

# Recycling and Reuse Technology Transfer Center

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### **Production of Limonene during the Pyrolysis of Scrap Tires ASMS, Portland, OR**

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Selective Chemical Production of Limonene During the Pyrolysis of Scrap Tires  
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Recycling of scrap tires has become an increasingly important 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, activated carbon, 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. 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 biodegradable, a natural solvent, environmentally safe with excellent solvency, miscibility and high wetting, penetrating and detergent properties. 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.

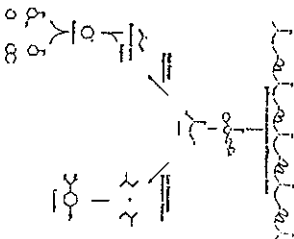


Figure 1: A proposed mechanism of the depolymerization of polyisoprene rubber and the high and low energy mechanisms which take place during pyrolysis.

In order to evaluate the potential of scrap tire pyrolysis three different reactors were built. These reactors 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 level. This reactor was also used to study the temperature effects on the pyrolysis process and to determine the different product ratios of these 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 temperatures ranged from 300-1000°C. In order to determine the optimal pyrolysis temperature, 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 products from this initial reactor were also used in the FT-ICR analysis.

The second reactor, built to study the effects of gas constriction during product formation, was made of a 12mm dia. by 90cm long copper tubing with 3mm dia. holes drilled in the furnace region, four holes at every

12mm interval. This tubing was surrounded by pyrex tubing with a diameter of 7cm and was 75cm long. The tire pieces used were predominantly natural or polyisoprene rubber taken from the lower sidewalls of scrap automobile tires (approximately 12mm X 12mm and 6mm 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 Lindburg 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 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 1.5 Amp. vacuum pump to displace the atmosphere. Furthermore, the heater coil was insulated with Sauerisen ceramic paste to reduce any effects of the nichrome on the ensuing chemistry. The wire was wound in a spiral orientation with a 12mm dia., 3mm in between each wind and was approximately 12.5cm in length. The nichrome wire was hooked up to a Fisher variable-120V auto transformer (Variatec) and the temperature was monitored using a tp 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.

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 (Figure 1). 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 decrease the amount of soot and environmentally hazardous products produced. Using this approach the amount of limonene produced has been increased from an average of 51% of the recovered liquid product to above 90% recovery (Figure 2).

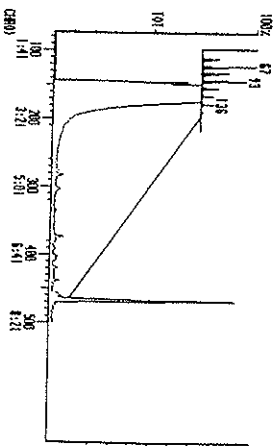


Figure 2: A chromatogram obtained from the liquids collected from the open coil reactor.

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