

# The catalytic cracking of the off-spec polyisoprene rubber thermolysis products

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**Abstract.** The catalytic cracking of the off-spec polyisoprene rubber thermolysis products over a mesoporous zeolite has been studied on a laboratory unit with a fixed-bed reactor. The effect of the reaction temperature and the feed space velocity on the feedstock conversion degree and the yield of gas and gasoline has been studied. The data obtained has shown that at rates below 2 h<sup>-1</sup>, a high gas generation and a low yield of liquid products are observed, while at rates above 3 h<sup>-1</sup>, the total yield of gas and gasoline decreases. In the course of the work, it has been noted that the reduction in conditional conversion occurs with an increase in the feed rate. The maximum yield of gasoline observed at a feed rate of 3 h<sup>-1</sup> and amounted to 35.6 %, gas yield was inversely proportional to the feed rate, and the coke yield changed slightly. With an increase in the feed rate, the content of C<sub>3</sub>-C<sub>4</sub> in gas increases. To achieve high conversion or a high gasoline yield, the optimal feed rate should be 2 and 3 h<sup>-1</sup>, respectively. The products obtained in this process can be used as the motor fuel components.

## 1 Introduction

Catalytic cracking is one of the most important processes ensuring the deeper oil refining and increased yield of light fractions: high-octane gasoline and light gas oil. The conventional raw materials for catalytic cracking units are oil fractions boiling within 200-550 °C [1], although some units may process heavier materials [2, 3] such as vacuum gas oil, tar, fuel oil, hydrocracking residue, deasphaltizate, etc. Some catalytic cracking units using gasoline fractions as raw materials are aimed at producing light products [4]. In a number of studies, catalytic cracking of alternative feedstocks such as vegetable oils [1, 5, 6], biomass, and various hydrocarbon-containing materials [2, 7, 8] has been studied.

The ever-growing production of polymeric materials leads to the growth of their waste at landfills that occupy large areas causing damage to the environment. This requires qualified processing and disposal of this waste [9], which has great environmental and economic significance. Among the known polymer waste disposal techniques, the most universal ones are thermal and catalytic cracking [10, 11]. The thermal cracking fuels are characterized by low stability, since due to the gasoline and diesel fractions exposure at certain temperature and time, a significant change in their chemical composition occurs

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caused by tarring and drift of physicochemical properties such as viscosity, density, and fractional composition. In this regard, these fractions can be used as fuel components only after appropriate treatment. The catalytic processing of polymer waste [12-14] is the most advanced recycling area.

The problem of catalytic cracking of polymer waste is the need to meter them when supplying into the reactor that requires their pretreatment. It is advisable to carry out the process in several stages: at the first stage, the feedstock is thermally cracked and further sent to the second-stage catalytic reactor and then fractionated. There is another technique for the feedstock treatment — the dissolution of polymer materials in the relevant oil fractions [12, 13], followed by catalytic cracking. The advantages of catalytic cracking of polymer waste as compared to other chemical feedstock processing techniques are the reduced energy costs and the ability to control the process selectivity to the target products. It should be noted that many polymer feedstocks such as synthetic rubber and its production waste do not virtually contain sulfur and heavy metals negatively affecting the catalyst activity [15] that allows their environment-friendly processing. In the paper, this issue has been considered on the example of polyisoprene rubber production waste.

## 2 Materials and Techniques

The catalytic cracking of the low-temperature polyisoprene rubber waste pyrolysis products has been carried out in a fixed-bed unit using a wide-pore NaX zeolite as a catalyst, which is highly active in the cracking of linear hydrocarbons. The temperature in the reaction zone and the feed space velocity ranged from 400 to 550 °C and 1 to 5 h<sup>-1</sup>, respectively.

Kinematic viscosity at 25 °C has been determined according to GOST 33-2000. The content of double bonds has been determined using the iodine number technique according to GOST 2070-82. Flashpoint has been determined according to GOST 6356-75. The hydrocarbon density has been determined according to GOST R 51069. The product structure has been studied according to the <sup>1</sup>H NMR technique on a JEOL JNM-ECA 600 spectrometer. Chromatographic analysis has been performed on a CrystalLux-4000M chromatograph in the temperature programming mode.

The research object was a wide hydrocarbon fraction obtained by the thermolysis of polyisoprene rubber waste. The physicochemical properties of the wide thermolysis fraction are given in Table 1.

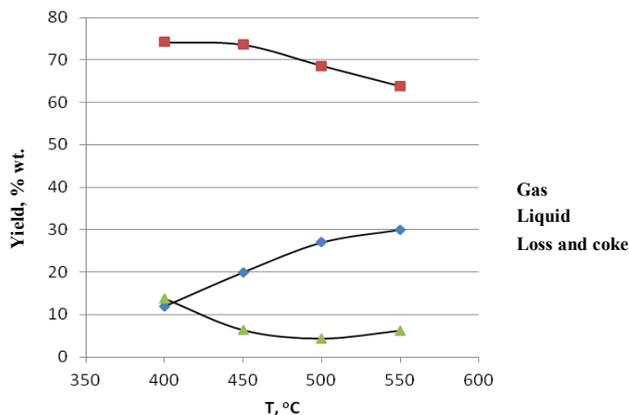
**Table 1.** Physicochemical Properties of the Source Fuel Fraction

Indicators	Value
Kinematic viscosity at 20 °C, mm/s <sup>2</sup>	2.69
Boiling range, °C	40-320
Density at 20 °C, kg/m <sup>3</sup>	830
Refractive index	1.48
Appearance	Dark green

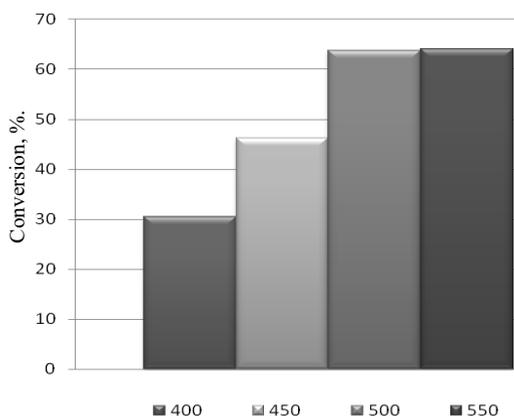
## 3 Experimental Technique

When studying the catalytic cracking of a wide fraction of the polyisoprene rubber waste thermolysis, the basic variable process parameters have been the temperature and the feed contact time. A preliminary series of experiments to study the effect of the feed rate on the yield of light products at a temperature of 500 °C has shown that at a rate below 2 h<sup>-1</sup>, a

high gas generation and a low yield of liquid products are observed, while at rates above 3 h<sup>-1</sup>, the total yield of gas and gasoline decreases. Therefore, a series of experiments have been conducted at various temperatures and a feed rate of 2 h<sup>-1</sup>. The process conditions and the results obtained are given in Figures 1 and 2.

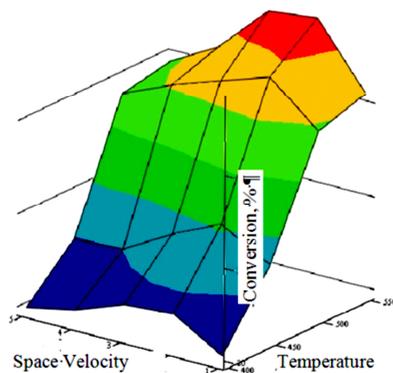


**Fig. 1.** Dependence of the Gas, Liquid, and Solid Product Yields on the Cracking Temperature.



**Fig. 2.** Temperature Dependence of a Wide Fraction Catalytic Cracking Conditional Conversion (Gas + Gasoline).

Fig. 2 diagram shows that with an increase in the process temperature from 400 to 550 °C, the gas product yield increases by 18 % and the liquid product yield decreases by 10 %. The loss-and-coke curve has a minimum at 500 °C. At 450 °C, the liquid product yield is close to the maximum. However, the total conversion into gas and gasoline fractions at 450 °C is 46 %, while at 550 °C it is 63 %. The dependence of the conditional conversion (gas + gasoline) on temperature and feed space velocity is shown in Figure 3. The highest valuable product yields are observed at a temperature within 500–550 °C and a feed rate of 2–3 h<sup>-1</sup>.



**Fig. 3.** Dependence of the Catalytic Cracking Conditional Conversion on Temperature and Space Velocity

The outcomes on the effect of operational parameters on the catalytic cracking of a wide fraction of the polyisoprene rubber production waste thermolysis allow suggesting that with increasing feed space velocity, the total gasoline and gas yield increases, which leads to increasing feedstock conversion and decreasing yield of light gas oil. With increasing process temperature, the liquid product yield decreases and the yield of gas sharply increases with a maximum gasoline yield of 37 % at 500 °C.

The basic physicochemical properties of the products obtained are given in Table 2. They show that with increasing process temperature, the product viscosity and density, and the final boiling point (FBP) decrease.

**Table 2.** Physicochemical Properties of Liquid Conversion Products.

Process temperature	400	450	500	550
Kinematic viscosity at 20 °C, mm/s <sup>2</sup>	1.7	1.629	1.12	1.105
Boiling range, °C	115-295	82-289	44-283	43-280
Density at 20 °C, kg/m <sup>3</sup>	825	818	815	809
Refractive index	1.461	1.458	1.46	1.458
Appearance	Light green, transparent	Yellow, transparent	Yellow, transparent	Yellow, transparent

Each liquid fraction has been divided into gasoline (FBP < 200 °C) and light gas oil (FBP > 200 °C) ones. The main physicochemical properties of these fractions are given in Table 3. The properties of gasoline fractions obtained are similar to those obtained from conventional raw materials. Reactions over NaX-type zeolites proceed mainly by a radical-chain mechanism, and the resulting gasoline fractions have a wide distribution of products, despite this, the motor octane numbers of gasoline range from 68 to 75 with higher MONs achieved at higher process temperatures. The products obtained are characterized by high iodine number; catalytic cracking gasoline is used as commercial gasoline component. E.g., A-92 gasoline is produced with the addition of 10 to 85 % catalytic cracking gasoline, i.e. by compounding, on-spec indicators can be achieved.

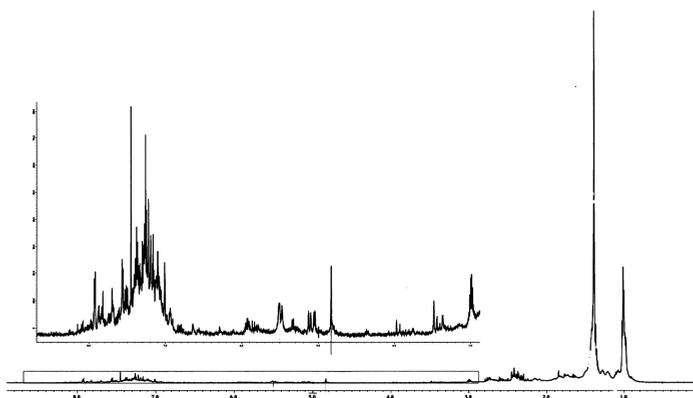
Analysis of the Table 3 data shows that the basic properties of the light gas oils obtained in this research and in catalytic cracking of traditional raw materials are similar, although

the first one has a lower FBP. With increasing process temperature, the cetane index and iodine number decrease, as is typical.

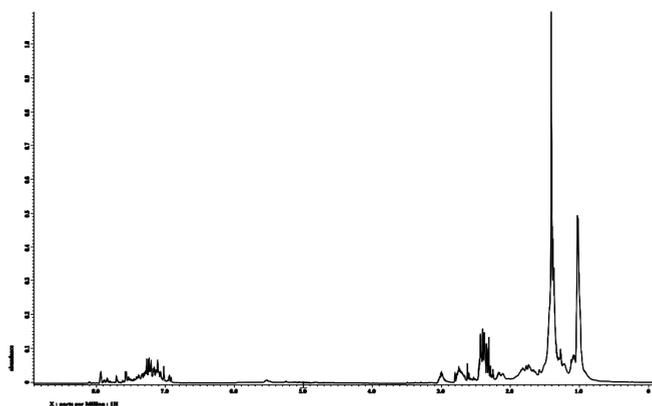
**Table 3.** Physicochemical Properties of Gasoline Fraction of Catalytic Cracking of a Wide Fraction of the Polyisoprene Rubber Production Waste Thermolysis.

Process temperature	400	450	500	550
<b>Gasoline Fraction</b>				
Boiling range, °C	115-200	82-200	44-200	43-200
Density at 20 °C, kg/m <sup>3</sup>	787	794	778	789
Kinematic viscosity at 20 °C, mm/s <sup>2</sup>	0.719	0.722	0.716	0.723
Refractive index	1.464	1.468	1.464	1.466
Iodine number, gJ <sub>2</sub> /100 mL	22.2	23.1	24.5	22.5
Appearance	Light yellow, transparent	Light yellow, transparent	Colorless, transparent	Colorless, transparent
<b>Light Gas Oil</b>				
Boiling range, °C	200-295	200-289	200-283	200-280
Density at 20 °C, kg/m <sup>3</sup>	839	830	831	836
Kinematic viscosity at 20 °C, mm/s <sup>2</sup>	2.15	2.14	1.556	1.678
Refractive index	1.487	1.487	1.494	1.495
Iodine number, gJ <sub>2</sub> /100 mL	18	16.5	17	16.6
Cetane index (GOST 27768-88)	53	52	46	44
Appearance	Green, transparent	Yellowish-green, transparent	Yellow, transparent	Yellow, transparent

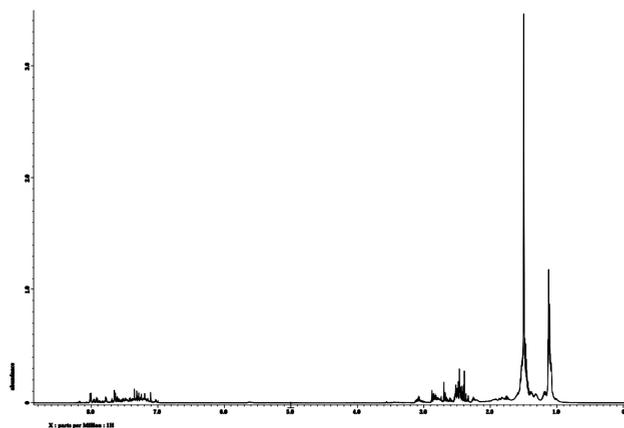
The analysis of the feedstock and the products obtained has been carried out by quantitative nuclear magnetic resonance spectroscopy. Fig. 4-6 show <sup>1</sup>H NMR spectra of the feedstock and the products obtained, and Table 4 provides the characteristics of the fragmental structure of the samples, i.e. the quantitative content of aromatic hydrogen (*H<sub>ar</sub>*); double bond hydrogen (*H<sub>ol</sub>*); hydrogen of groups directly attached to the benzene ring (*H<sub>α</sub>*); hydrogen of all methylene and methine fragments, as well as methyl groups located in the β-position to the benzene ring (*H<sub>β</sub>*); hydrogen of all methyl groups of saturated compounds, as well as those in the γ-position to the benzene ring (*H<sub>γ</sub>*).



**Fig. 4.** 1H NMR Spectrum of Feedstock.



**Fig. 5.** 1H NMR Spectrum of the Catalytic Cracking Gasoline Fraction ( $T_{cr} = 500\text{ }^{\circ}\text{C}$ , feed space velocity is  $2\text{ h}^{-1}$ ).



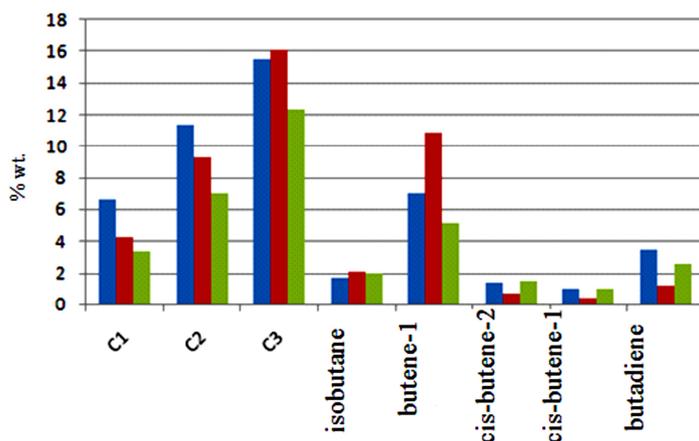
**Fig. 6.** 1H NMR Spectrum of Light Catalytic Cracking Gas Oil ( $T_{cr} = 500\text{ }^{\circ}\text{C}$ , feed space velocity is  $2\text{ h}^{-1}$ ).

**Table 4.** Fragmental Structure of Feedstock and Products of Catalytic Cracking of a Wide Fraction of the Polyisoprene Rubber Production Waste Thermolysis.

	H <sub>ar</sub> , %	H <sub>ol</sub> , %	H <sub>α</sub> , %	H <sub>β</sub> , %	H <sub>γ</sub> , %
Feedstock	7.78	0.98	14.05	54.02	23.17
<b>Gasoline Fraction</b>					
T <sub>cr</sub> =500	11.76	2.49	16.84	48.84	20.07
T <sub>cr</sub> =450	8.29	0.84	16.65	48.72	25.5
T <sub>cr</sub> =400	7.25	1.35	13.78	47.9	29.74
<b>Light Gas Oil</b>					
T <sub>cr</sub> =500	12.37	0.41	18.79	47.1	21.32
T <sub>cr</sub> =450	6.52	0.29	11.85	55.17	26.17
T <sub>cr</sub> =400	6.1	0.8	11.1	56.4	26

From Table 4, it follows that with increasing the process temperature, the share of aromatic hydrogen  $H_{ar}$  and, accordingly,  $H_{\alpha}$  signals increases. This indicates an increase in the content of aromatic compounds in cracking products, which explains some of the trends given in Table 3. The increase in the content of aromatic compounds is caused not only by the formation of unsaturated compounds during the process but also their presence in the feedstock, which may undergo cyclization and dehydrogenation in wide zeolite pores.

Fig. 7 provides the composition of cracking gases at various feed rates and a temperature of 500 °C. The composition of the gas phase varies insignificantly with the share of C<sub>3</sub>-C<sub>4</sub> in the gas composition of 65 % on average. Propylene and butene-1 make up a high proportion (15 %) of wet gas.



**Fig. 7.** Cracking Gas Composition (Feed Space Velocity is 2,3, and 4 h<sup>-1</sup>, T = 500 °C).

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