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Abstract:

Recycling of scrap tires has become an increasingly problematical environmental issue. In the United States alone, scrap tires generated has reached an amount of 2 million tons per year. Although these tires contain many useful and valuable products, approximately 70% are disposed of in landfill sites, open dumps, or are stockpiled. Pyrolysis permits a method of separating the hydrocarbon oils and high grade steel. Although current methods of pyrolysis permit the production of hydrocarbons such as limonene, the low yield of valuable compounds limits the economics of the process. Modeling the chemistry of pyrolysis using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR) indicates that two energy dependent reaction mechanisms exist. One being a radical cation mechanism and the other a low energy dimerization mechanism. Based on proposed mechanisms, a pyrolysis method that increases the amount of condensable limonene produced compared to conventional techniques has been demonstrated. It has been determined that the amount of limonene produced during pyrolysis can be increased by decreasing the reactor residence time of isoprene gas, which is produced during the thermal degradation of polyisoprene rubber. This reaction can be achieved by using a perforated vessel which permits rapid condensation to occur and therefore decreases the amount of soot and environmentally hazardous products produced.

INTRODUCTION

Estimates of the generation of scrap tires produced in the United States are on the order of 2 million tons per year (1). Although these tires contain a high percentage of useful hydrocarbons, steel and carbon black, approximately 70% are disposed of in landfill sites, open dumps, or stockpiled. These practices result in serious environmental problems as well as losing the potential economic value of residual hydrocarbons and steel. Because tires do not degrade, they are not good candidates for landfill, and open dumping may result in accidental fires which produce high pollution emissions. Other common fates include tire shredding for combustion or as a additive to road asphalt. While these approaches provide a simple method of waste reduction, air emission concerns are inherent and optimal recovery of the energy and chemical materials is not obtained.

Recently, pyrolytic recycling of scrap tire (*thermal decomposition in the absence of O₂*) is receiving renewed interest because of its ability to produce hydrocarbon oils that can be used as fuel additives. These hydrocarbons typically have high energy content on the order of 40-50 MJ/kg (*1700 BTU/lb*) (2). In addition, pyrolysis also permits the recovery of the high grade steel and carbon in the form of smokeless fuel, carbon black, or activated charcoal. A recent evaluation of pyrolytic recycling of scrap tires indicates that it can be an economically viable process if marketable products could be collected (3).

Due to the economic and environmental attractions, a number of bench scale and pilot studies for tire pyrolysis have been recently reported (3,4,5,6). These systems typically use inert atmospheres and decompose the rubber at temperatures ranging from 700°-900°C. Under these conditions, the maximum collectable yield of the hydrocarbon product is generally only 30% of the tire mass(7). However, when the temperature was decreased to 500°-700°C, the yield of hydrocarbon oil was increased to 40-50% of the tire mass (2).

Although the reduction of temperature permits both a savings in the process energy required and an increase in the amount of condensable hydrocarbon, low temperature pyrolysis also produces a viscous mixture of high molecular weight carbon compounds (C₁₀-C₂₀) having a

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high C:H ratio (*e.g. creosote and polycyclic aromatics*). These compounds can reduce the effectiveness of pyrolysis resulting in poor thermal degradation of the rubber and making product reclamation difficult if not impossible. In addition, the difficulty in removing these hydrocarbons often leads to the build up of combustible materials in pyrolysis ovens.

One material of interest that is produced in high quantities during the pyrolytic decomposition of tires is limonene. Limonene has many extremely fast-growing industrial applications. It is used in the formulation of industrial solvents, resins and adhesives and as a dispersing agent for pigments. It is also used as a feedstock for the production of fragrances and flavorings. Limonene is biodegradable, a natural solvent, environmentally safe with excellent solvency, rinseability and high wetting, penetrating and detergent properties(8,9). It has been used in a wide range of applications including water-based degreasers, natural lemon scented all-purpose cleaners, hand cleaners and replacements for chlorofluorocarbon solvents to clean electronic circuit boards.

Other products found in the liquid fraction are not analogs of isoprene and are produced by thermally energetic chemical reactions in the reactor oven. These compounds consist of a mixture of aromatics and aliphatics which are not easily recyclable. Therefore, optimization of the chemical reaction occurring during pyrolysis which produce valuable compounds, such as limonene, could enhance the economics of recycling scrap tires.

An understanding of the reaction mechanisms that lead to the formation of these hydrocarbons allows for a better understanding of the chemistry of pyrolysis. This is necessary in order to determine if soot formation can be controlled, or if the products can be produced or put back into the pyrolysis process as fuel for the pyrolysis oven.

Work has been done by Pakdel (8) utilizing Fourier transform infrared spectroscopy (FT-IR) and gas chromatography mass spectrometry (GC-MS) in order to analyze the liquid fraction of pyrolysis products. Although this method provides a clear picture of the product distribution, it is too slow when analyzing reactions which occur in the gas phase. No information regarding the mechanism of gas phase product formation can be provided.

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Because of instrumental limitations, the chemistry of the thermal degradation of scrap tires is not greatly understood. It is therefore nearly impossible to optimize the production of the economically viable compounds such as limonene. If the mechanism of product formation were understood, catalysts and or changes to the reaction environment may be produced to optimize the production of valuable chemicals.

Due to the high energy present during pyrolysis, the likely reaction mechanism is either a neutral free radical or ion molecule reaction(10,11). These reactions proceed with high reaction rates and are therefore similar to ion-molecule reactions occurring in the gas-phase. Fourier transform ion cyclotron mass spectroscopy(FT-ICR MS) provides an excellent analytical technique which gives quantitative and qualitative information regarding gas phase ion/molecule reaction pathways. Experiments are conducted in a low pressure atmosphere ca. 2×10^{-7} torr, which maintains a low concentration and collision rate. Under these conditions, the reaction products and pathways of fast reactions can be observed. This allows gas phase reactions to be closely monitored to gain understanding of the mechanisms of product formation. This approach has been used by John Eyler and others, to determine the reaction mechanism of combustion processes using a gas-phase ion molecule model(16,17,18). The benefits of FT-ICR and its analytical capabilities regarding ion molecule reactions in the gas phase have been discussed elsewhere (12,13,14,15,16).

Through the use of the FT-ICR, a mechanism of soot formation during the pyrolytic decomposition of tires, has been proposed. Based on this proposed mechanism a new reactor design has been constructed and tested. Using this approach, the production of limonene has risen above 90% of the liquid fraction, which is the highest percentage reported to date. This is approximately 45% of the tire by weight. With this new product distribution, the recycling of tires by pyrolysis becomes economically viable.

Experimental

Three different reactors were built and were used to thermally decompose scrap tire

rubber and collect the liquids made from them. The first reactor built was initially used to investigate the possibility of modeling the pyrolysis process on the bench scale system (figure 1). This reactor was also used to study the temperature effects on the pyrolysis process and to determine the differing product ratios of those effects. The reactor was based on a preparative flash vacuum pyrolysis apparatus. A 30 gram piece of scrap tire was placed in a quartz pyrolysis tube and thermally decomposed in a Lindburg furnace. The products were collected in a liquid nitrogen cold trap which was allowed to equilibrate to room temperature following product collection. Upon equilibration, the gaseous products were collected in a gas sampling bulb. Separate analysis of the liquid fraction and gaseous products was carried out using FT-ICR. Additional analysis of the liquid product fraction was performed using GC/MS.

The second reactor, built to study the effects of gas constriction during product formation, was made of a $\frac{1}{2}$ " dia. by 36" long copper tubing with $\frac{1}{8}$ " dia. holes drilled in the furnace region, four holes at every $\frac{1}{2}$ " interval (figure 2). This tubing was surrounded by pyrex tubing with a diameter of $1\frac{1}{2}$ " and was 30" long. The tire pieces used were predominately natural or polyisoprene rubber taken from the lower sidewalls of scrap automobile tires (approximately $\frac{1}{2}$ " X $\frac{1}{2}$ " and $\frac{1}{4}$ " thick). These tire pieces were placed between the copper tubing and the pyrex wall in the region of the drilled holes. The heater was a Lindberg tube furnace. The temperature of the oven was brought up to 400°C before the reactor tube was placed into the oven. After 5 min. of thermal decomposition the reactor tube was removed. Two liquid samples were collected from this reactor. The liquid that was created inside of the copper tubing and the liquid that was created between the copper tubing and the pyrex glass wall.

A third bench scale reactor was constructed (see figure 3) to optimize limonene production based on the proposed mechanism. The reactor consisted of an open heater coil located in a cooling jacket. The cooling jacket was initially cooled with liquid nitrogen to ensure all resulting products would be condensed for analysis. A vacuum environment was created using a Welch 1.5Amp. vacuum pump to displace the atmosphere. Furthermore, the heater coil was insulated with Sauereisen ceramic paste to reduce any effects of the nichrome on the ensuing

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chemistry. The wire was wound in a spiral orientation with a 1/2" dia., 1/8" in between each wind and was approximately 5" in length. The nichrome wire was hooked up to a Fisher variable 120V auto transformer (variac) and the temperature was monitored using a n/p thermocouple. Six 10 gram samples of scrap tires were loaded into the reactor (60-70 grams total) and temperature was brought up to approximately 250°C and from this point, the tires were allowed to decompose for 5 minutes. During this 5 minutes the temperature was ramped at a constant rate to approximately 425°C. After 5 minutes, the variac was turned off and the liquid was collected.

The liquid portions retrieved from the reactors were cleaned as follows: first, a small amount of methylene chloride was added to the liquid samples to extract both polar and non-polar components. This solution was placed in a separatory funnel and agitated. The organic layer was separated from the nonorganic and polar organic layers. The organic sample was filtered to remove any solid particulate from the sample using a 50ml burette filled with 100-200 mesh type 60A special Mallinckradt silicar silica gel. The sample was loaded on the buret and washed using additional methylene chloride. The resultant filtrate was rotary evaporated to remove the excess solvent. These oils were then added to either methylene chloride or trichlorotrifluoroethane solvents for the gas chromatographic/ mass spectrometry analysis.

Gas chromatographic/mass spectrographic analysis (GC/MS) was performed on a Finnigan MAT ITD 800 GC/MS and associated vacuum system controlled by an IBM compatible PC 386. A 30 meter DB5 phase column with a 0.25 mm I.D. was used in the chromatographic separation. The temperatures of the injection and detection ports were both 250c with Helium carrier gas. The mass spectra were recorded at an ionizing energy of 70eV. Mass spectral data and chromatographic peak areas were determined using the integrated data system. Identification of the compounds was performed using a NIST library and confirmed by interpretation of the fragmentation data.

Gas phase reaction experiments were performed on an IonSpec OMEGA 50 Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR) with a high field Walker Scientific electromagnet held at 1.03 Tesla. Background pressures of $8.5 * 10^{-10}$ torr were

maintained in the vacuum system analyzing chamber by a Blazers 330 liter/second turbomolecular pump backed by an Alcatel direct drive roughing pump. Gaseous reagents were set and maintained using a Varian leak valve. Experimental pressures ranging from 2×10^{-7} - 3×10^{-7} torr in the 5 cubic centimeter analyzer cell were measured using a Bayard-Alpert type ionization gauge. The gaseous samples were ionized by electron impact from a 20 millisecond electron beam at an electron energy of 60-70 eV. The filament current ranged from 1.2 - 1.6 μ A. Data was collected using the IonSpec OMEGA 50 data system.

Results and discussion:

During preliminary experiments a small tube furnace was used to thermally decompose the sample to determine the distribution of liquids, solids and gases formed during the vacuum pyrolysis process. It was determined that vacuum pyrolysis at 396°C gives 3 phases. First, a solid phase which represents ca. 38% in weight of the pyrolysis products, essentially constituted of activated carbon. Second, a liquid phase which represents ca. 60% of the bulk product. Finally, the gaseous phase, which represented only ca. 2% of the bulk. This phase comprises the likely precursors for the gas phase reactions leading to the products found in the liquid phase, which is of the primary interest.

Results from the GC/MS analysis of the liquid fraction of pyrolysis products after equilibrium of the liquid trap are found in Table 1. The mixture consists of a complicated distribution of many products, largely aliphatic C₈-C₁₀ isomers. Limonene (molecular weight 136), the major product of vacuum pyrolysis comprises of approximately 50% of the total liquid product distribution, which can be explained by the dimerization of isoprene. The other half of the distribution is comprised of unsaturated hydrocarbons such as cyclohexene, toluene, and ethyl benzene. These later compounds are similar to the soot compounds produced during the combustion or open burning process. Combustion reactions are predominately high energy reactions similar to the ion molecule gas phase reactions associated with the reactions found in the

FT-ICR. During the above tests, it was determined that the product distribution formed during pyrolysis could be modeled using FT-ICR MS(20).

By modeling the products formed during the gas phase reactions, via FT-ICR mass spectrometry, the initial impact spectrum of the pyrolysis products was determined (Figure 4). In the resulting mass spectrum, five important peaks were observed: $C_3H_3^+$ ($m/z=39$), $C_3H_5^+$ ($m/z=41$), $C_3H_8^+$ ($m/z=44$). Although 44 could indicate CO_2 or C_2H_4O , it seems improbable because pyrolysis is thermal decomposition in the absence of oxygen. Furthermore, isolation of $m/z=44$ produces a hydrocarbon series which is inconsistent with the former compounds. In addition, $C_4H_8^+$ ($m/z=56$) and $C_5H_7^+$ ($m/z=67$) resulting from C_5H_8 by loss of a proton were observed. At a reaction time of 2.5 seconds, extinction of ions having m/z 44 and appearance of $C_5H_9^+$ ($m/z=69$), $C_6H_9^+$ ($m/z=81$), $C_7H_{11}^+$ ($m/z=95$) and $C_8H_{11}^+$ ($m/z=107$) was observed (Figure 5). These peaks correspond to the low molecular weight unsaturated hydrocarbons found in the liquid fraction. It is important to note that the largest peak in the reaction product spectrum occurs at m/z 81 which corresponds to gas-phase reaction products that are analogous to the cyclohexene found in the liquid fraction formed during pyrolysis of scrap tire. The good correlation between the products formed from the gas-phase reactions of isoprene compared to the pyrolysis products indicates that the pyrolysis reactions can be effectively modeled in the gas phase (10). These spectra indicate that the reactions which occur during the pyrolysis form these products by gas phase reactions.

These experiments indicate that two energy dependent reaction mechanisms exist. One being a radical cation mechanism and the other a low energy dimerization mechanism. High energy reactions follow a neutral free radical or ion molecule pathway and produce the high C:H ratio (soot) compounds and the low energy dimerization reactions which form the low C:H ratio compounds such as limonene. During pyrolysis both of these mechanisms occur. However, they occur at different rates at the different respective temperatures depending on the location and residence time of the gases within the high temperature region of the oven. The low energy reactions typically occur in the cooler regions at the extremes of the oven where the temperature is

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below 200°C. The high energy reactions occur when the gases formed during pyrolysis have long residence time in the high energy regions of the oven.

The proposed mechanism is summarized in figure 6; poly-isoprene rubber thermally decompose in a B-scission de-polymerization fashion. This decomposition produces the individual isoprene units. At this point individual isoprene molecules are in the gas phase free to react. As the temperature is increased, the high energy mechanism starts to predominate over the low and soot is now being produced at a higher rate. This is because at this point, the high energy regions are predominate in the reactor. As the temperature increases more, the limonene that is being produced or has been produced, starts to decompose or undergoes a reverse Diels alder reaction and reverts back into its individual isoprene units and proceeds via the radical mechanism. Under these conditions soot becomes the predominate product. Ovens which constrict the expansion of gases and therefore increase the residence time within the high temperature region will selectively produce soot like compounds having low C:H ratios.

To test the effects of gas constriction and residence time within the oven on product distribution a second reactor oven was constructed (figure 2). This dual tube arrangement provides the ability to compare different oven constrictions simultaneously. The central tube of the reactor has an open cross sectional area of ca. 5 cm² compared to the open cross sectional area available in the outer tube of ca. 50 cm². Because of the relative open area of the two exit tubes, the expansion of isoprene in the central tube should be more constricted and therefore have a higher residence time in the high temperature region of the oven. The liquid fractions from both of the tubes were collected separately and analyzed using GC-MS. The percent of limonene collected from the exterior tube (A) was determined to be >60% of the liquid fraction compared to ~50% collected form the internal tube (B). It is important to note that the significant increase in the relative amount of limonene collected from the exterior tube which has the larger cross sectional area and therefore shorter residence time of the isoprene subunits in the high temperature regions of the oven. This observation is consistent with the concept that the reaction distribution can be significantly altered if the residence time of the isoprene subunits is reduced by

providing a more rapid transference of the gaseous isoprene into a cooler condensation region. This suggests that the limonene is not a product of high energy gas-phase reactions and must be produced by a different mechanism. Isoprene which quickly expands out into a cooler region of the pyrolysis apparatus can dimerize to form the limonene found in the liquid fraction. Therefore if an apparatus is constructed to provide rapid removal of the isoprene produced during pyrolysis to a cooler condensation region, the amount of limonene produced should be increased, resulting in a more economically viable process.

Liquid samples were collected from the third reactor, an open coil heater(Figure 3) which permits rapid expansion and low residence times in the high energy regions. The resulting chromatogram is shown in figure 7. It is important to note that only one peak is observed at a retention time (r.t.) of 410 (with the exception of the Methylene chloride solvent peak at r.t. 150). The percentage yield of limonene based on this approach has an observed increase of greater than 90%. The elimination of all other components in the mixture is consistent with a selective production of limonene by reducing the residence time of the evolved gases. This approach reduces the high energy reactions and therefore reduces any unwanted side products.

Conclusion

The factors dealing with the recycling of tires through the pyrolytic cycle are not presently economically viable. This is due to the low amounts of profitable chemicals produced in the different systems . To make pyrolytic recycling of tires more economically favorable, either limonene or another economically viable compound will have to be produced in a much higher percentage.

These experiments indicate that the pyrolysis process can be successfully modeled at the bench top level. These results found at the microscale are comparable to Christian Roy's results which were done at the macroscopic scale, indicating that we have modeled pyrolysis at the bench top level. Furthermore, comparison of FT data is also consistent with the bench top data from the reactor and the macroscopic data from Christian Roy's work. Therefore, a gas-phase reaction mechanism effectively models the macroscopic model. This ability to model pyrolysis at the

molecular level lets us study the chemistry of pyrolysis. The extremely good correlation between the gas phase data for the high energy products and those observed by Christian Roy, indicates that our mechanism is consistent with the mechanisms occurring at the macroscopic level.

Using this mechanism and our understanding of the chemistry of pyrolysis, we have designed a new reactor which reduces the residence time of the depolymerization process. These results from this reactor show a dramatic increase in the amount of limonene formed, from 50% to greater than 90% limonene. This increase in the production of limonene greatly improves the economic viability of pyrolysis and makes the pyrolysis of scrap tires an economically viable method of recycling the growing stockpile of scrap tires.

The high limonene content of the oil fraction was associated with the decreased residence time of the isoprene gas in the high temperature areas of the oven during the thermal degradation of polyisoprene rubber. This was achieved by using the coiled heater reactor (figure 3) which permitted rapid condensation to occur and therefore allowed the isoprene gases to dimerize and form limonene. Furthermore, by allowing the above process to take place, the isoprene was not allowed to form radicals thereby forming the unwanted environmentally unfriendly soot products.

The ideas presented here illustrate a pyrolytic method that increases the amount of condensable limonene produced compared to conventional pyrolysis techniques of scrap tire carcasses. The high percentage of limonene in the oil fraction of the scrap tire vacuum pyrolysis will have a positive effect on the economics of the thermal decomposition process. This in turn makes the process of pyrolytic decomposition economically favorable.

Acknowledgments

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Figure 1 Shown is the diagram of the pyrolysis reactor used to determine the differing product ratios, temperature effects on those ratios, and the possibility of modeling the pyrolysis process on the bench top level.

Figure 2 Shown is the pyrolysis reactor used for studying the effects of retention time on the pyrolysis liquid product formation. The different diameters controls the conductance limitation which in turn determines the oven residence time of the released gases.

Figure 3 A diagram of a vented pyrolysis reactor used for the optimization of limonene. The open geometry minimizes the residence time of the released gases therefore minimizing the production of soot.

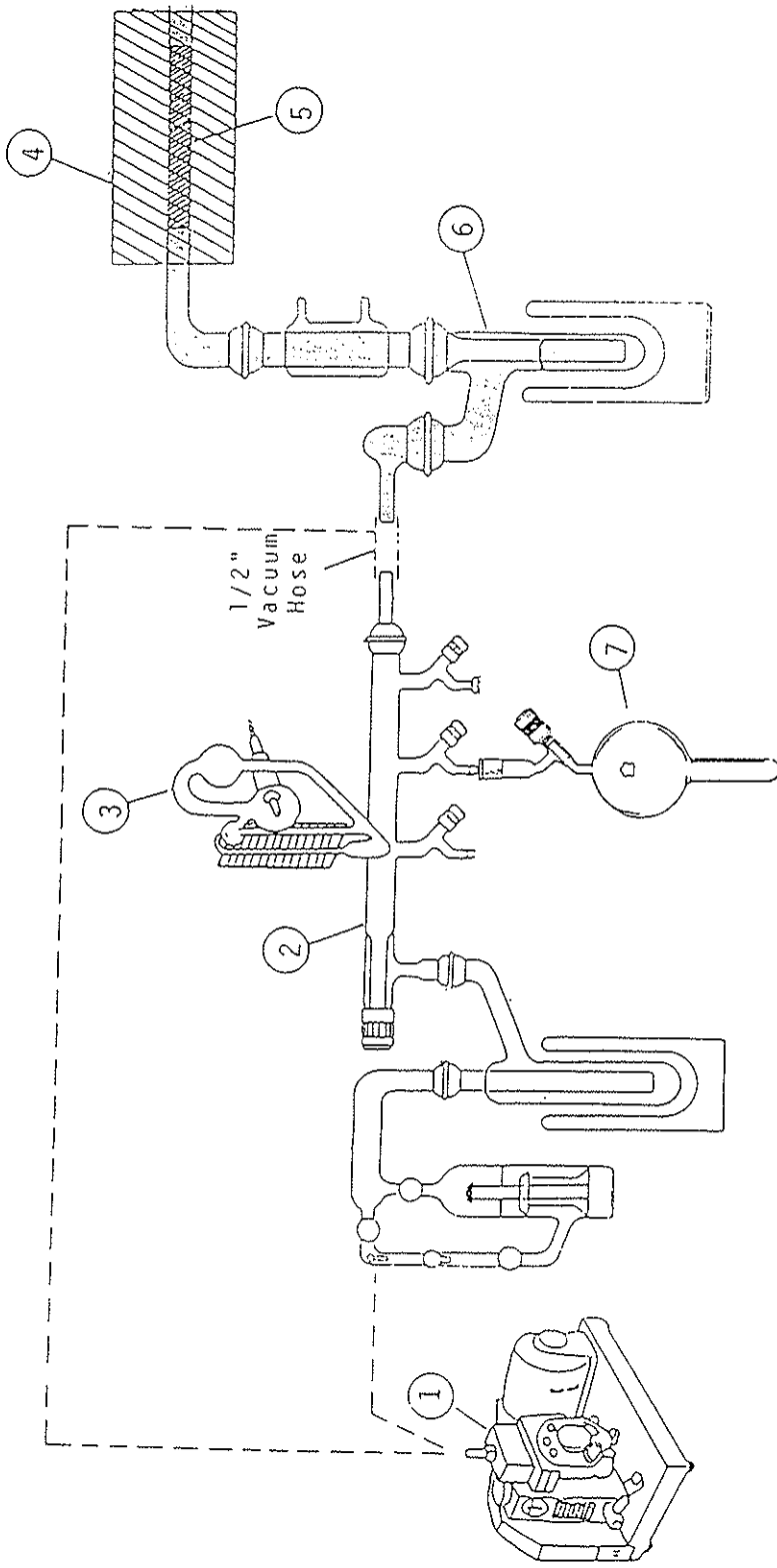
Table 1 Liquid product distribution of the pyrolysis of scrap tires using the reactor from figure 1. Chromatogram and pyrolysis product distribution formed by vacuum pyrolysis of scrap tire

Figure 4 Initial electron impact mass spectrum of the products collected during pyrolysis of scrap tires.

Figure 5 Shown is the spectra of the gas phase reaction products of isoprene following a 2.5 second reaction delay. It is important to note that the peak at m/z 81 corresponds to the molecular weight of cyclohexene, which is found in the liquid fraction of pyrolysis products. Also observed in the spectrum are peaks at 95 and 107 which correspond to the formation of toluene and xylene. This strong correlation between the gas phase reaction products observed in the FT-ICR and the products found during pyrolysis of scrap tires illustrates the ability to model the mechanism of pyrolysis using gas phase methods.

Figure 6 Shown is the proposed mechanism of the depolymerization of polyisoprene rubber and the high and low energy mechanisms which take place during pyrolysis.

Figure 7 Shown is the chromatogram obtained from the liquids collected from the reactor found in figure 3. It is important to note the absence of any peaks other than the limonene peak indicating the selective production of limonene.



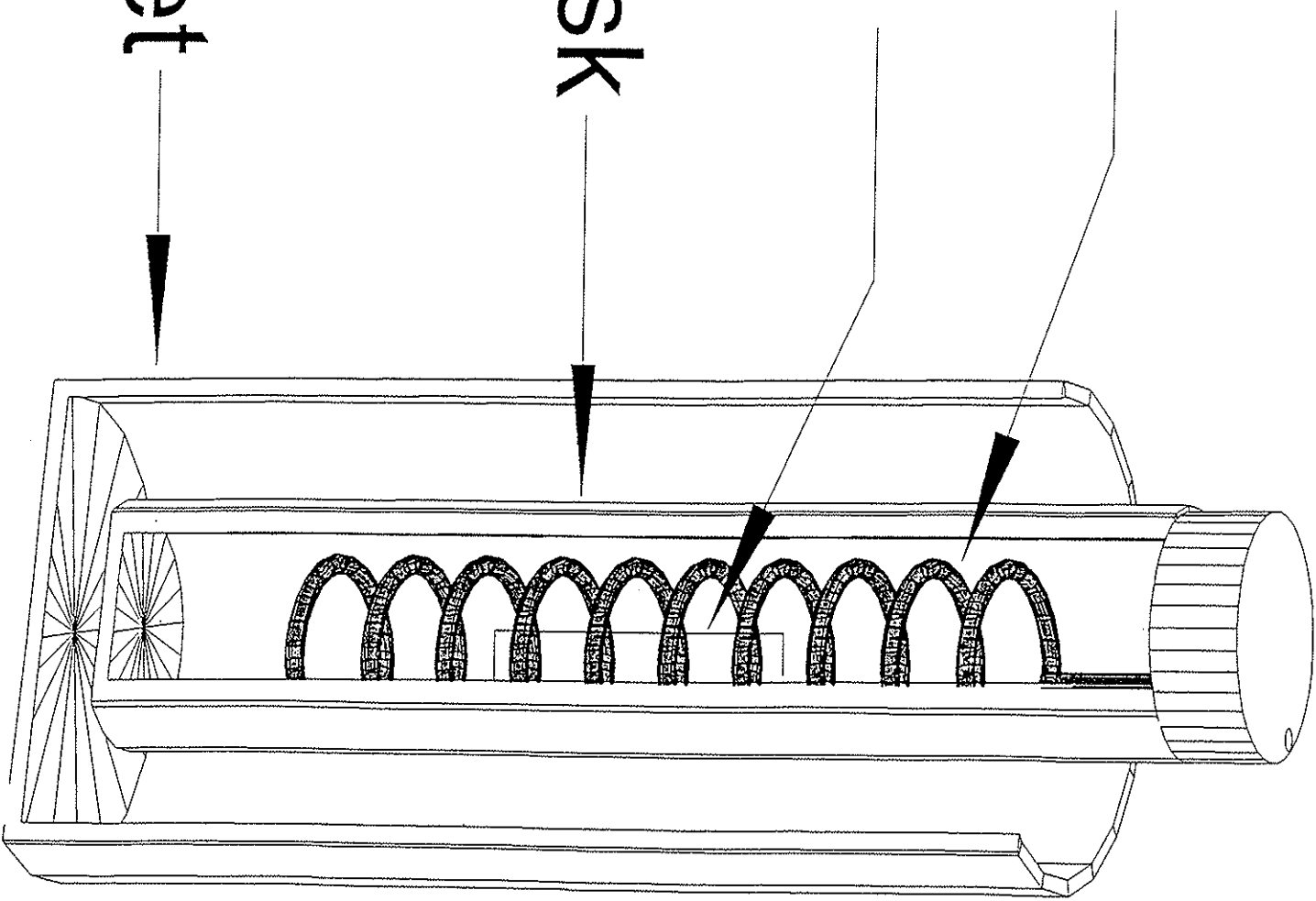
- | | |
|---|---|
| <ol style="list-style-type: none"> 1. 4 cfm Direct drive vacuum pump 2. Vacuum Line 3. Mercury manometer 4. Lindburg tube furnace | <ol style="list-style-type: none"> 5. Quartz sample tube 6. Liquid nitrogen cold trap 7. Gas sampling bulb |
|---|---|

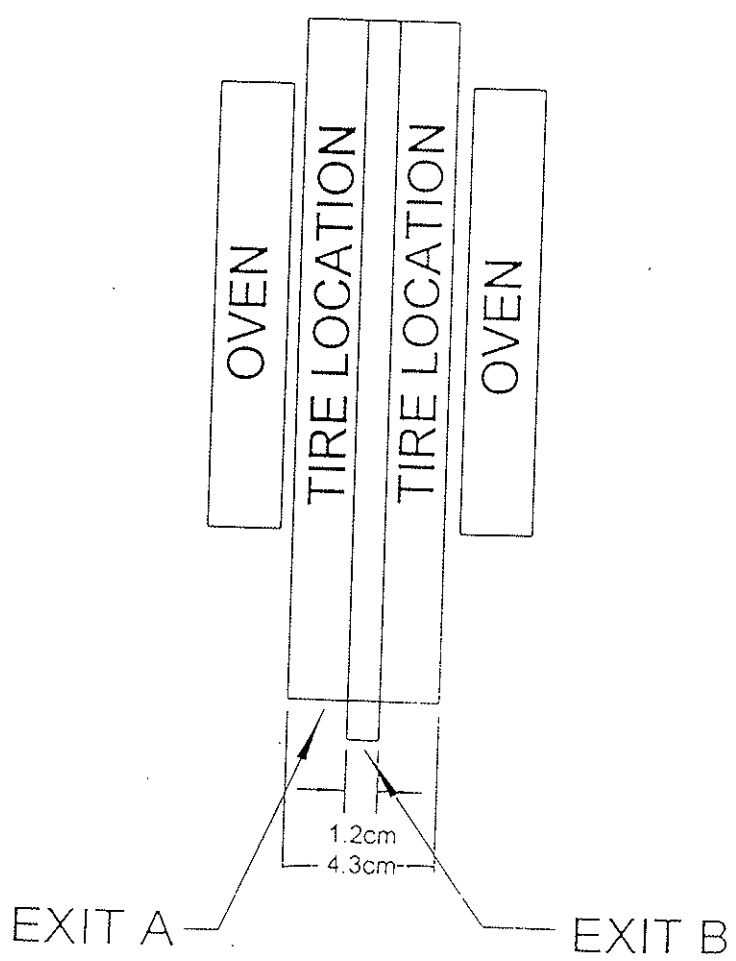
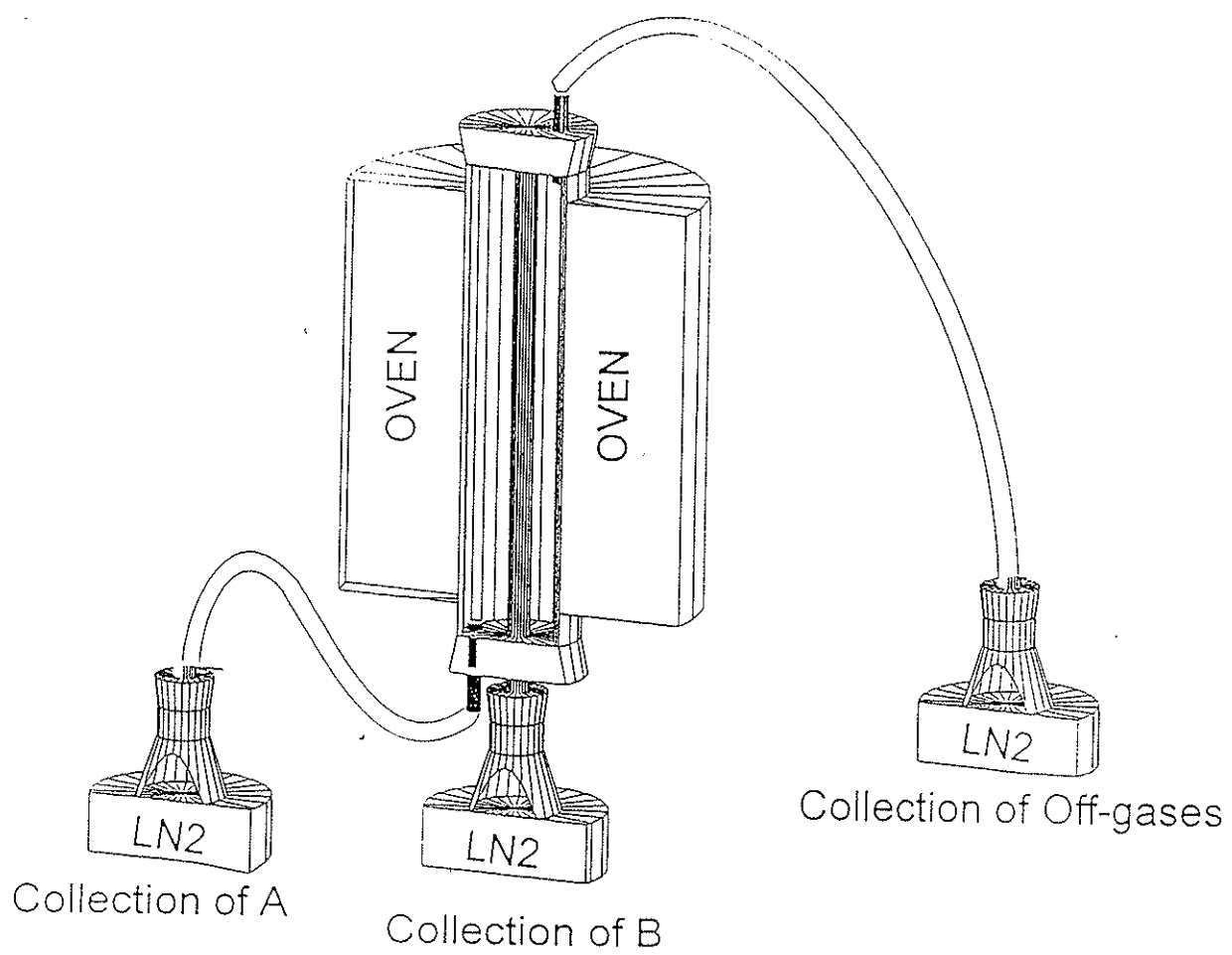
Heater Coil

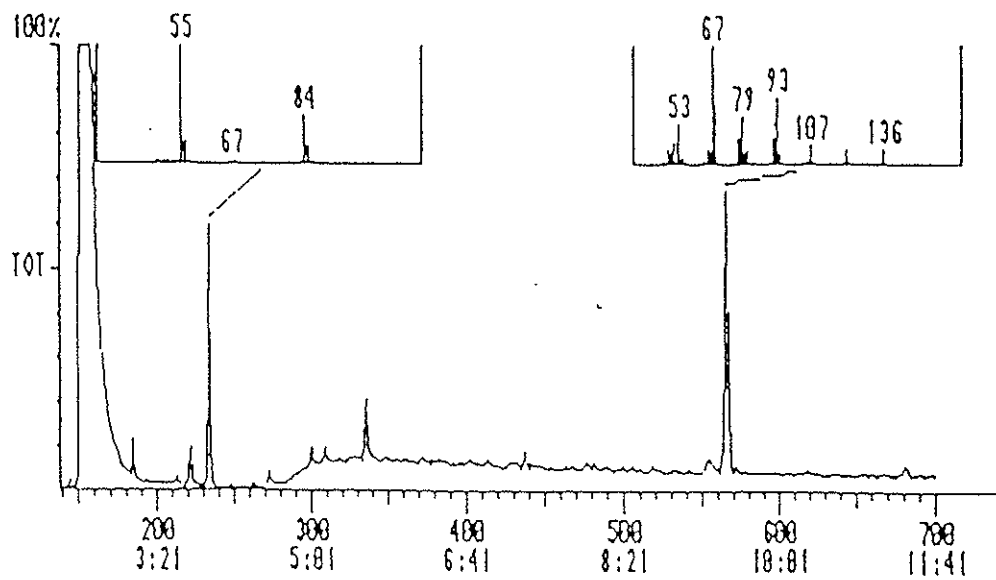
Tire Location

Collection Flask

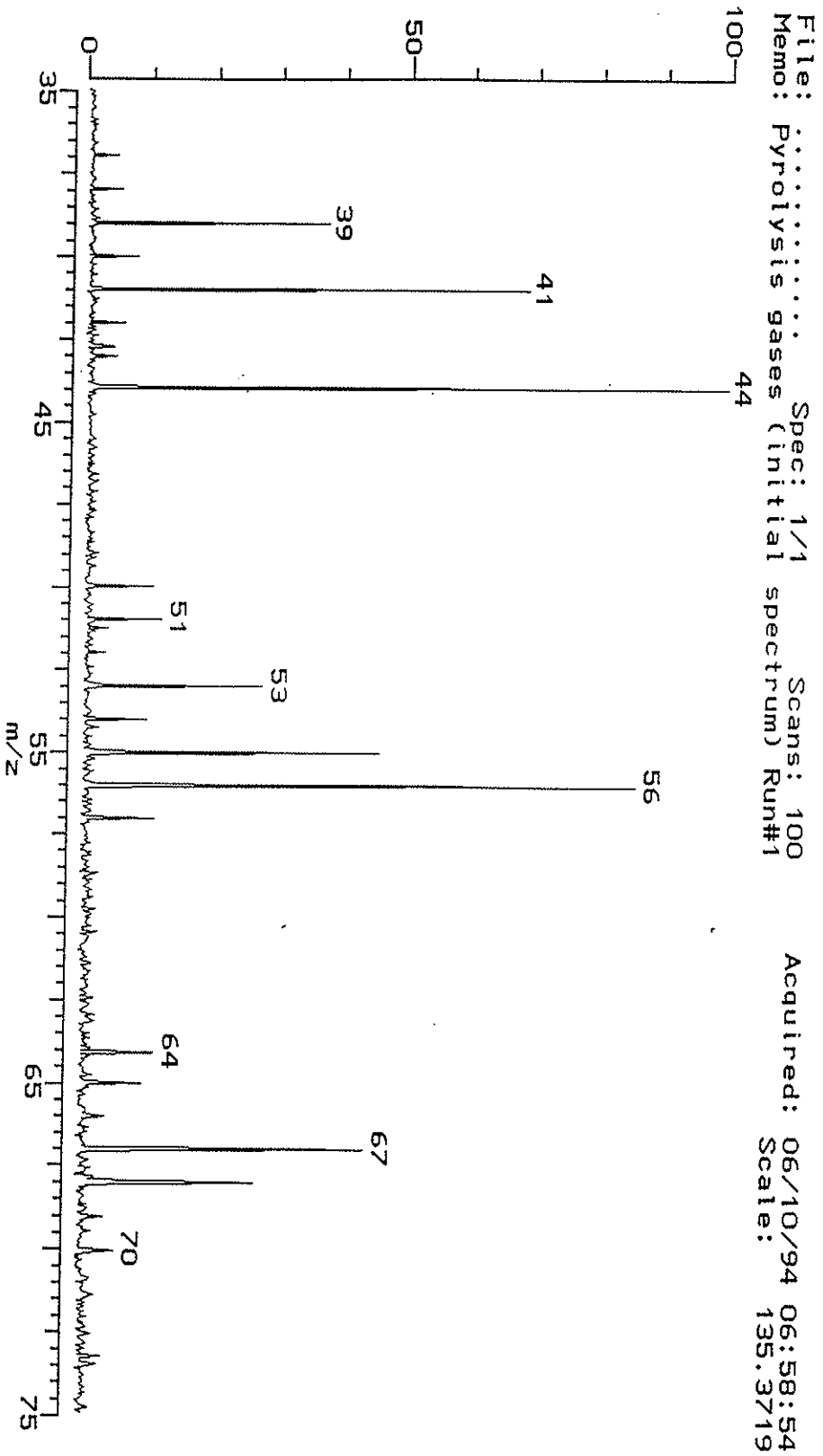
Cooling Jacket



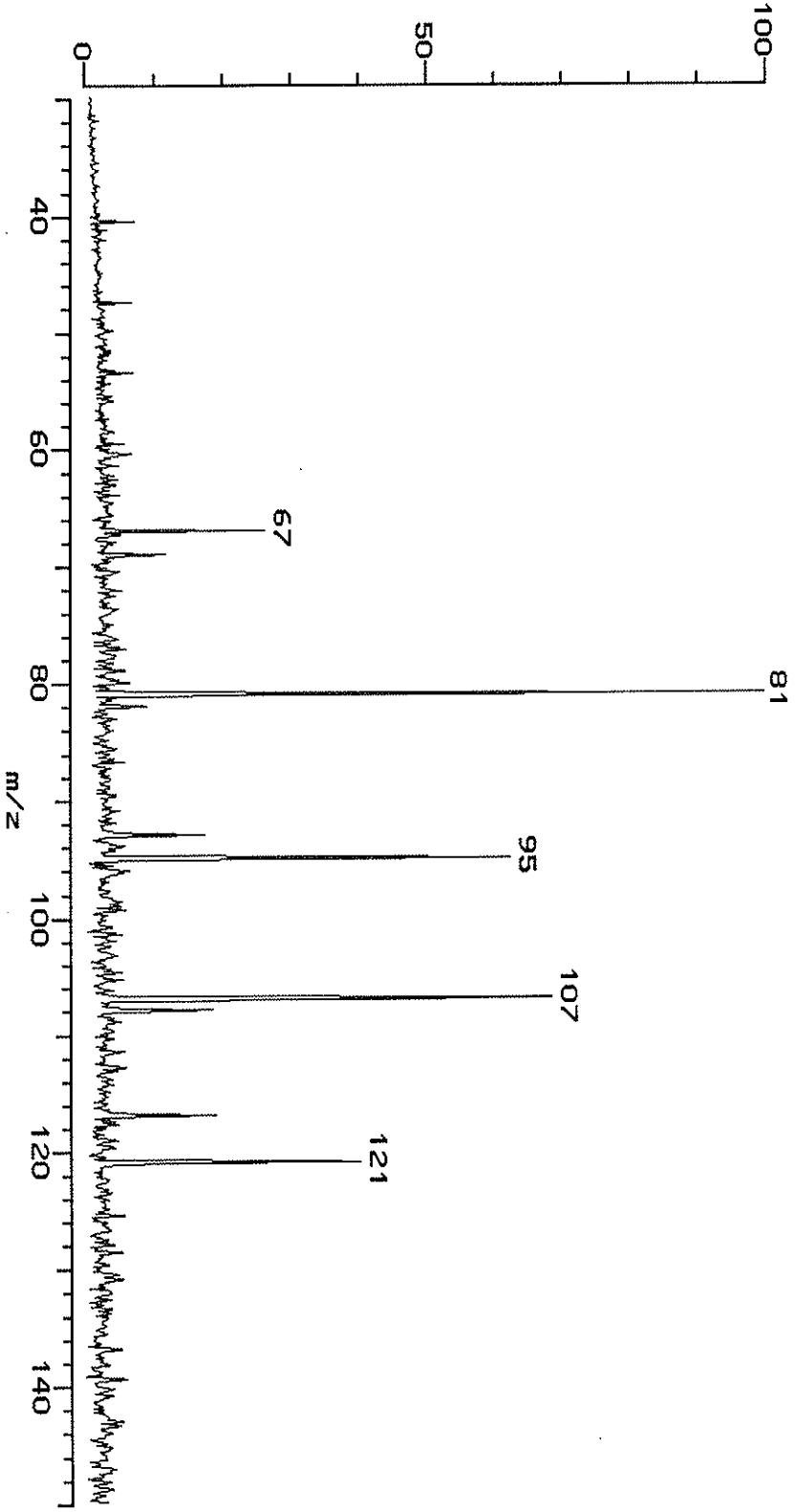


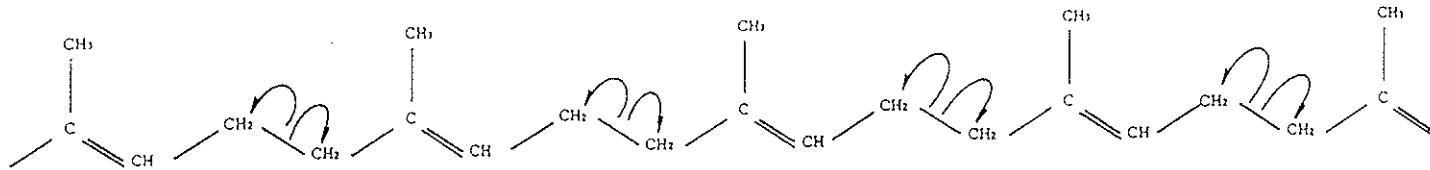


<u>Name</u>	<u>Emperical Formula</u>	<u>%</u>	<u>M.W.</u>
Cyclohexene/2,4-hexadiene	C ₆ H ₁₀	15	82
3-Methyl-1-Cyclohexene	C ₇ H ₁₂	2	82
Toluene	C ₇ H ₈	6	92
1,3-Cyclooctadiene	C ₈ H ₁₂	3	108
Ethyl Benzene	C ₈ H ₁₀	3	106
O-Xylene	C ₈ H ₁₀	2	106
Styrene	C ₈ H ₈	8	104
Camphene	C ₁₀ H ₁₆	2	136
M-Methylstyrene	C ₉ H ₁₀	2	118
1,2-Dimethyl-3-Ethylbenzene	C ₁₀ H ₁₄	4	134
Limonene	C ₁₀ H ₁₆	51	136

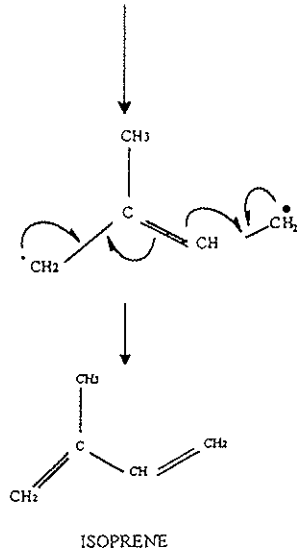


File: Spec: 1/1 Scans: 10 Acquired: 11/06/95 14:02:41
Memo: Scale: 329.3193





β-Sission de-polymerization of Polyisoprene Rubber



High Energy
Fragmentation

Low Temperature
Dimerization Reaction

