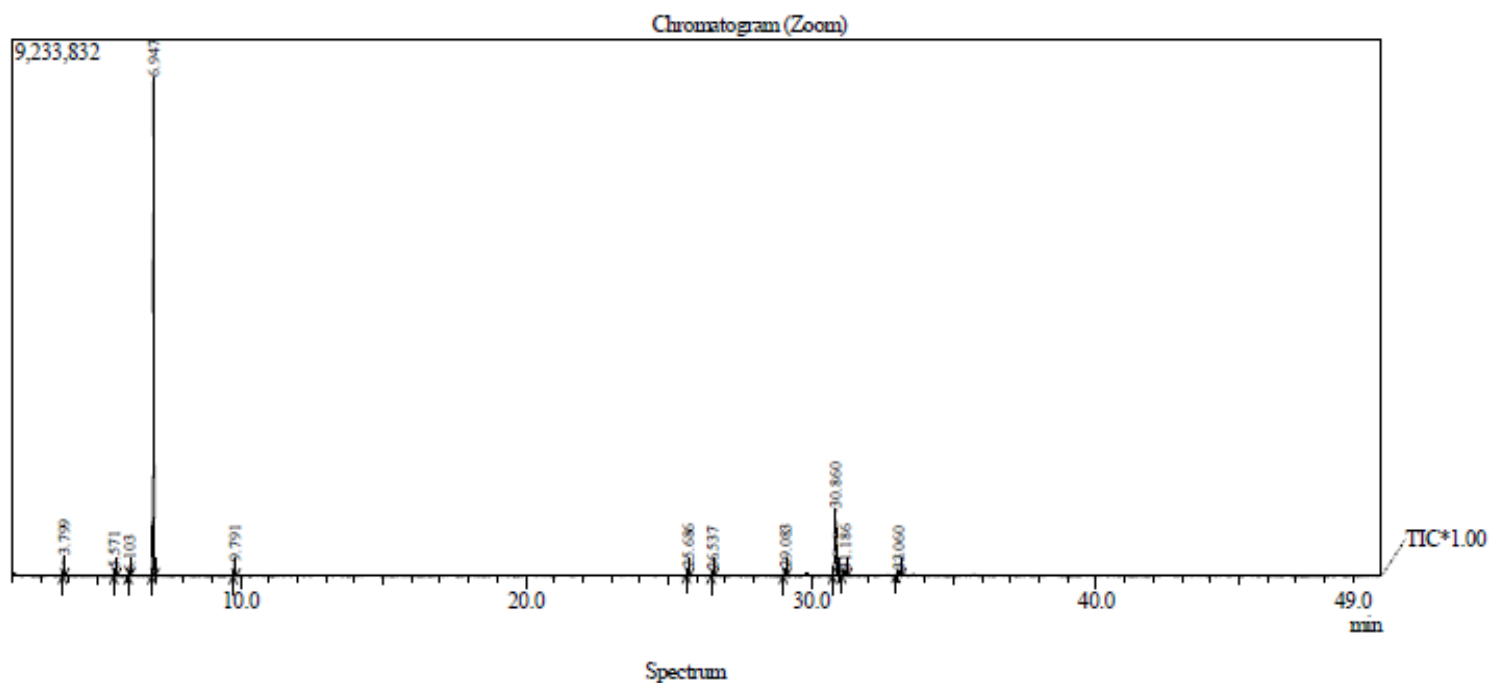


Figure 64: GC/MS spectrum for sample 46

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.799	3.765	3.840	290232	1.26	211229	2.08	1.37		Toluene
2	5.572	5.560	5.660	230781	1.00	111050	1.10	2.08		
3	6.947	6.880	7.010	16245144	70.39	8230046	81.21	1.97		Styrene
4	9.793	9.750	9.845	270142	1.17	128156	1.26	2.11		.alpha.-Methylstyrene
5	25.693	25.640	25.735	255765	1.11	99256	0.98	2.58		Bibenzyl
6	26.544	26.500	26.595	151389	0.66	56848	0.56	2.66		1,2 diphenylpropane
7	29.089	29.030	29.160	335335	1.45	106349	1.05	3.15		1,3 diphenylpropane
8	30.860	30.755	30.960	4880779	21.15	1131474	11.17	4.31		Dimer
9	31.191	31.080	31.275	419015	1.82	59589	0.59	7.03		
				23078582	100.00	10133997	100.00			

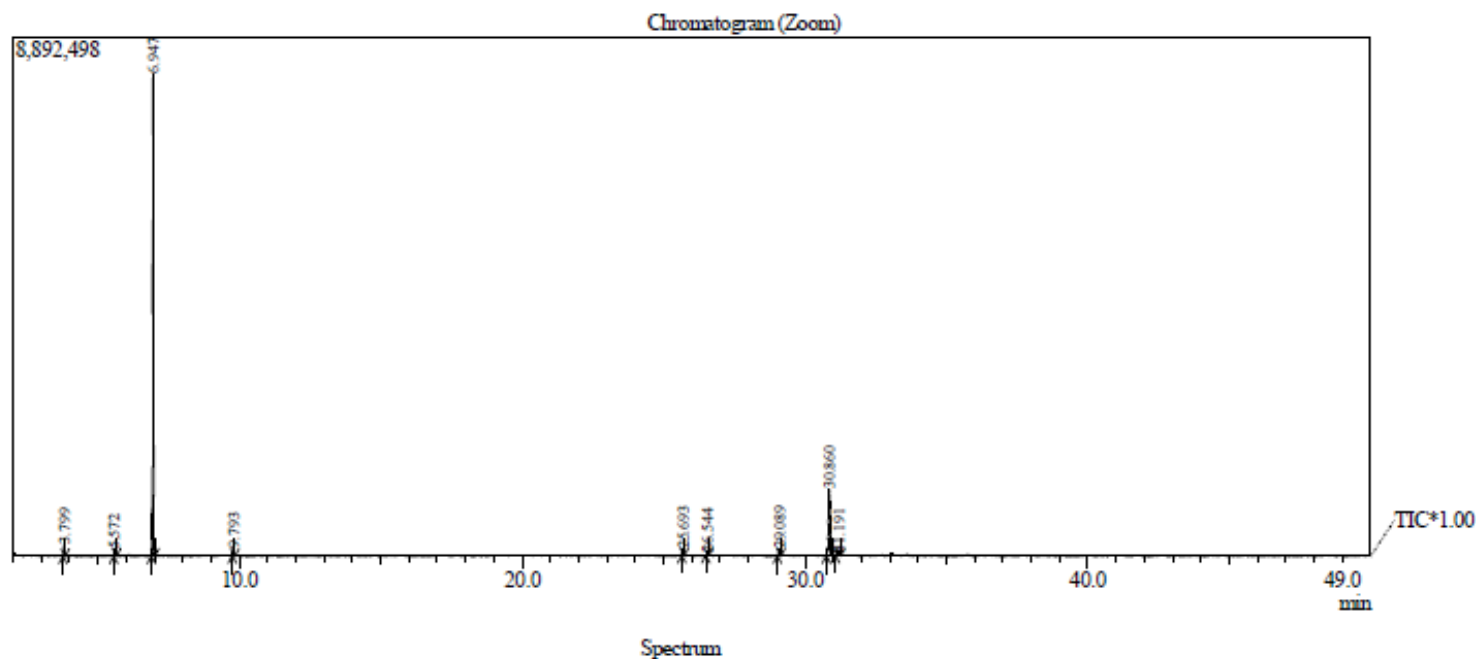


Figure 65: GC/MS spectrum for sample 47

Peak Report TIC										
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.802	3.770	3.835	303978	1.45	223281	2.36	1.36		Toluene
2	5.579	5.555	5.670	207719	0.99	97636	1.03	2.13		
3	6.106	6.070	6.145	108961	0.52	62148	0.66	1.75		Ethylbenzene
4	6.950	6.885	7.010	14978300	71.43	7667827	81.00	1.95		Styrene
5	9.797	9.750	9.845	418860	2.00	206126	2.18	2.03		.alpha.-Methylstyrene
6	25.692	25.645	25.750	234227	1.12	88642	0.94	2.64		Bibenzyl
7	26.545	26.500	26.590	147472	0.70	56457	0.60	2.61		1,2 diphenylpropane
8	29.090	29.025	29.150	287205	1.37	87848	0.93	3.27		1,3 diphenylpropane
9	30.863	30.755	30.965	3900161	18.60	916455	9.68	4.26		Dimer
10	31.197	31.095	31.285	382697	1.83	59747	0.63	6.41		
				20969580	100.00	9466167	100.00			

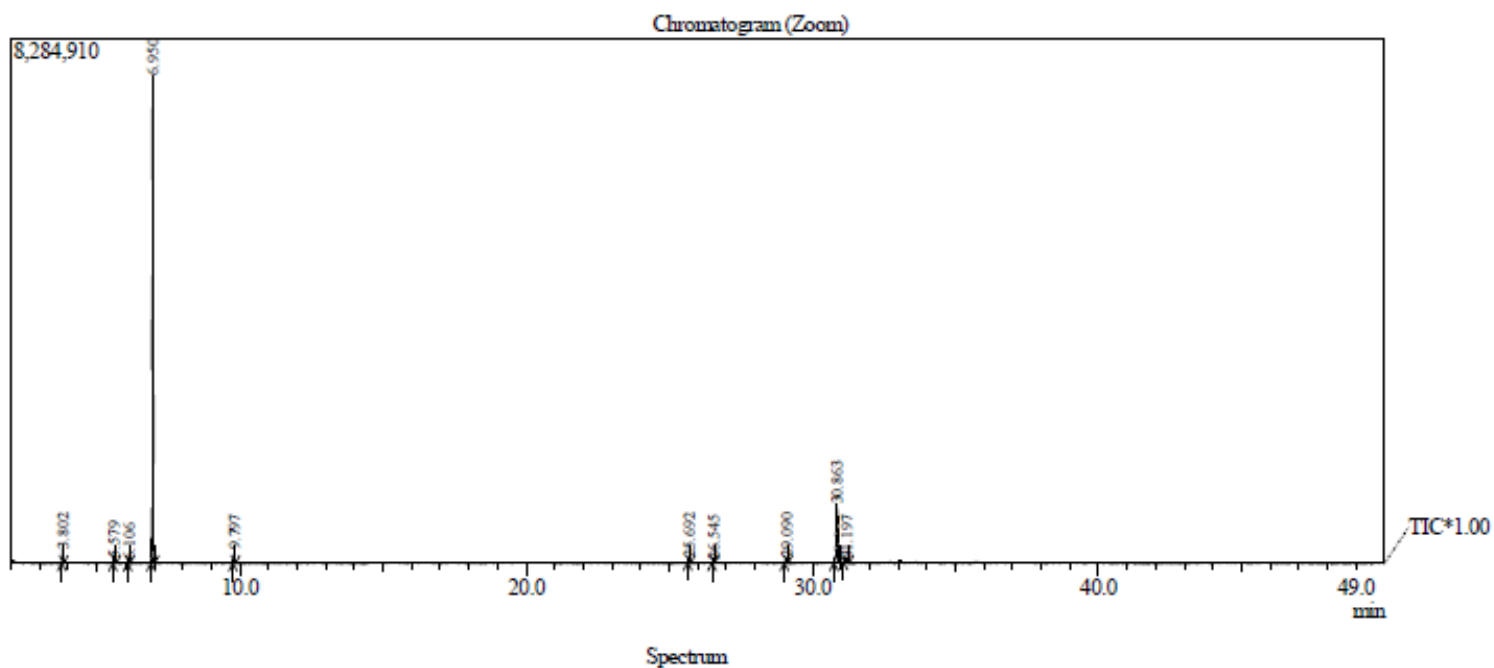


Figure 66: GC/MS spectrum for sample 48

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.805	3.765	3.840	590452	2.09	433105	3.53	1.36		Toluene
2	5.577	5.565	5.645	239996	0.85	127590	1.04	1.88		
3	6.110	6.070	6.150	186449	0.66	103999	0.85	1.79		Ethylbenzene
4	6.957	6.890	7.015	19213052	67.94	9592325	78.22	2.00		Styrene
5	9.799	9.750	9.850	707718	2.50	339238	2.77	2.09		.alpha.-Methylstyrene
6	29.095	29.030	29.170	803095	2.84	244531	1.99	3.28		1,3 diphenylpropane
7	29.764	29.720	29.810	134872	0.48	46664	0.38	2.89		
8	29.870	29.810	29.930	233209	0.82	70211	0.57	3.32	V	
9	30.871	30.765	30.985	4539010	16.05	1039635	8.48	4.37		Dimer
10	31.210	31.095	31.295	679244	2.40	116506	0.95	5.83		
11	33.071	32.975	33.205	950572	3.36	149300	1.22	6.37		
				28277669	100.00	12263104	100.00			

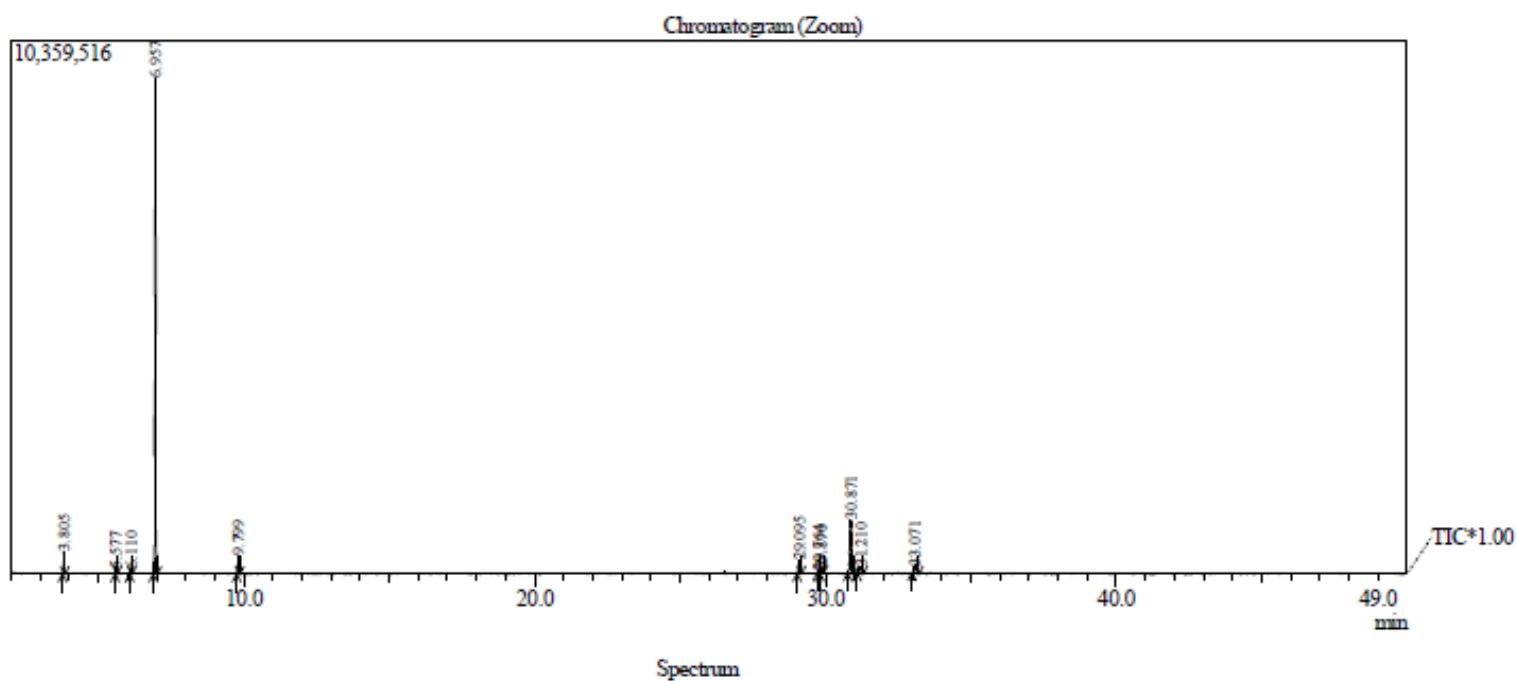


Figure 67: GC/MS spectrum for sample 56

Peak Report TIC													
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name			
1	3.811	3.775	3.850	531287	1.59	394586	3.12	1.35		Toluene			
2	5.586	5.560	5.660	219919	0.66	117018	0.93	1.88					
3	6.116	6.080	6.170	217496	0.65	118283	0.94	1.84		Ethylbenzene			
4	6.964	6.900	7.025	17378550	51.93	8675016	68.57	2.00		Styrene			
5	9.809	9.760	9.860	922949	2.76	447146	3.53	2.06		.alpha.-Methylstyrene			
6	25.619	25.575	25.670	166429	0.50	60969	0.48	2.73					
7	25.716	25.670	25.775	109812	0.33	41502	0.33	2.65	V	Bibenzyl			
8	26.499	26.455	26.535	85476	0.26	36180	0.29	2.36					
9	29.095	29.010	29.200	1782410	5.33	390861	3.09	4.56		1,3 diphenylpropane			
10	29.770	29.700	29.820	309853	0.93	75220	0.59	4.12					
11	29.878	29.820	29.945	502066	1.50	128083	1.01	3.92	V				
12	30.889	30.765	30.990	7268315	21.72	1567030	12.39	4.64		Dimer			
13	31.221	31.090	31.330	1824991	5.45	278227	2.20	6.56					
14	33.119	32.985	33.255	2147675	6.42	320351	2.53	6.70					
				33467228	100.00	12650472	100.00						

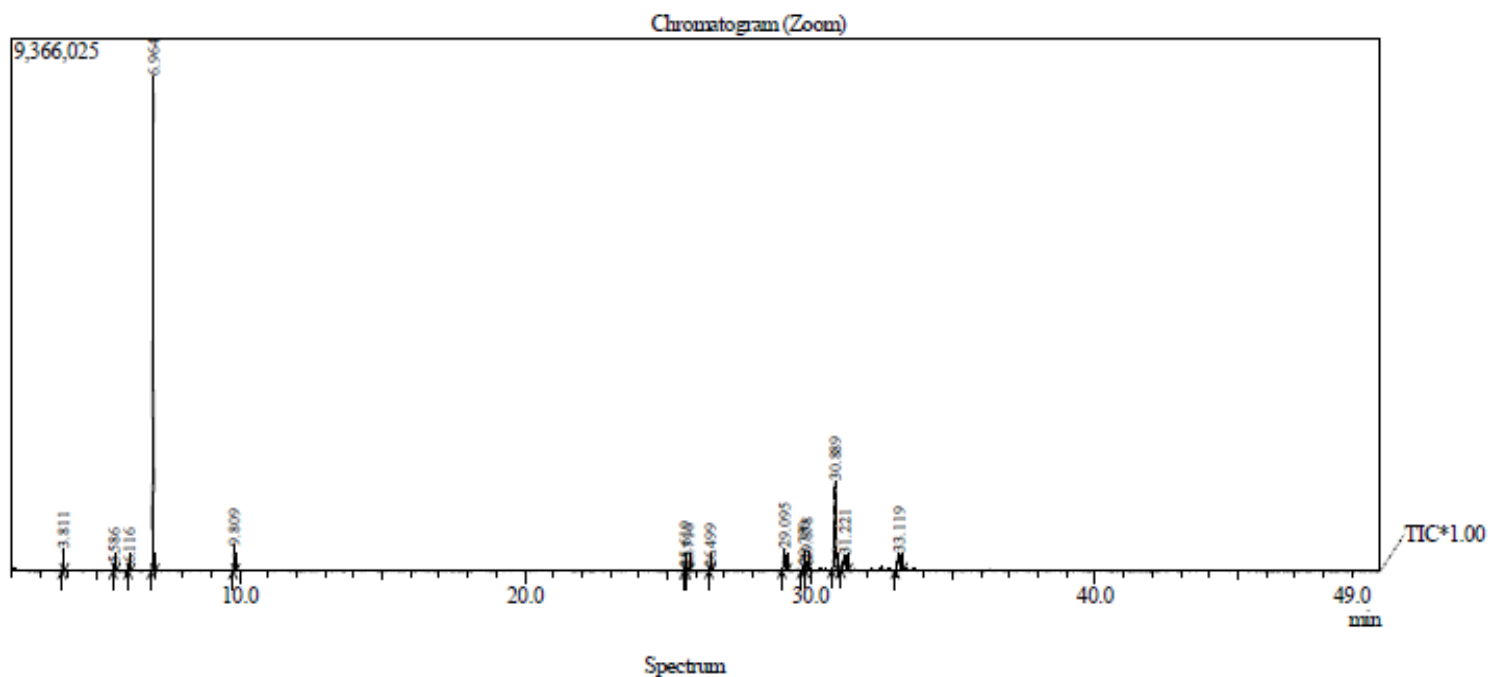


Figure 68: GC/MS spectrum for sample 57

Peak Report TIC												
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name		
1	3.818	3.785	3.855	363660	1.66	260889	2.54	1.39		Toluene		
2	5.596	5.570	5.670	211112	0.96	110737	1.08	1.91				
3	6.125	6.080	6.170	690107	3.15	385295	3.76	1.79		Ethylbenzene		
4	6.971	6.915	7.025	15576586	71.17	7982732	77.81	1.95		Styrene		
5	8.003	7.965	8.045	88057	0.40	45942	0.45	1.92				
6	9.819	9.765	9.875	1048075	4.79	502005	4.89	2.09		.alpha.-Methylstyrene		
7	25.722	25.685	25.775	87677	0.40	33838	0.33	2.59		Bibenzyl		
8	26.574	26.540	26.630	75656	0.35	30007	0.29	2.52		1,2 diphenylpropane		
9	29.121	29.055	29.195	612169	2.80	186197	1.82	3.29		1,3 diphenylpropane		
10	29.898	29.850	29.955	125596	0.57	39528	0.39	3.18				
11	30.887	30.800	30.995	2232020	10.20	523301	5.10	4.27		Dimer		
12	31.230	31.175	31.315	336531	1.54	80085	0.78	4.20				
13	33.113	33.035	33.215	438446	2.00	78159	0.76	5.61				
				21885692	100.00	10258715	100.00					

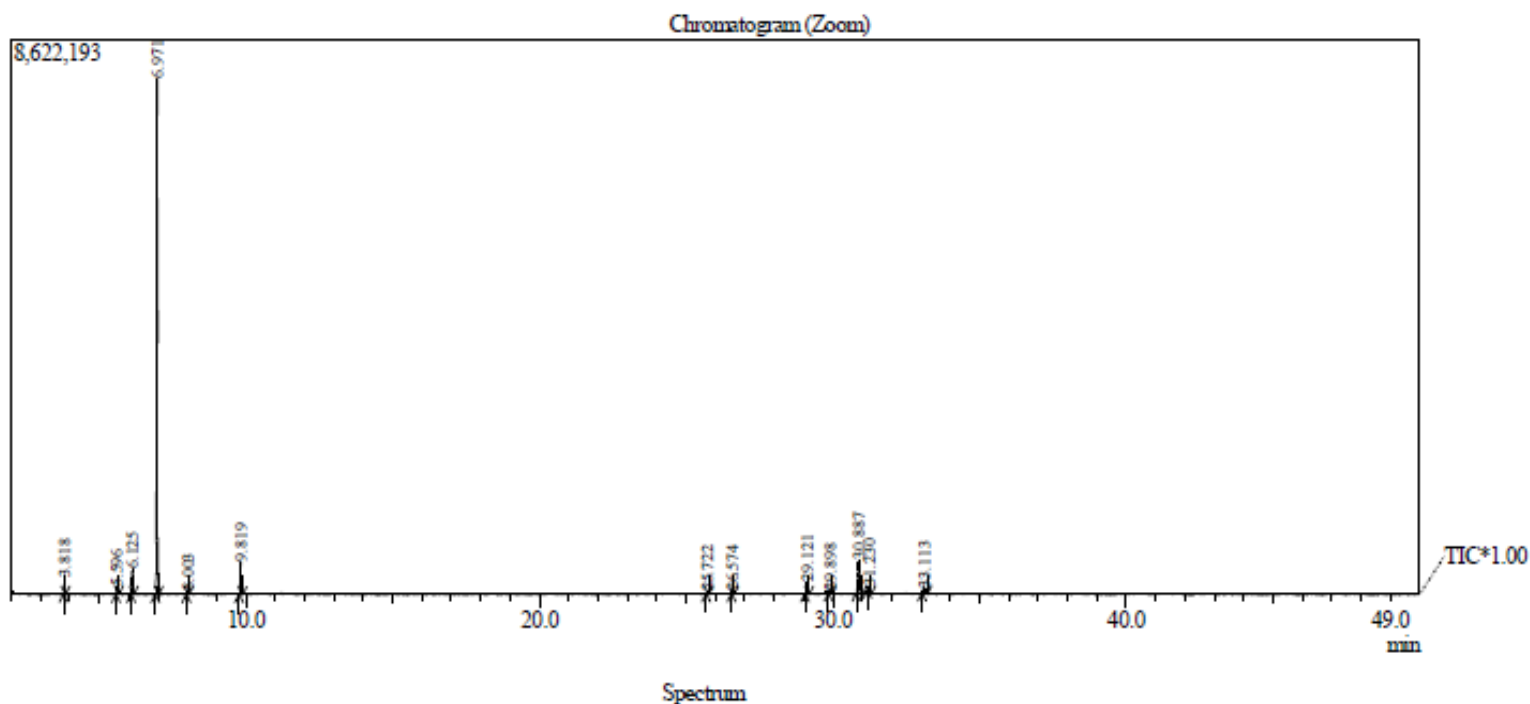


Figure 69: GC/MS spectrum for sample 58

Peak Report TIC											
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name	
1	3.818	3.785	3.850	174876	1.26	124481	2.08	1.40		Toluene	
2	5.596	5.580	5.660	193880	1.40	106651	1.78	1.82			
3	6.127	6.090	6.170	177579	1.28	102800	1.72	1.73		Ethylbenzene	
4	6.965	6.910	7.020	8109957	58.40	4317291	72.07	1.88		Styrene	
5	9.818	9.770	9.870	476616	3.43	223854	3.74	2.13		.alpha.-Methylstyrene	
6	29.118	29.050	29.185	859582	6.19	260731	4.35	3.30		1,3 diphenylpropane	
7	29.789	29.735	29.840	172990	1.25	53568	0.89	3.23			
8	29.902	29.840	29.950	226863	1.63	57798	0.96	3.93	V		
9	30.010	29.950	30.050	128481	0.93	31109	0.52	4.13	V		
10	30.888	30.795	30.985	1974129	14.22	467771	7.81	4.22		Dimer	
11	31.239	31.120	31.325	878792	6.33	158797	2.65	5.53			
12	33.106	33.030	33.235	513394	3.70	85192	1.42	6.03			
				13887139	100.00	5990043	100.00				

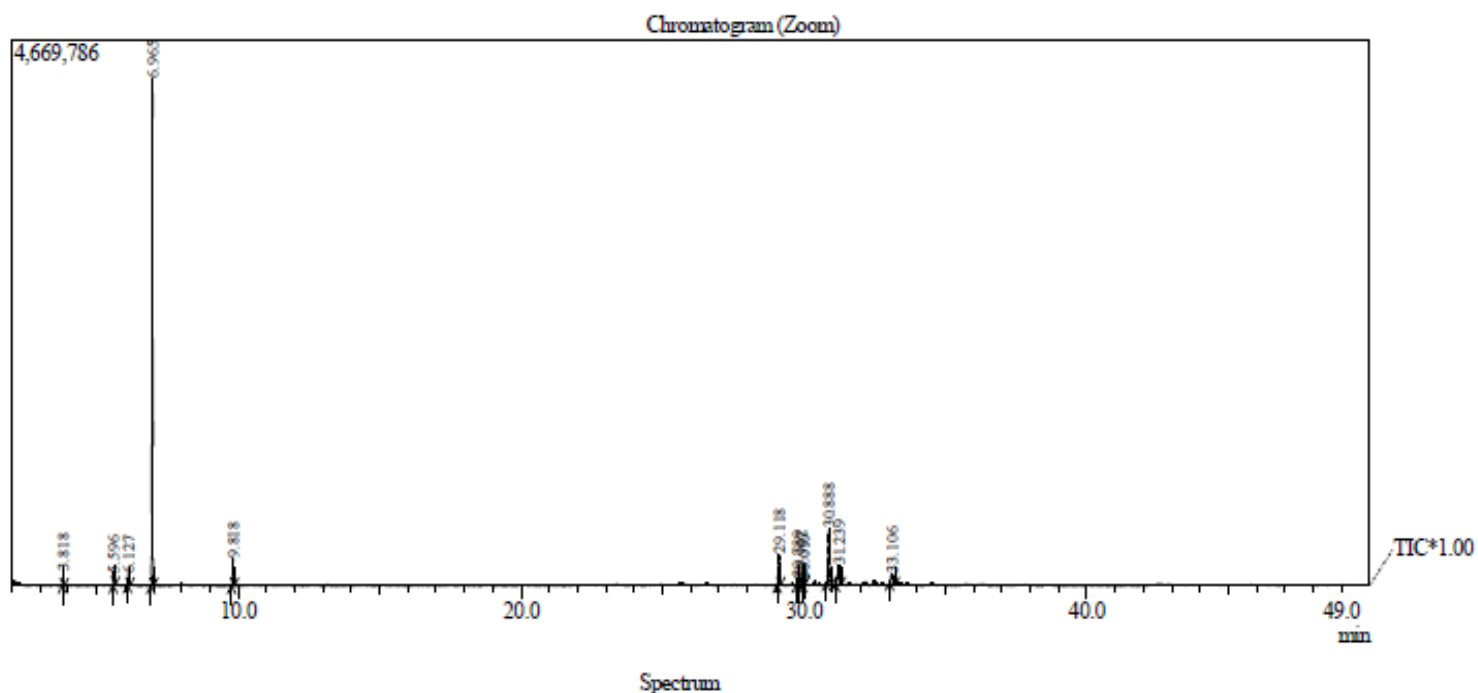


Figure 70: GC/MS spectrum for sample 59