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A New Pyrolysis Reactor for Increased Limonene Yield in Scrap tire Pyrolysis

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A New Pyrolysis Reactor for Increased Limonene Yield in Scrap Tire Pyrolysis

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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. 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 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.

Because of past 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. Following the determination of the different mechanisms for product formation, 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. 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.

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).

These experiments indicate that two energy dependent reaction mechanisms exist. One being a radical cation mechanism and the other a low energy dimerization mechanism (21). 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

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 that the poly-isoprene rubber thermally decomposes in a B-scission de-polymerization fashion (8). 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.

Based on the above mechanism, a second pyrolysis reactor was constructed (see figure 3) to optimize limonene production. The reactor consisted of an perforated heating coil located in a condensation jacket. This design permits rapid expansion and low residence times in the high energy regions and therefore selectively accesses the low temperature dimerization reaction to form Limonene. Liquid samples were collected from the reactor and analyzed using GC-MS. 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 pyrolitic cycle are not presently economically viable. This is due to the low amounts of profitable chemicals produced in the different systems. To make pyrolitic 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. 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 results from the bench-scale reactor presented here indicate that this process can be up-scaled to a industrial level. Because the production of the isoprene gases will effectively displace any combustible atmosphere, there is no need to produce a pyrolysis environment using inert gases or vacuum equipment, thus reducing the cost of the technique. Furthermore, an open design in a pyrolysis reactor is consistent with a continuous feed, flow-through reactor. A continuous feed pyrolysis system would provide an effective method of dealing with the increasing backlog of scrap tires produced in this country. Finally, a perforated reactor design permits the separation of the three phases produced during pyrolysis. As seen in the block diagram of the proposed continuous feed system (Figure ??), a perforated oven also permits instant separation of the solid and liquid fractions produced by expansion of the condensable hydrocarbons into the two different regions of the oven.

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 of the economics of the thermal decomposition process. This in turn makes the process of pyrolytic decomposition economically favorable.

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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.

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