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USING TWO-DIMENSIONAL GAS CHROMATOGRAPHY WITH MSD TO DETERMINE THE COMPOSITION OF WASTE TIRE PYROLYSIS PRODUCTS

The method of two-dimensional gas chromatography coupled with mass-spectrometry detection has been used for determination of pyrolysis liquid which is a mixture of waste tire pyrolysis products. Six and a half thousand organic compounds have been identified: saturated, unsaturated, and aromatic hydrocarbons, as well as derivatives of thiophene, and cyclic amino-compounds. The pyrolysis liquid is similar to the diesel fuel by its composition and can be used as alternative fuel.

Key words: two-dimensional gas chromatography, mass spectrometry, pyrolysis, and rubber tires.

Nowadays, waste disposal is one of pressing problems. New technologies allow us to use waste as a raw material for industry. This helps preserve purity and safety of environment. Thermal decomposition (pyrolysis) holds a prominent place among the technologies of organic material recycling. This waste also includes the used and unsuitable road tires. Thanks to the intensive development of road transport the amount of tires to be disposed increases. The old tires pollute the environment, are characterized by high resistance to decomposition under the natural conditions, and can be stored for an indefinitely long period, which. Therefore, the development of technologies for processing the used tires is a key issue. One of the effective ways of disposing the tires is their pyrolysis.

The schematic diagram of pyrolysis unit is showed in Fig. 1. It includes a reactor for thermal decomposition, a reactor heating system, a pipeline for waste gases, and a tank for their accumulation.

When heating the reactor up to 400—600 °C the shredded tires undergo pyrolytic decomposition. This decomposition is associated with release of a large volume of gaseous substances, as well as with creation of the liquid fraction, a pyrolysis liquid, and the solid residue (pyrocarbon) which is a carbon with adsorbed organic matter. The gases generated during pyrolysis are used as a fuel; some of them are used to heat the reactor. The pyrolysis fluid is also used as an alternative fuel. However, for a final decision on the possible areas of its application and safety it is necessary to determine its composition.

This task is quite difficult inasmuch as the pyrolysis fluid is a complex mixture of thermal decomposition products. To identify them it is necessary to separate these compounds. The adequate and nearly exclusive method required for this resolution is two-dimensional gas chromatography. The method is based on the fact that the analyzed substance is separated in the long nonpolar capillary column, and then enters the short polar capillary column where the compounds which have not been divided in the first column are finally separated. Identification of individual compounds is conducted using the mass-spectrometry detection technique.

THE EXPERIMENT

The *Pegasus* 4D system for two-dimensional gas chromatography manufactured by *LECO* is used for the study. The system includes an *Agilent* 6890 GC gas chromatograph with a BPX-5 non-polar capillary column (30 m × 0.25 mm × 0.25 m), a BPX-50 polar column (1.7 m × 0.1mm × 0.1 mm), a cryoscopic modulator, and a time-of-flight mass spectrometer. The chromatograph injector temperature is 340 °C; the stream flow separation is 1 : 200. The program for changing the temperature of thermostat columns includes heating up to 70 °C (during 1 minute) followed by raising the temperature at a rate of 5 °C/min up to 330 °C (during 10 minutes); the carrier gas is helium. The mass spectroscopic study was performed by electron impact ionization with ionization energy of 70 eV. The *ChromaTOF* software based on deconvolution algorithm was used to process the data [1].

DISCUSSION OF RESEARCH RESULTS

More than 6500 substances have been identified on the chromatogram (Fig. 2) obtained as a result of research. These substances are placed in the order determined by their molecular weight during the passage through the first non-polar column and by volatility of these substances and their polar properties during the separation in the second polar column (Fig. 3).

The volatile substances with low molecular weights move faster and are placed in the lower left corner of chromatogram. As the molecular weight and polarity increase, the organic compounds shift to the top right corner of chromatogram. According to the above, in the bottom of chromatogram there are located saturated and unsaturated hydrocarbons. Among them, there are diene hydrocarbons because of the structure of rubber decomposed. Above this area, there are a lot of monoaromatic compounds (benzene, thiophene, and their derivatives); higher, there are located the diaromatic

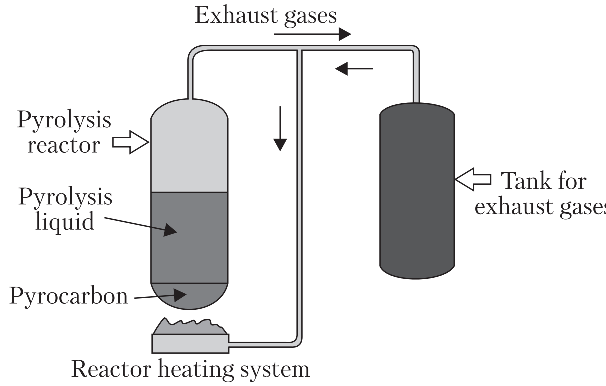

Fig. 1. Schematic diagram of installation for pyrolysis of tires

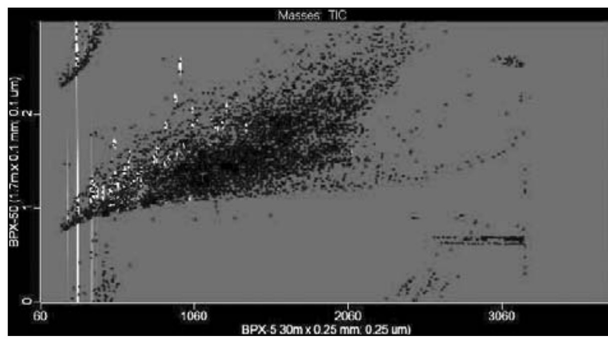

Fig. 2. GC x GC chromatogram of pyrolysis mixture

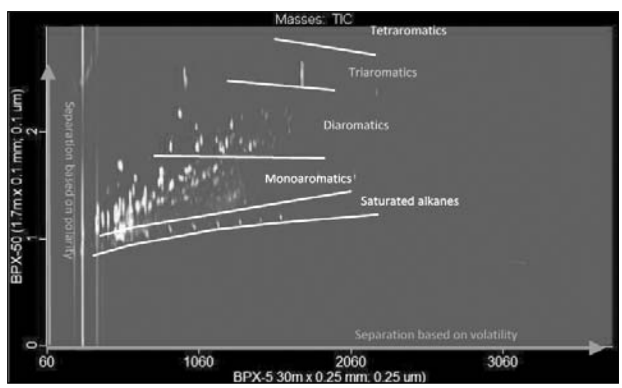

Fig. 3. GC x GC chromatogram of pyrolysis mixture. Location of compounds

agents (derivatives of naphthalene, benzofuran, benzothiophene, benzothiazole, indole, and quinoline). At the top of chromatograms, there are three zones (derivatives of anthracene, phenanthrene, fluorene, dibenzofuran, and dibenzothiaphene) and

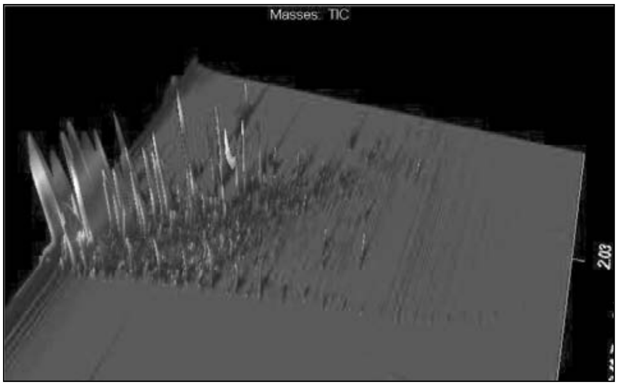

Fig. 4. 3D GX x GX chromatogram of pyrolysis mixture

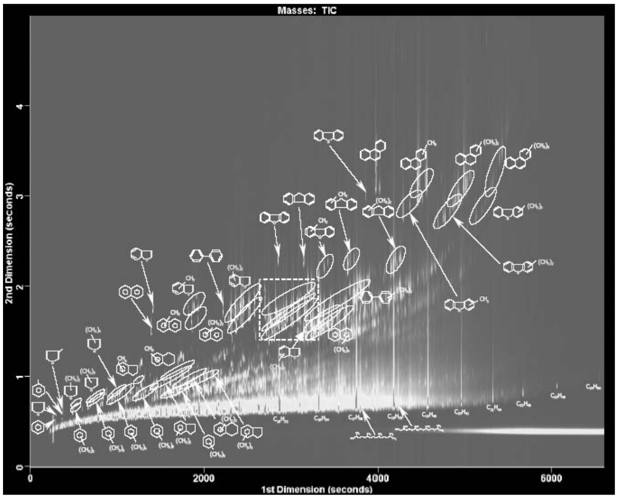

Fig. 5. GX x GX of diesel fuel [2]

tetraaromatic compounds (derivatives of pyrene and benzanthracene).

Fig. 4 shows the 3D chromatograph where the intensity of peaks in the lower right portion is much greater than in the upper right one. This means that the major part of pyrolysis mixture is low molecular weight volatile fractions which basically determine the properties of pyrolysis mixture as an alternative fuel.

In addition to hydrocarbons the pyrolysis fluid contains many compounds to which atoms of nitrogen, sulfur, and halogens are included. The nitrogen compounds are organic amines, nitrosobis compounds, heterocyclic compounds, as well as derivatives of pyridine, indole, quinoline, and acridine.

The sulfur compounds mainly are derivatives of thiophene (monoaromatic compounds) and dibenzothiophene (traromatic compounds). The mixture contains a small amount of halogen-containing compounds, mainly in the form of derivatives of monoaromatic hydrocarbons.

Thus, the pyrolysis liquid formed by tire thermal decomposition is a complex mixture of organic compounds, chiefly hydrocarbons. The composition of this mixture is similar to that of the petroleum products, in particular, the diesel fuel (Fig. 5).

In the two-dimensional chromatogram of diesel fuel the organic compounds are placed in accordance with the above-described principle. The normal alkanes in the form of strips are located in the bottom part of chromatogram. Further, the compounds are located from the bottom upwards as follows: the aromatic group (derivatives of benzene and thiophene); the group of naphthalene, indene, and benzothiophene compounds; the triaromatic group (derivatives of fluorene and dibenzofuran). In the upper right area, there are located phenanthrene derivatives and dibenzothiophene.

Due to the fact that the composition of pyrolysis liquid formed as a result of tire thermal decomposition is similar to that of petroleum, the use of pyrolysis mixture as an alternative fuel is sufficiently justified.

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ИСПОЛЬЗОВАНИЕ ДВУХМЕРНОЙ ГАЗОВОЙ ХРОМАТОГРАФИИ С МАСС-СПЕКТРОМЕТРИЧЕСКИМ ДЕТЕКТИРОВАНИЕМ ДЛЯ ОПРЕДЕЛЕНИЯ СОСТАВА ПРОДУКТОВ ПИРОЛИЗА С ОТРАБОТАННЫХ АВТОМОБИЛЬНЫХ ШИН

Метод двухмерной газовой хроматографии в сочетании с масс-спектрометрическим детектированием использован для определения пиролизной жидкости – смеси продуктов пиролиза отработанных автомобильных шин. Идентифицированы около 6500 органических соединений: насыщенных, ненасыщенных, ароматических углеводородов, производных тиофена, циклических аминосоединений. По содержанию соединений пиролизная жидкость близка к дизельному топливу и может использоваться в качестве альтернативного топлива.

Ключевые слова: двухмерная газовая хроматография, масс-спектрометрия, пиролиз, автошины.

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ДВОМІРНОЇ ГАЗОВОЇ ХРОМАТОГРАФІЇ З МАС-СПЕКТРОМЕТРИЧНИМ ДЕТЕКТУВАННЯМ ДЛЯ ВИЗНАЧЕННЯ СКЛАДУ ПРОДУКТІВ ПІРОЛІЗУ З ВІДПРАЦЬОВАНИХ АВТОМОБІЛЬНИХ ШИН

Метод двомірної газової хроматографії в поєднанні з мас-спектрометричним детектуванням використано для визначення складу піролізної рідини – суміші продуктів піролізу відпрацьованих автомобільних шин. Ідентифіковано близько 6500 органічних сполук: насичених, ненасичених, ароматичних вуглеводнів, похідних тіофену, циклічних аміносполук. За вмістом сполук піролізна рідина близька до дизельного палива і може використовуватись як альтернативне паливо.

Ключові слова: двомірна газова хроматографія, мас-спектрометрія, піроліз, автомобільні шини.

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