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Salvaging of Waste Automobile Tires with the Use of Thermal Solvolysis

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Abstract

Main regularities of thermal solvolysis of comminuted rubber in organic solvents and variations of its application to salvage waste tires have been considered. The advantages of the technology to process tires with the use of heavy petroleum residue as a solvent have been disclosed.

INTRODUCTION

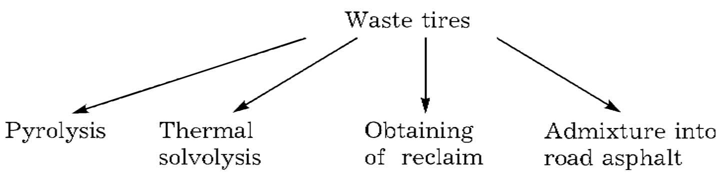
Processing of a great amount of waste tires is a serious environmental problem [1] and to solve the problem, the development of environmentally sound technologies is required that involve obtaining of valuable commercial products. Scheme 1 presents the basic directions for processing the waste tires.

Thermal solvolysis of comminuted rubber from waste tires to generate marketable products is under investigation as an alternative to the pyrolysis process. Main products of the processes of pyrolysis and thermal solvolysis of waste tires are gases, liquid products, and a fixed residue that represents a rubber extender, commercial-grade carbon, and inorganic admixtures. During pyrolysis of tires, the obtained gases are used to heat the pyrolysis reactor, whereas the fixed residue is used to yield sorbents or instead of marketable commercial-grade carbon, and the liquid products, as fuel admixtures. In view of comparatively sophisticated instrumentation and low quality of the obtained products, the pyrolysis technology has not found widespread use.

Thermal solvolysis of comminuted rubber is conducted in the medium of solvent at lower temperatures as compared to pyrolysis, which makes it possible to increase the amount of liquid products at the expense of the reduced gas-making, and also to adjust their quality through varying the solvent composition.

During the study of thermal solvolysis of tire rubber in various organic solvents, the following results are acquired that have formed the basis for the development of the process to salvage waste tires [2]:

1. The dissolution degree of the waste tires in various individual and commercial-grade solvents comprises 65–70 % at the temperatures of 300–400 °C. The insoluble residue constitutes a fine-dispersed commercial-grade carbon and the inorganic admixtures that are used in



Scheme 1.

production of tires. The yield of gases at 300 °C does not exceed 1 %.

2. Liquid products of thermal solvolysis of tires are represented for the most part by substances (oils) that are 90 % hexane-soluble. An average molecular mass of oils that have been produced at 300 °C comprises 1000–2000. These products consist preferentially of rubber oligomers that are constituents of tires. With an increase of solvolysis temperature, further splitting of oligomers to yield the compounds with the average molecular mass of 400 is observed, which is accompanied with the reactions of ring formation and aromatization.

3. As regards the process of thermal solvolysis, organic solvents are classified into those inert (that do not enter into reaction with the products of rubber thermolysis) and active (that form new compounds with intermediate reactive products of the disintegration of tire rubber).

4. During thermal solvolysis of tires in liquid asphalt, the rubbers that are constituents of tires completely decompose as a result of thermal reactions with the solvent components, to form the liquid compounds that are well compatible with oil products.

The acquired results make it possible to distinguish the following advantages of the process of thermal solvolysis of waste tires over the pyrolysis process:

1. Milder conditions for carrying out the process owing to the application of solvent and to a decrease of the process temperature down to 300–400 °C (the pyrolysis temperature is 400–600 °C).

2. Possible use of coarser pieces of rubber (fine-dispersed chips are applied during the pyrolysis, which is caused by a low thermal conductivity of rubber).

3. Enhanced conversion degree of tire rubber into liquid products that is as high as 65 % at 300 °C (during the pyrolysis, this magnitude can be as high as 45 % at the same temperature).

4. A decrease in the yield of gases down to 1 % at 300 °C (5 % during the pyrolysis).

5. The possibility to modify consumer properties of the products of thermal solvolysis by solvent selection and through adjusting the temperature of the process.

Being dependent on the solvent composition, two process flow diagrams to salvage the waste tires are possible.

The stage of preliminary grinding of tires is common for both versions. As of now, various processes of tire grinding are suggested and practically implemented to yield comminuted rubber with separating of a metal cord. As a rule, the target product of these processes is fine-dispersed comminuted rubber with the particle size of no more than 3 mm, and in specific cases, from 0.3 to 0.8 mm (depending on the direction of its application). Meanwhile, when close-grained chip is produced, its production cost increases drastically.

Coarse comminuted rubber with the particle size of 5–20 mm has been used in this work during thermal solvolysis (applying larger chip is admitted too). This comminuted rubber can be acquired from the functioning manufacturers that salvage waste tires or it can be obtained directly in thermal solvolysis units through application of the familiar, well-proven technologies of mechanical grinding.

SALVAGING OF WASTE TIRES WITH THE USE OF THERMAL SOLVOLYSIS

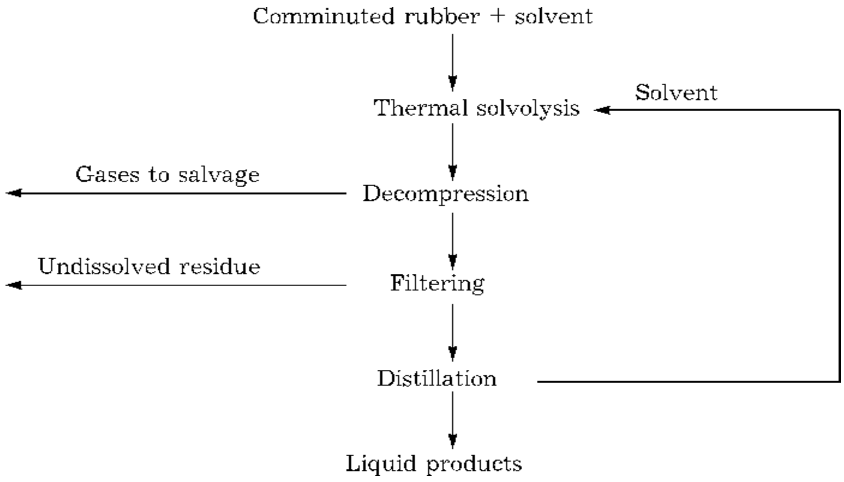
The first version

The process is conducted at the temperatures of 350–400 °C (Scheme 2) and involves application of recirculating organic solvent with low molecular weight.

In this case, it is possible to separate the fixed residue from liquid products by means of filtering and to use it as a substitute of commercial-grade carbon or as a sorbent. It is suggested that liquid products are used in combination with solvent as an admixture to fuel or as raw material for petrochemical processes.

In addition, incorporation of the stages of solvent separation and its recycling back into the process of thermal solvolysis is possible together with the independent use of liquid products in the same directions.

The following demands are imposed on the solvent: availability, low cost, thermal stability, the interval of boiling points of 110–160 °C. It



Scheme 2.

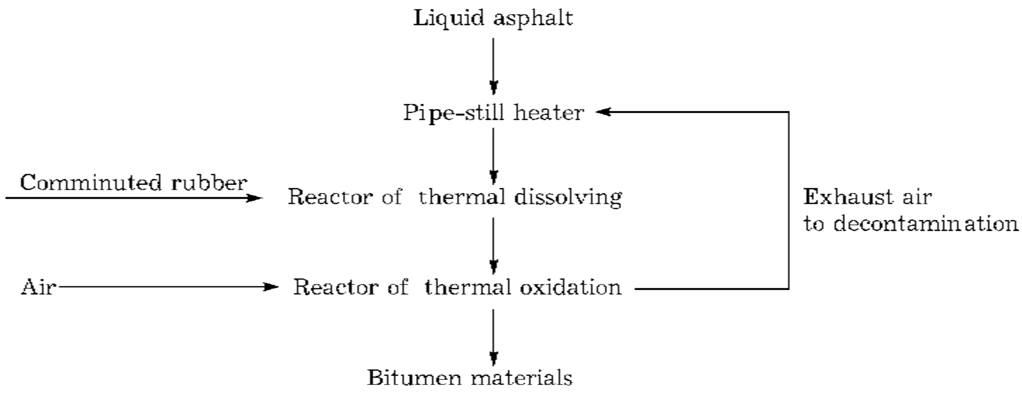
is recommended to utilize the technical fractions that are produced in petroleum refining and that meet these requirements, or commercial products after the appropriate preparation. Particularly, Nefras-S 50/170 can be used as a solvent after a fraction with a boiling range of 105–145 °C has been taken.

The quantity of gases can amount from 1 to 5–7 % of the mass of the initial comminuted rubber depending on the process temperature. They consist preferentially of light hydrocarbons (C_1–C_5). The undissolved residue constitutes the filler of rubber, namely, fine-dispersed carbon black and inorganic admixtures. The yield of the residue is 25–30 %, and that of liquid products, up to 70 % from the mass of initial rubber. Their characteristics and composition depend, mainly, on the temperature of the stage of thermal solvolysis. Kind of manufactured tires has practically no effect on the degree of rubber conversion into soluble products [2].

There is no non-reclaimed waste and emissions in thermal solvolysis. The gases that evolve at different technological stages are exposed to salvaging by the combustion in a pipe-still heater that is applied to heat the feedstock.

The second version

This version (Scheme 3) involves application of heavy commercial solvents. The process includes two stages: thermal solvolysis and the subsequent thermal oxidation by air. Heavy petroleum residue after atmosphere-vacuum distillation of oil (liquid asphalts), the oxidized liquid asphalts (bitumen), the asphalt from propanoic deasphaltizing, and the residue of



Scheme 3.

viscosity breaking can be used as a solvent. From the economic point of view, it is advisable that lower-priced products, liquid asphalts are applied. By virtue of the fact that the process is conducted under atmospheric pressure, the solvent may not contain the fractions that boil lower than 360 °C.

By the analogy with bitumen, with the oxidized liquid asphalts, the product of the process can be used for the same purposes [3]: as an organic astringency in road building, as an insulation and structural bitumen, and as a component of anticorrosive insulator for pipelines. Soot particles and liquid products of thermal solvolysis of tire rubber serve as modifiers for the obtained bitumen materials.

Here are the basic features of bitumen modification by the products of thermal solvolysis by tire rubber.

1. Carbon black plays the part of structuring agent, as it reduces the temperature effect upon the physical properties of bitumen and improves the properties of road surfacing such as mechanical strength, crack resistance, and frost resistance [2, 4]. Meanwhile, carbon black solids available in bitumen reduce the value of the "elongation" index, or ductility, which is not the basic index though during the assessment of the properties of the products that are obtained by the developed process.

2. Liquid products of dissolving the tire rubber act as a plasticizer that lowers the

TABLE 1

Physicomechanical properties of bitumen materials

Sample	Softening point (Ring and Ball Method), °C	Penetration, mm, at a temperature of, °C		Elongation, cm	Adhesion to mineral materials, %	
		0	25		Marble	Granite
Liquid asphalt	34	177	68	65	20	30
Combined product of thermal solvolysis from the experiment 1*	36	228	164	–	90	80
The same from the experiment 2*	50	48	33	30	100	100
BPR 40/60	51	40–60	10	40	25–100	25–100
Combined product of thermal solvolysis from the experiment 3*	49	88	21	–	100	100
BPR 60/90	47	61–90	20	–	25–100	25–100
The same from the experiment 4*	49	104	22	–	100	100
BPR 90/130	43	91–130	28	–	25–100	25–100

*The experiment 1: T = 300 °C; the experiments 2–4 differ in the liquid asphalt : rubber ratio and in the oxidation time.

softening point. The combination of the processes of thermal dissolving and thermal oxidation makes it possible to control physical properties of the bitumen. There is no non-reclaimed waste and emissions with this technology. The main possible contaminant of the environment is the exhaust air from the stage of thermal oxidation; therefore, the process must include the stage of its decontamination. Small quantities of gases evolve at the stage of thermal solvolysis too. Their salvaging is made simultaneously with the neutralization of the exhaust air through its combustion in a pipe-still heater.

Evaluation test has been performed for the bitumen that has been produced by the given technology in compliance with the indices that are used for tests of road asphalts.

Table 1 gives the basic indices of the quality of road asphalts for the initial liquid asphalt.

To compare the obtained bitumen materials with standard road bitumen, the requirements for petroleum road bitumen of BPR 40/60, BPR 60/90, and BPR 90/130 grades (State Standard GOST 22245–90) are given here, too.

It is evident that upon the modification of liquid asphalt by carbon black and liquid products of thermal dissolving of rubber, the softening point varies only slightly and the penetration index rises dramatically.

The subsequent air thermal oxidation of the combined product of solvolysis leads to a rise in the softening temperature, to a decrease of penetration, and to an increase in the binding force of the bitumen to mineral materials. All the modified bitumen show excellent adhesion: the adhesion to marble and granite ranges up to 100 %.

Varying the ratio of comminuted rubber and the oil residue, and the conditions of thermal solvolysis and thermal oxidation, we can obtain modified bitumen with various characteristics, including those meeting the norms of current standards in the basic indices.

The obtained bitumen can be used in road building or as an admixture to standard bitumen to enhance their adhesion to mineral materials.

The developed technology of salvaging the waste tires in heavy technical solvents shows the following advantages:

1. The use is made of standard and inexpensive instrumentation.

2. The process occurs at atmospheric pressure.

3. Modified bitumen with various properties for different fields of application can be produced.

4. There are no harmful emissions and waste; the exhaust air after the stage of thermal oxidation is reclaimed by its delivering to a pipe-still heater.

Economic efficiency will be ensured by obtaining the high-quality road asphalts around low-cost and available raw material, tire rubber, and petroleum residue, as well as bitumen raw material for alternative directions of application.

CONCLUSION

A non-waste technology of salvaging the waste tires has been developed with application of the process of thermal solvolysis in heavy petroleum residue to yield bitumen materials. The basic regularities of bitumen modification by the products of thermal solvolysis of tire rubber have been revealed. The combination of the processes of thermal solvolysis and thermal oxidation makes it possible to control physicomechanical properties of bitumen. The produced modified bitumen that feature excellent adhesion to marble and granite can be used independently in road building or as an admixture to standard bitumen to enhance their adhesion to mineral materials.

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