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THE DIRECTIONS OF PRODUCTS' USE OF RUBBER WASTE PROCESSING

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In the modern world environmental issues related to the disposal of production and consumption waste are of particular importance. At the same time the relevance of development is dictated not only by environmental aspects but also by the limitations of natural raw materials and the search for alternative energy sources. Therefore, when recycling industrial and consumer waste, an important direction is the production of energy and chemical products obtained today from traditional oil and gas raw materials. Industrial and consumer waste (suitable for processing to produce raw materials for energy and industry) includes rubber products that have lost their consumer qualities during operation, but at the same time have the potential for recycling to produce products for various purposes [1].

Every year in Russia from 650 to 750 thousand tons of waste tires, tires and inner tubes are generated, while the share of recycling is only 13%. Of the total volume of recycled waste, 20-25% is processed, about 20% is burned, and the rest is sent for disposal [2]. This picture can characterize Kuzbass as a region with a developed fuel and energy complex and, accordingly, great number of equipment (mainly large-tonnage dump trucks). As a result of open-pit mining activities, a large amount of rubber waste is generated, such as large dump truck tires. Provided that all mineral extraction sites, including coal, planned for licensing, must provide for predominantly open-pit mining of reserves [3], one should not expect a decrease in the amount of corresponding rubber waste (requiring disposal).

Current methods for processing rubber waste (RW) cannot reduce waste and lead to its accumulation in landfills that occupy significant areas. To a greater extent, this is due to the lack of demand and low quality of the resulting products [4-7]. Therefore, to solve the problem of waste disposal, especially in industrial regions, it is necessary to develop existing thermal processing technologies with an expansion of the range of resulting products.

A promising processing method is a recycling method that combines the stage-by-stage RTO pyrolysis processes and subsequent activation of the resulting solid residue [8, 9] with the production of gaseous, solid and liquid products in one technological scheme. The first stage of the technology under consideration is the process of high-temperature pyrolysis of crumb rubber in an inert environment, which results in the formation of a solid carbon product, pyrolysis gas and a condensed liquid phase; at the second stage, the process of carbon dioxide gasification of the solid product is carried out to produce carbon-containing gas and solid residue at temperatures of 950-1000^{o}C.

The solid carbon residue obtained because of pyrolysis in traditional technologies is considered for use as a composite fuel [10], pigment for the production of paints and varnishes [11] or sorbent [5]. At the same time, studies carried out by a few authors have shown that TCO for tire pyrolysis has a rather low specific surface area (≈40-50 m2/g) and a poorly developed structure, which indicates that TCO in this form cannot be used as sorbent, and requires additional activation processes [7-9,12]. In the proposed two-stage technology, the solid residue of the pyrolysis process is not considered as the final product but is a raw material for the second stage of processing.

In addition, the liquid fraction is a mixture of heavy hydrocarbons and is used in the traditional approach as heating fuel. In this case, the conditions of pyrolysis influence the composition of the resulting liquid phase, so under certain parameters of the pyrolysis process such valuable products as o-Cymene and D-Limonene are formed [13]. During the experimental testing of the proposed technology during the pyrolysis of rubber crumbs from tires of mining dump trucks, about 40% of o-Cymene and D-Limonene were obtained in the pyrolysis liquid, which is a promising composition for their industrial production. O-Cymene and d-Limonene are widely used in various areas of production: solvent for fats, rubbers, petroleum products; intermediate raw materials in chemical synthesis (terpinhydrate, terpineol, carvone, flotation reagents); disinfectant and brightening reagent; perfume and pharmaceutical industry. Comparing d-Limonene with the industrial extraction solvent hexane, the study authors concluded that the properties of these solvents are comparable, and the use of d-Limonene as an alternative to hexane has the potential to eliminate environmental safety concerns [14]. Traditionally, these substances are obtained through fractional distillation of citrus oils, and annual production reaches 70 thousand tons per year. After the separation of high-margin o-Cymene and D-Limonene, the remaining part of the liquid product of the pyrolysis process can be considered in technologies for processing coal raw materials into liquid chemical products [15].

The gas phase of the pyrolysis process is a mixture of mainly H2 (up to 70%) and CH4, the content of other gases is within 1% [7-9]. The traditional use of this gas is combustion to support the endothermic reactions of the pyrolysis process. It means that this product does not have purchasing power and can only be disposed of on site. It should be noted that gas containing up to 70% hydrogen can be a source of hydrogen fuel with a low carbon footprint. Thus, pyrolysis gas, which contains up to 70% hydrogen, can become a promising raw material for producing pure carbon. Today, hydrogen is an industrial gas used in the production of ammonia, methanol, and oil refining. The concentration of hydrogen from gas mixtures can be carried out using cryogenic air separation units, adsorption, and membrane methods. The most attractive process is the membrane method. This method has greater mobility, simplicity, and reliability.

At the second stage of processing waste rubber products, the solid residue from the pyrolysis process is processed in a carbon dioxide atmosphere at temperatures sufficient for the Boudoir reaction to occur (900-1000°C). The result of the Boudoir reaction is the production of a gaseous product consisting mainly of CO (up to 86%) and a solid residue. In this case, compared to TOC obtained after the pyrolysis process, there is an increase in the micro-/mesoporous structure and specific surface area. Thus, the solid residue after the second stage of processing has the characteristics of a carbon sorbent that can compete with industrial activated carbons in the market. Recent events such as a fuel leak at the “Primteploenergo” boiler house [18] and an industrial disaster at CHPP-3 in “Kayerkan” [19] have shown the particularly important role of sorbents in ensuring environmental safety.

It should be mentioned that the generator gas (formed at the second stage of processing) is a mixture of CO and CO2 with a predominance of CO (up to 86%) in the composition. The heat of combustion of 14-16 MJ/Nm3 makes this gas an attractive raw material for the production of electrical and thermal energy and maintaining endothermic reactions occurring during disposal and providing electrical energy for related processes. This increases the energy efficiency of the processing process, which in conventional technologies is a limitation for their industrial and large-scale implementation. In addition, the use of carbon dioxide as a gasifying agent helps reduce CO2 emissions due to its liquefaction after combustion of CO in a CCGT unit during the generation of electrical and thermal energy. The implementation of recycle solves the issue of providing the process with a gasifying agent that does not increase costs in the production of target products, as in the case of using water vapor as a gasifying agent.

As a result of a review of thermal methods for recycling industrial rubber waste, it was revealed that their large-scale implementation is hampered by the low level of demand for the resulting products, associated with their inferior quality compared to analogues on the market. Therefore, to increase the volume of rubber waste recycling, it is necessary to diversify the resulting products with a focus on energy and chemical products that are in demand in the markets.

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