Investigation of Obtaining Modifiers from Industrial Waste for Polymer Composite Materials

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**Abstract.** The purpose of this study is to investigate the chemical composition of pyrolysis residues obtained from gas-chemical enterprises in Turkmenistan and Uzbekistan. Using various physical and chemical methods, the composition of the pyrolysis residue was determined. The residue is a heavy, dark brown liquid with an unpleasant odor, primarily consisting of arenes and olefins. The average molecular weight of the pyrolysis product was found to be 267 amu, with a density of 0.986 g/sm³. The yield of the residue was approximately 10%, depending on the feedstock processed during pyrolysis. The olefin content comprised 48.11%, while arenes 43.00%. Additionally, is paraffins, naphthenic hydrocarbons, and resins were detected. This ongoing research aims to explore the potential applications of these industrial wastes as chemical modifiers in polymer composite materials.

**Keywords:** Pyrolysis product, pyrolysis residue, by-products of pyrolysis, chemical composition.

# INTRODUCTION

Pyrolysis residues are a highly aromatized hydrocarbon mixture that is formed as a secondary product as a result of processing natural gas by cracking in the production of ethylene and propylene at polymer plants in Turkmenistan (Kiyanli plant) and Uzbekistan (Shurtan and Ustyurt gas chemical complexes) [1, 2].

Processing of raw materials and expansion of production of targeted products is a developing (leading, driving) force for the petrochemical industry of our time. This is explained by the fact that the pyrolysis of hydrocarbon feedstock is the main process for the production of ethylene and propylene, as well as pyrolysis gasoline. [3, 4, 5, 6, 7, 8].

High-quality processing of these types of products is the basis for the production of benzene, toluene, xylene, ethylbenzene, styrene, divinyl, cyclopentadiene, naphthalene and other valuable types of hydrocarbons [9].

Based on this point of view, it should be noted that the development of the petrochemical complex and the production of new, import-substituting chemical products, which is based on the processing of hydrocarbon raw materials, is one of the important tasks [10, 11, 12].

To achieve competitive advantages in both local and global markets, it is crucial to develop effective methods for the chemical processing of readily available, low-cost raw materials. Therefore, studying the physical and chemical composition of these materials is an important scientific challenge.

At the enterprises of Turkmenistan and Uzbekistan, where the most advanced, modern technological equipment is installed, 386 thousand tons of high-quality polyethylene, 81 thousand tons of polypropylene (in Turkmenistan) and 512 thousand tons of various commercial types of high-quality polyethylene, 83 thousand tons of polypropylene and various liquid commercial products are produced every year. pyrolysis products (in Uzbekistan).

Pyrolysis residues are secondary raw materials for the production of naphthalene, phthalic anhydride and other valuable chemical products necessary for the industry. Due to the fact that modern technologies make it possible to produce more valuable and more necessary products from combustible materials, the heavy parts of liquid pyrolysis products are raw materials with effective potential for further use.

Currently, this residue is not processed at chemical plants in both Turkmenistan and Uzbekistan. In this regard, for the processing of waste from gas-chemical complexes, new research aimed at the development of complex technologies is especially necessary.

In this context, collaborative research has undertaken a study to analyze the chemical composition of pyrolysis condensate residues. Gas condensate serves as the primary raw material for thermal pyrolysis processes.

# METHODOLOGY

In this study the pyrolysis residue composition from the Kiyanli plant in Turkmenistan was determined. Laboratory analyses were conducted using standard physical and chemical methods, complemented by infrared (IR) spectroscopy and high-performance adsorption chromatography.

Physical and chemical properties of the pyrolysis residue were determined in according to the national Technical Specifications (TU) 13684330-02-2020.

The quantitative composition of organic compounds in the pyrolysis residue was analyzed using a Agilent Technologies 7890 gas chromatography coupled with a model 5975 MSD mass selective detector.

The complex hydrocarbon composition of the samples was further characterized by adsorption chromatography on silica gel, allowing for the separation and identification of hydrocarbon classes [13, 14].

Structural features of the hydrocarbons were examined by Fourier Transform Infrared (FTIR) spectroscopy in the spectral range of 4000 to 400 sm⁻¹ using a ThermoFisher Scientific IR spectrophotometer [15, 16, 17, 18, 19, 20].

# RESULTS AND DISCUSSIONS

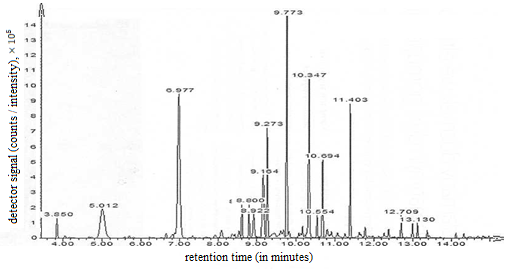
The yield of the studied pyrolysis waste depends on the raw material processed and is approximately 10%. The average molecular weight of the residue is 267 amu, with a viscosity of 5.02 cSt and a density of about 0.986 g/sm³. The physical and chemical properties of the pyrolysis residue are summarized in Table 1.

The content of isoparaffin-naphthenic hydrocarbons in the residue is 7.99%, while the combined amount of aromatic and olefin hydrocarbons reaches 91.11%. The resin fraction constitutes approximately 0.9% of the sample (Figure 1).

The olefin content was further quantitatively determined the bromine number, which was found to be 28.83 g Br₂/100 g of sample. This corresponds to an olefin content of up to 48.11% in the pyrolysis residue (see Table 2).

**TABLE 1.** Physio-chemical indicators of pyrolysis residue

|  |  |  |
| --- | --- | --- |
| Physico-chemical indicators | Standard for the product | Meaning |
| Appearance | Thick brown liquid | Thick brown liquid |
| Density, d20, g / sm3 | not less than 0.895 | 0.986 |
| Average molecular weight, amu | - | 267 |
| Flash point (closed cup), o C | at least 40 | 45 |
| Viscosity, 40 o C, cSt | at least 4 | 5.02 |
| Mechanical mixtures | No | No |
| Yield in relation to feedstock, % | - | 10 |

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**FIGURE 1.** Chromatogram pyrolysis residue

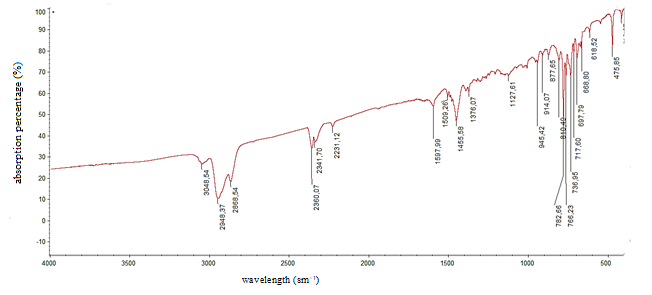
**TABLE 2.** Chemical composition of the pyrolysis residue

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Carbon number** | **Isoparaffins** | **Naphthenes** | **Olefins** | **Arenas** | **Total** |
| 2 | 0 | 0 | 0 | 0 | 0 |
| 3 | 0 | 0 | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | 0 | 0 |
| 5 | 1.02 | 0.12 | 4.35 | 0 | 5.49 |
| 6 | 0.52 | 0.23 | 6.71 | 18.6 | 26.06 |
| 7 | 0.84 | 0.58 | 9.41 | 9.05 | 19.88 |
| 8 | 1.32 | 0.14 | 11.02 | 6.12 | 18.6 |
| 9 | 1.25 | 0.71 | 2.05 | 5.89 | 9.9 |
| 10 | 1.06 | 0.18 | 5.67 | 2.52 | 9.43 |
| 11 | 0 | 0 | 7.09 | 0.82 | 7.91 |
| 12 | 0 | 0.02 | 1.81 | 0 | 1.83 |
| Total | 6.01 | 1.98 | 48.11 | 43.00 | 99.1 |

Pyrocondensate is further classified into three groups based on boiling points (Table III): pyrolysis distillate (boiling range from 35°C to 160°C), heavy pyrolysis resin (boiling range from 160°C to 190°C), and waste product (boiling point above 344°C) [21, 22, 23, 24, 25].

**TABLE 3.** Hydrocarbon and fractional composition of the pyrolysis residue of polymer production

|  |  |
| --- | --- |
| Indicators | Meaning |
| Mass fraction of sulfur, % | 0.02 |
| Bromine number, g Br2 /100 g | 28.83 |
| Isoparaffino -naphthenic hydrocarbons, % | 7.99 |
| Olefins + aromatic hydrocarbons, % | 91.11 |
| Including: olefins, % | 48 .11 |
| Aromatic hydrocarbons, % | 43.00 |
| Resins, % | 0.9 |
| Fractional composition: | |
| Initial boiling point, o C | 35 |
| Distillation start temperature, oC | 80 |
| Boil-off, oC: |  |
| 10% | 160 |
| 20% | 196 |
| 30% | 205 |
| 40% | 205 |
| 50% | 209 |
| 60% | 221 |
| 70% | 251 |
| 80% | 300 |
| Boiling point, oC | 344 |
| Exit, % | 85 |
| Residue in flask, % | 15 |

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**FIGURE 2.** Infrared spectrum of the pyrolysis residue

As in the data given below in Table IV, aliphatic hydrocarbons mainly contain chains of different lengths (n>6) (CH2) n - CH 3 (Figure 2).

**TABLE 4.** Structural composition of aliphatic hydrocarbons

|  |  |
| --- | --- |
| **Structural composition** | **Corresponding absorption band** |
| CH2 – groups aliphatic chains | Stretching vibration of the C– H bond 2868 and 2948 sm-1;  Pendulum vibrations of the C- H bond ( n>6) group ( CH2 )n |
| CH3 – groups | Structural vibration of the (СH3)2 group at 1127 sm-1 plane bending vibrations of the C–H bond at 1376 and 1455 sm-1 |

Structural analysis of the composition of aliphatic and aromatic hydrocarbons (Table V) reveals that the absorption band around 3000 sm⁻¹ corresponds to the stretching vibrations of the C–H bonds in the aromatic ring. Additionally, an absorption band observed below 900 sm⁻¹ indicates the presence of C–C and C–P bonds [15, 18, 19].

These physical and chemical results suggest that the pyrolysis residue contains alkylbenzenes with a single substituent as well as alkyl chains substituted at positions 1, 2, and 3 by three alkyl groups (Figure 2).

**TABLE 5.** Structural composition of aliphatic hydrocarbons

|  |  |
| --- | --- |
| **Structural composition** | **Corresponding absorption band** |
| Absorption bands belonging to the aromatic ring | of the C=C ring bonds are 2231; 1597; 1455 sm-1;  The strain vibration on the C=C bond plane is 717; 697; 668 sm-1 ;  The strain vibration on the C–H bond plane is 945; 914 sm-1 ;  The bending vibration beyond the C–H bond plane is 877; 810; 73 6 sm-1 ; |
| Dialkylbenzenes with two alkyl chains in the 1,2 position | The deformation vibration on the C – H bond plane is 1127 sm-1 ;  The deformation vibration beyond the C – H bond plane is 73 6 sm-1 . |
| Dialkylbenzenes with two alkyl chains in the 1,3 position | The deformation vibration on the C – H bond plane is 914  sm-1 ;  The deformation vibration beyond the C–H bond plane is – 810 sm-1 ; |
| Dialkylbenzenes with two alkyl chains in the 1,4 position | The deformation vibration on the C – H bond plane is 1127 sm-1;  The deformation vibration beyond the C–H bond plane is – 782 sm-1; |
| Dialkylbenzenes with three alkyl chains in the 1,3,5 position | The deformation vibration on the C – H bond plane is 945  sm-1;  Deformation vibration beyond the bond plane C – H is – 877 sm-1; |
| R1HC = CHR2 | The bond stretching vibrations (=C–H) (trans) are 3018  sm-1;  Deformation vibrations on the C–H bond plane in the  (–C=C–H) group (trans) are 1376 sm-1;  The deformation vibration behind the C–H bond plane in the (–C=C–H) group (trans) is 945.877 sm-1; |

Analysis of the infrared spectra of aromatic hydrocarbons (Table 5) indicates the presence of monoolefins containing a single pair of double bonds of the —HC=CH— type in the pyrolysis residue. These compounds include hydrocarbon chains with the general structure R¹HC=CHR². Additionally, the presence of dialkylbenzenes with two alkyl substituents in the 1,3- and 1,4-positions, as well as trialkylbenzenes with three alkyl groups in the 1,3,5-positions, has been confirmed.

# CONCLUSION

An IR spectroscopic study of the structural features of the hydrocarbons in the pyrolysis residue revealed the presence of aliphatic chains of varying lengths (n > 6) with the general structure (CH₂)ₙ–CH₃, olefinic chains of the R¹HC=CHR² type, as well as dialkylbenzenes with two alkyl substituents in the 1,3- and 1,4-positions, and trialkylbenzenes with three alkyl chains in the 1,3,5-positions.

The results obtained indicate the possibilities of using the pyrolysis residue in chemical modification processes for the development of composite materials. Such materials have a wide range of uses both in the chemical industry and for materials used in construction and mechanical engineering. The research contributes to the broader effort to repurpose industrial waste as chemical modifiers in composite systems.

From the point of view of environmental and chemical safety, it should be noted that pyrolysis residues contain a number of substances, particularly aromatic hydrocarbons and olefins, potentially hazardous when used uncontrollably. However, when these components are incorporated into a polymer matrix, their mobility is significantly reduced, which limits their migration into the environment or contact with users. This approach, described in several studies, enables the effective utilization of industrial waste without increasing environmental risks. Additionally, the use of pyrolysis residues contributes to reducing the volume of waste disposal and enhances resource efficiency, aligning with the principles of sustainable development. In the future, toxicological and thermal studies of the resulting composites are planned to confirm their environmental safety.

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