

<https://doi.org/10.3176/oil.1997.1.05>

UTILIZATION OF RUBBER WASTE IN MIXTURE WITH OIL SHALE IN DESTRUCTIVE THERMAL PROCESSING USING THE METHOD OF SOLID HEAT CARRIER

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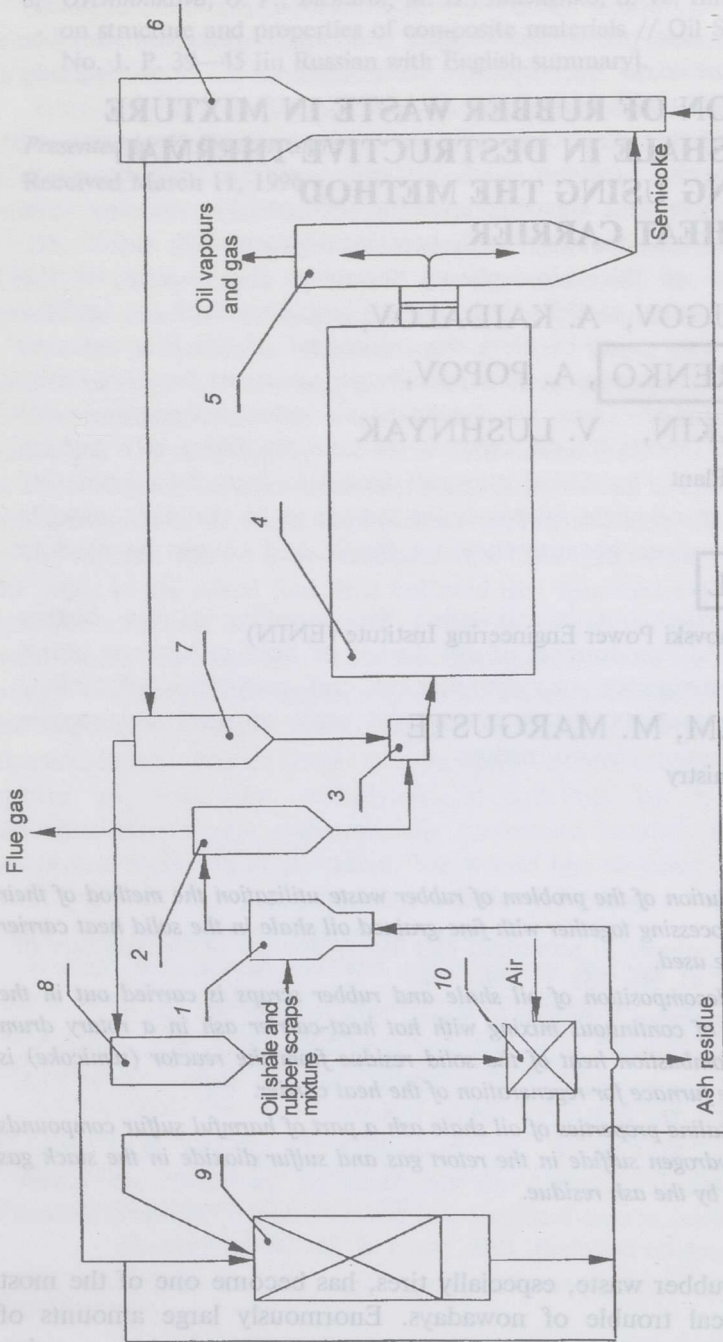
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For the solution of the problem of rubber waste utilization the method of their thermal processing together with fine-grained oil shale in the solid heat carrier unit can be used.

Thermal decomposition of oil shale and rubber scraps is carried out in the conditions of continuous mixing with hot heat-carrier ash in a rotary drum reactor. Combustion heat of the solid residue from the reactor (semicoke) is used in the furnace for regeneration of the heat carrier.

Due to alkaline properties of oil shale ash a part of harmful sulfur compounds such as hydrogen sulfide in the retort gas and sulfur dioxide in the stack gas are bound by the ash residue.

Utilization of rubber waste, especially tires, has become one of the most serious ecological trouble of nowadays. Enormously large amounts of worn tires are disposed of every year. Their storage results in a growing number of environmental problems. Rubber waste is not easily biodegradable under the action of natural factors. Rubber waste is flammable and tires in flames are hard to extinguish. Moreover, burning tires produce compounds intensively polluting natural surrounding.



Flow sheet of the thermal processing of rubber waste in the mixture with oil shale using the method of solid heat carrier:
 1 - drier, 2 - dry shale separator, 3 - mixer, 4 - reactor, 5 - dust removal chamber, 6 - furnace, 7 - heat carrier cyclone,
 8 - ash cyclone, 9 - waste heat boiler, 10 - air

Rubber tires are made from synthetic or natural caoutchouc - a polymerization product of unsaturated hydrocarbons. At vulcanization 0.5-3.5 % sulfur is added. Soot as a filler and some other special components (e.g. zinc oxide) are also added to caoutchouc, and tires are reinforced with textile and/or metal cord.

Potential power resources of rubber waste are comparable to specific heat of combustion of a high-quality coal (about 32 MJ/kg). However, direct combustion of tires in boilers for producing electricity and high-pressure steam would be economically not effective because capital investments needed for special measures to protect nature against pollutants were too high. During combustion of tires toxic volatile compounds are formed and most of sulfur present in tires also passes on into the flue gases. The storage of combustion residues is also too expensive.

The possibilities of retorting of rubber waste - i.e. its thermal destruction for producing gas and oil - have been studied already [1]. Shredded tires were processed in rotating retorts with external heating at 520-580 °C [2]. The volatile products formed were pyrolyzed on smouldering coal in the presence of air. The gas yield was 1.5-2.5 kg per one kg of rubber mass. The combustion value of gas was very low - only 3.7-5 MJ/kg. This process is characterized by an unbalanced heat balance: about 20 % of the potential heat power of the initial matter remain in the solid residue of thermal decomposition. Furthermore, calcium hydroxide must be added into reactor for binding sulfur and chlorine present in retorting products.

Consequently, neither combustion nor thermal decomposition represent effective methods for utilization of tires because both processes are accompanied by serious engineering, ecological and economical problems, and solid residues of processing are inapplicable.

In this paper a complex method for utilization of rubber waste, primarily tires, is presented. The requirements enforced by nature protection agencies are also considered. The method enables to produce liquid and gaseous products from the organic material of tires, and electricity on account of potential thermal power of rubber waste. The process consists in thermal decomposition of shredded tires in the mixture with fine-grained oil shale at the unit SHC-3000 using the method of solid heat carrier.

Flow sheet of the thermal processing of rubber waste in the mixture with oil shale using the method of solid heat carrier is given in the Figure.

The mixture of oil shale fines and waste tire particles (≤ 25 mm) is supplied by conveyor to drier 1 where flue gas (t about 700 °C) is also fed in. The dried mixture enters, through dry shale cyclone 2 and dry shale conveyor, mixer 3, where it is mixed with hot (750-800 °C) heat-carrier

ash. The mixture of shale, tires and heat-carrier ash enters rotary drum reactor 4. The mixture is heated up to a temperature ~450-550 °C, organic part of the mixture undergoes destruction and a gas-vapour mixture is formed. Then the mixture and spent shale are directed to the dust separator 5 and, after passing special cyclones and cleaning, the gas-vapour mixture is directed to the condensation unit, where heavy and middle oils, gas turbine fuel fraction, gasoline fraction and high-calorific gas are separated.

Table 1. Results of Laboratory Retorting of Scrap Tires
(Ash Content of Rubber Crumb $A^d = 3.32\%$,
Sulfur Content $S^d = 1.23\%$)

Indices	Value
Product yield (rubber mass basis), %:	
Oil	52
Pyrogenetic water	1
Solid residue (semicoke)	39
Gas	6
Volume yield of retort gas (at 0 °C and 760 mm Hg), 1/kg	39.1
Oil characteristics	
Density d^{20}_4 , g/cm ³	0.9277
Phenol content, %	2.7
Iodine value, g of iodine per 100 g of oil	90.6
Kinematic viscosity at 20 °C, cSt	5.95
Refraction index n^{20}_D	1.5270
Flash point (in closed crucible), °C	+7
Pour point, °C	-27.5
Water-soluble acids and bases	Not present
Fractional composition of oil	
Initial boiling point, °C	95
10 % distil at t , °C	125
20 % distil at t , °C	188
30 % distil at t , °C	227
40 % distil at t , °C	276
50 % distil at t , °C	306
60 % distil at t , °C	335
70 % distil at t , °C	355
75 % distil at t , °C	360
Benzo(a)pyrene content of oil, µg/kg	3
Semicoke	
Ash content of solid residue A^d , %	6.33
Combustible content of residue, %	93.47

Solid residue of retorting from separator 5 is supplied by conveyor to the furnace, where the organic material not gasified in the reactor is finally burned in the air flow. During combustion the temperature of residual ash reaches 750-850 °C. The combustion products formed in the furnace are directed to cyclone 7 where most ash is removed. The ash

collected by cyclone 7 serves as a heat carrier for shale-and-tires heating and is directed to the mixer. The ash collected by cyclone 8 is removed from the cycle after cooling in the ash heat exchanger 10 where the air which is directed into the furnace is heated up.

Due to alkaline properties of oil shale ash the bulk of sulfuric compounds formed at thermal processing (hydrogen sulfide, sulfur dioxide) and other acidic compounds present in products are bound through chemisorption.

Quantitative indices of decomposition of waste tire particles have been determined in laboratory experiments of retorting under standard conditions in retorts with external heating (final temperature 520 °C) (Table 1).

Later on full-scale tests of thermal processing of the mixture of oil shale with rubber were carried out. The throughput rate of the solid heat carrier unit SHC-3000 at Estonian Power Plant is 3000 tonnes of shale per day [4, 5].

In the first experiment, the ratio of fine-grained oil shale and tire particles was 9 : 1 (Table 2).

Table 2. Characteristics of Mixture, %

Indices	Value
Oil shale	
Moisture W^r_t	11.16
Ash content A^d	51.97
Carbon dioxide $(CO_2)^d_M$	24.46
Sulfur S^d_t	1.50
Content of organics in dry matter	23.57
Tire (79% inner and 21% outer tires)	
Ash content A^d	3.33
Sulfur S^d_t	1.02
Yield of products in the standard aluminum retort, % on tire basis:	
Oil	33.02
Gas	29.58

During the first experiment 21.45 tonnes of scrap tires in the mixture with 193 tonnes of oil shale were processed (Tables 3 and 4). The oil yield was 143.6 kg per 1 tonne of the initial mixture. The increase in oil yield due to the presence of rubber was 31.57 % (on rubber basis), the number being close to the results of laboratory experiment.

Table 3. Fractional Composition of Oil (Oil Shale and Rubber Ratio 9 : 1)

Indices	Value
Heavy oil	43.24
Middle oil	28.97
Gas turbine fuel fraction	5.98
Gasoline fraction	21.81

Total oil obtained at processing the mixture contained more low-boiling fractions compared to pure oil shale retort oil. Sulfur content of total oil is lower but other indices (iodine value, viscosity) are comparable with those of shale oil.

Chemical composition and heat value (40 MJ/m³) of the retort gas formed from the mixture also do not differ essentially from those indices determined for shale retort gas. Flue gases do not contain hydrogen sulfide and the content of sulfur dioxide is even lower than in flue gases of shale retorting (0.016 Vol.%).

Table 4. Characteristics of Oil Fractions

Indices	Gasoline fraction	Gas turbine fuel fraction	Middle oil	Heavy oil
Density d_{4}^{20} , g/cm ³	0.8267	0.9690	1.0373	1.0575
Sulfur, %	0.79	0.64	0.39	0.54
Iodine value, g of iodine per 100 g of oil	126.7	122	-	-
Mechanical impurities	-	0.11	0.12	1.77
Viscosity, °E:				
at 20 °C	0.98	4.53	-	-
at 30 °C	-	1.22	2.96	11.8
Fractional composition:				
5 % distil at t , °C	114	244	280	287
10 % distil at t , °C	123	250	297	305
20 % distil at t , °C	136	256	310	332
30 % distil at t , °C	147	262	322	345
40 % distil at t , °C	161	268	333	(37 %) 360
50 % distil at t , °C	170	277	340	-
60 % distil at t , °C	179	286	352	-
70 % distil at t , °C	183	300	(68 %) 362	-
80 % distil at t , °C	199	320	-	-
90 % distil at t , °C	217	340	-	-

Chemical composition of the ash sample taken from the hydraulic ash disposal system during thermal processing of the mixture at the solid heat carrier unit was as follows, %:

SiO ₂ - 21.38	Al ₂ O ₃ - 6.47	Fe ₂ O ₃ - 3.16
CaO - 29.69	MgO - 3.99	Na ₂ O - 0.42
TiO ₂ - 0.12	K ₂ O - 3.63	ZnO - 0.22
SO ₃ - 2.55	S _S ^d - 0.60	(CO ₂) _M ^d - 19.00
Water of constitution - 7.91		
Organic matter - 0.86		

Optimum ratios for the mixture oil shale:rubber waste were chosen experimentally, and for this purpose a series of full-scale tests was carried out. Maximum share of scrap tires in the mixture is 20 %.

The results of thermal decomposition of the mixture oil shale fines and tire particles 4 : 1 are given in Tables 5 and 6.

Table 5. Characteristics of Mixture, %

Indices	Value
Oil shale	
Moisture $W r_t$	13.08
Ash content A^d	51.30
Carbon dioxide $(CO_2)^{d_M}$	21.56
Sulfur S^d_t	1.55
Content of organics in dry matter	27.14
Tire	
Ash content A^d	20.44
Sulfur S^d_t	0.94
Yield of products in the standard aluminum retort, % on tire basis:	
Oil	49.20
Gas	3.67

During this experiment 1500 tonnes of rubber scraps were processed (tires, children toys, various packings, etc.). The oil yield was 205.8 kg per one tonne of the mixture (46.74 %, on rubber basis).

Table 6. Characteristics of Oil Fractions

Indices	Gasoline fraction	Gas turbine fuel fraction	Middle oil	Heavy oil
Density d^{20}_4 , g/cm ³	0.8200	0.9024	1.0220	1.0362
Sulfur, %	0.63	0.93	0.64	0.53
Iodine value, g of iodine per 100 g of oil	111.8	93.8	39.9	87.1
Fractional composition:				
5 % distil at t , °C	135	207	273	283
10 % distil at t , °C	141	212	286	287
20 % distil at t , °C	150	219	303	324
30 % distil at t , °C	157	225	319	341
40 % distil at t , °C	163	232	330	353
50 % distil at t , °C	169	238	340	363
60 % distil at t , °C	175	244	353	-
70 % distil at t , °C	183	251	(65 %) 356	-
80 % distil at t , °C	192	259	-	-
90 % distil at t , °C	209	275	-	-

Ash contained no heavy metal oxides. The content of silicon, aluminum and calcium oxides only unessentially exceeded these values determined for shale ash.

Whereas rubber contains less sulfur than oil shale, enlarging the share of rubber in the mixtures is not accompanied by an increase in the content of sulfuric compounds in oil, flue gas and retort gas.

Since the ash content of tires varies between 2.5-4.5 %, and other rubber wastes contain less ash than oil shale, too, the share of rubber waste in the mixture may not exceed 20 %, otherwise the normal run of pyrolysis will be disturbed because the quantities of ash formed would not be sufficient for producing heat carrier in amounts needed for the process.

The method of utilization of rubber waste processing them in the mixture with oil shale by the method of solid heat carrier is patented [5]. During ten months in 1996, 13 thousand tonnes of rubber waste were utilized at the unit SHC-3000 at Estonian Power Plant.

Conclusion

Useful retorting products - oil and gas (summarily 59-62 %, on rubber mass basis) are produced at destructive thermal processing of the mixture consisting of oil shale fines and rubber scraps. Heat power of remained semicoke is used for realization of the process. Ash removed from the process contains only $\leq 1\%$ of the organic matter.

Application of the well-known method of solid heat carrier for thermal decomposition of rubber waste, especially of worn tires, enables effectively to solve a most serious problem of environment protection and at the same time to reduce the amounts of processed shale even increasing the yields of oil and gas.

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Presented by I. Öpik

Received November 8, 1996