

The Composition of Pyrolysis Products of used Car Tires used as Liquid Fuel

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Abstract

Waste disposal technologies, which allow obtaining useful products, are one of the most powerful means of environmental protection through the rational use of waste as raw materials for industry. One of such technologies is the pyrolysis of used car tires. As a result of pyrolysis, gaseous, liquid and solid products are formed. These products are used as fuel, in particular, the liquid fraction can be used as diesel fuel.

The content of the liquid fraction was analyzed by the method of two-dimensional gas chromatography using TOF MS. More than 6600 compounds have been identified. The majority of the pyrolysis mixture consists of low-molecular volatile fractions the liquid fraction contains saturated, unsaturated, aromatic hydrocarbons, a significant number of compounds, which include nitrogen, sulfur and halogens atoms. When juxtaposing the chromatograms of the liquid fraction of the pyrolysis mixture with the chromatograms of petroleum products, in particular, diesel fuel, it can be seen that they largely contain the same components, which indicates that the properties of the liquid pyrolysis fraction are close to petroleum products of natural origin.

Keywords: Car Tires, Waste Disposal Technologies, Two-Dimensional Gas Chromatography Using TOF MS, Pyrolysis Mixture, Alternative Fuel

Introduction

The problem of recycling and utilizing household and industrial waste is one of the most pressing issues of modern times, as it helps prevent environmental pollution, improves ecological safety, and expands the raw material base for the production of useful products. One type of waste that requires recycling is rubber and latex products, with the majority of this waste consisting of automobile tires. Given the enormous number of vehicles in operation worldwide, as well as the large scale of tire production, the amount of tire waste is continuously increasing. This type of waste is highly resistant to decomposition under natural conditions and poses a significant environmental threat.

One of the most effective methods for recycling this type of waste is deep chemical processing through thermal decomposition (pyrolysis). During pyrolysis, high temperatures break

down polymer components, forming various monomolecular products. Pyrolysis decomposition technologies are implemented at industrial facilities in Ukraine.

The schematic of a pyrolysis plant (Figure 1) includes a reactor where thermodestruction processes occur at temperatures ranging from 400°C to 600°C. The resulting waste gases are collected in a storage tank and used to heat the pyrolysis reactor. Some of these gases can also be utilized in boiler houses or as fuel for other industrial processes. The main product of pyrolysis is pyrolysis liquid, which resembles petroleum products in consistency and odor. This liquid is used as an alternative fuel in boiler systems, and there have been successful attempts to use it as diesel fuel for agricultural machinery. The solid residue formed during pyrolysis, known as pyrocarbon, consists of carbon with adsorbed components of the pyrolytic mixture. It can be recy-

cled by reloading it into the pyrolysis reactor. However, pyrocarbon also has applications in other industries, such as metallurgy and the chemical industry.

Enterprises utilizing pyrolysis technologies are profitable and successful. Their operations address two critical issues: the disposal of used tires and the production of alternative fuel.

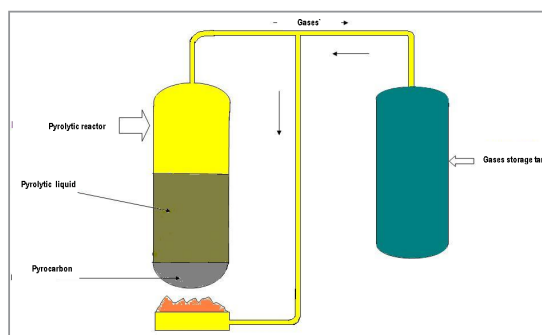


Figure 1. Schematic diagram of the pyrolytic installation

One of the key tasks associated with the operation of pyrolysis units is determining the composition of pyrolysis products, particularly pyrolysis liquid. This enables the improvement and development of pyrolysis methods and technologies, as well as the assessment of the safety of these products for human health.

From an analytical research perspective, this is a highly complex object, as it may contain a vast number of chemical compounds. The methods used for its analysis must exhibit high selectivity and the ability to identify individual compounds. These requirements are met by two-dimensional gas chromatography combined with mass spectrometry. The essence of the method is that the analyzed mixture is first separated on a non-polar gas capillary column and then, through a modulator, is introduced in small portions onto a short polar column.

Methods

The study utilized a two-dimensional gas chromatography system, Pegasus 4D by LECO, which includes an Agilent 6890 GC gas chromatograph equipped with a non-polar capillary column BPX-5 (30 m × 0.25 mm × 0.25 μm), a polar capillary column BPX-50 (1.7 m × 0.1 mm × 0.1 μm), a cryogenic modulator, and a time-of-flight mass spectrometer.

Gas Chromatography

- 1.dimension: BPX-5 (30 m x 0.25 mm x 0.25 μm)
- 2. dimension: BPX-50 (1,7 m x 0.1 mm x 0.1 μm)

- Injection Split 1:200,
- Oven program: 70°C (1 min), 5°C/min to 330°C (10 min)
- Secondary oven: 10°C above the main oven
- Modulator: 30°C above the main oven
- Modulation period: 3 s
- Hot pulse time: 0.7 s
- Carrier gas: He
- Flow: 1 ml/min
- Transferline temp. 280°C

Mass spectrometry

- Ionization type: EI (-70eV)
- Ion source temp.: 250°C
- Acquisition speed: 100 Hz
- Mass range: 35-700
- Detector voltage: 1550 V
- Solvent delay: 60 s
- Analysis time 63 min

The data obtained during the study was processed using ChromaTOF software.

Results

The use of two-dimensional gas chromatography allows for the separation of compounds based on their volatility in the first column and their polarity in the second polar column. As a result, the obtained chromatogram (Figure 2) identified approximately 6600 compounds.

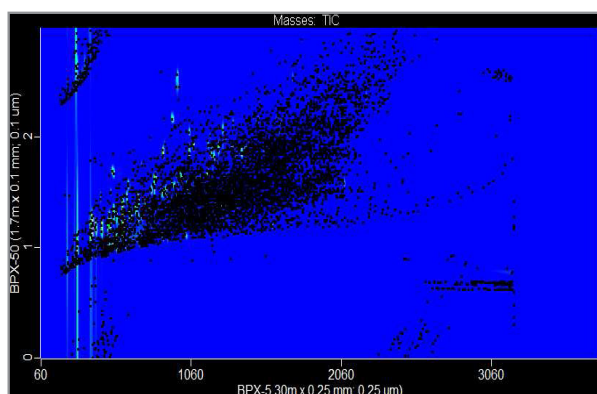


Figure 2: Chromatogram of the pyrolysis mixture.

On the obtained chromatogram (Figure 2), the x-axis represents the retention time of compounds in the first non-polar column, while the y-axis shows the retention time in the second polar column. Compared to conventional one-dimensional analysis, GC×GC provides significantly improved compound separation.

In Figure 3, the same chromatogram is presented in a three-dimensional space, where the height and intensity of the peaks are clearly visible.

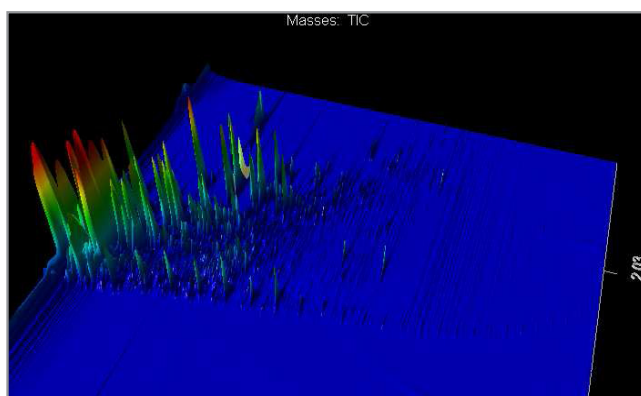


Figure 3: 3D Chromatogram of the pyrolysis mixture

The peak height and intensity correlate with the quantity of the substance in the mixture. The chromatogram shows that the most intense peaks are located on the left side, indicating a higher concentration of compounds with a shorter retention time. Based on their physical properties, these are volatile substances with lower molecular weight, which constitute the majority of

the pyrolysis mixture and play a significant role in defining its consumer properties as an alternative fuel.

Despite the complexity of such a chromatogram, it can be interpreted as a map, where specific classes of compounds are located in distinct regions (Figure 4).

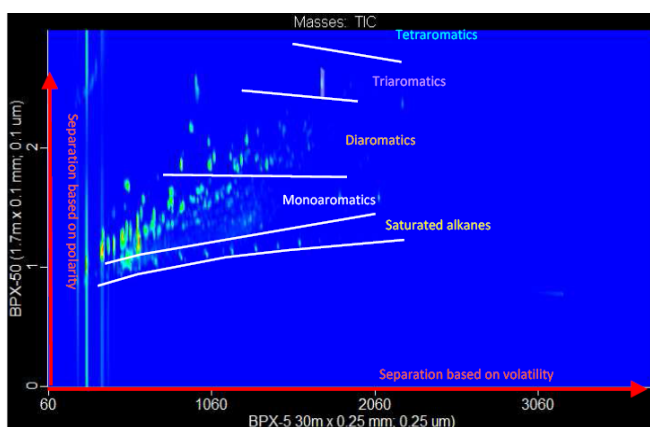


Figure 4: Components of the pyrolytic mixture

Saturated and unsaturated hydrocarbons appear as a band in the lower part of the chromatogram. The mixture contains a significant amount of diene hydrocarbons, which is attributed to the polymer structure (rubber) undergoing decomposition.

Above the region of unsaturated compounds, there is an area containing monoaromatic compounds, including benzene derivatives and thiophene. Higher up, diaromatic compounds appear, primarily naphthalene and indene derivatives. Above these compounds, tricyclic aromatic hydrocarbons, such as anthracene derivatives, are found. Polycyclic aromatic hydrocarbons (PAHs)

with four or more rings are practically absent in this mixture, which is significant since such compounds exhibit carcinogenic properties.

Apart from hydrocarbons, the pyrolysis liquid contains a considerable number of compounds incorporating nitrogen, sulfur, and halogens:

- Nitrogen-containing compounds include organic amines, nitroso compounds, and heterocyclic derivatives of pyridine, indole, quinoline, and acridine.

- Sulfur-containing compounds are mainly thiophene derivatives (monoaromatic) and dibenzothiophene.
- Halogenated compounds are present in small quantities, primarily as monoaromatic hydrocarbon derivatives
- It is useful to compare the chromatogram of this mixture with those of petroleum products, particularly diesel fuel (Figure 5) [1].

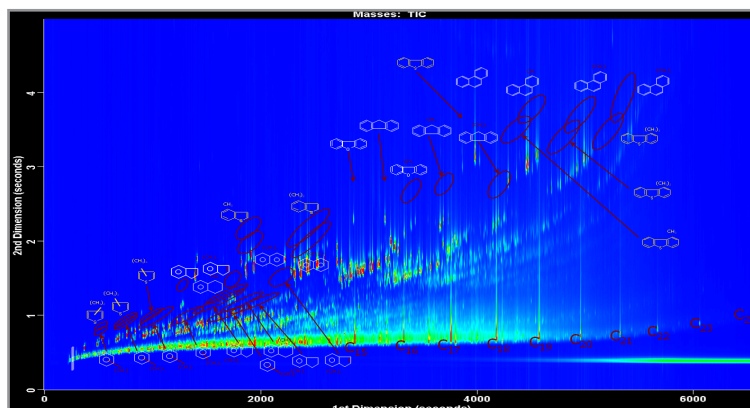


Figure 5: Chromatogram of Diesel Fuel

A comparison of these chromatograms reveals that they share a significant number of the same components, indicating that the pyrolysis mixture is chemically similar to petroleum-based fuels. This suggests that the processing methods for the pyrolysis mixture can be analogous to those used in petrochemistry. Thus, the pyrolysis-based recycling of rubber tires can be successfully

implemented for the production of alternative fuel, offering a sustainable solution for waste management and energy generation.

References

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