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# PYROLYSIS PROCESSING OF POLYMER WASTE COMPONENTS OF ELECTRONIC PRODUCTS

Anatoliy Ranskiy<sup>1</sup>, Olga Gordienko<sup>1</sup>, Bogdan Korinenko<sup>1</sup>, Vitalii Ishchenko<sup>1</sup>, Halyna Sakalova<sup>2,⊠</sup>, Tamara Vasylinych<sup>2</sup>, Myroslav Malovanyy<sup>3</sup>, Rostyslav Kryklyvyi<sup>2</sup>

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Abstract. The recycling of ABS plastic as a component of electronic and electrical equipment waste by the method of low-temperature pyrolysis is shown and substantiated as well as obtaining alternative sources of energy: pyrolysis liquid, gas mixture, and pyrocarbon. The main components of electronic and electrical equipment waste, which consists of plastic and refractory oxides, along with copper and iron compounds, were analyzed. The composition of precious, toxic, rare, basic metals, and plastic waste is given. It is shown that the waste of electronic and electrical equipment is a valuable secondary raw material and requires separate environmentally friendly processing technologies. The thermal destruction of ABS plastic as a component of waste electronic and electrical equipment at a technological installation of periodic action in the absence of air oxygen and an acidtype catalyst was investigated. Gasoline, naphtha, kerosene, and diesel fractions were obtained by distillation of the pyrolysis liquid, and their qualitative and quantitative composition was studied by gas chromatography. It was established that the vast majority of compounds in different fractions are saturated C8-C16 hydrocarbons of normal and isomeric structure.

**Keywords:** waste of electronic and electrical equipment, ABS plastic, pyrolysis, technology, chromatographic analysis, alternative energetics.

#### 1. Introduction

Chemical and biological degradation of man-made waste often leads to the pollution of all components of the environment: atmosphere, hydrosphere, and soil. In some cases, it is possible to use waste in industrial and environmental protection technologies.<sup>1</sup> Still, in most cases, it is necessary to foresee special technologies for cleaning polluted components of the environment, of which the most common are adsorption technologies.<sup>2-4</sup>

The relative share among solid household waste (SHW) and electronic and electrical equipment (EEE), that is obsolete or out of order (monitors, TVs, computers, radios, telephones, cameras, *etc.*) and requires environmentally safe disposal or recycling, is growing. The main components of EEE waste are plastic and refractory oxides (30 % each), as well as compounds of copper (~ 20 %) and iron (~ 8 %).<sup>5</sup> Even though EEE waste is only 2 wt % from the total amount of solid waste, they are valuable secondary raw materials containing plastic, precious metals (Au, Ag, Pt, Pd), and other (Cu, Fe, Al, Ni, Sn) metals.<sup>6</sup> Thus, considering the basic principles of the circular economy,<sup>7</sup> EEE waste must be processed using modern technologies. The main metals in EEE are Fe, Al, Cu, Pb, Ni, Sn, and Zn. According to some estimates, the content of ferrous metals in EEE waste reaches 15 % by mass.8 Less common metals in the composition of EEE waste are Bi, Co, Ga, St, Ta, as well as toxic metals: Ba, Be, Cd, Cr, and St,<sup>9</sup> which require separate environmentally safe technologies for their processing. Multicomponent EEE waste, in addition to dangerous toxic metals, also contains dangerous organic substances: brominated flame retardants, phthalates, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, benzene, toluene, xylene, ethylbenzene, battery electrolytes, etc.

EEE plastic waste contains various impurities and fillers in addition to the polymers themselves. Some of

<sup>&</sup>lt;sup>1</sup> Vinnytsia National Technical University, Department of Ecology, Chemistry and Environmental Protection Technologies, Khmelnytske shose 95, Vinnnytsia, Ukraine

<sup>&</sup>lt;sup>2</sup> Vinnytsia Mykhailo Kotsiubynskyi State Pedagogical University, Department of chemistry and methods of teaching chemistry, Ostrozkoho St. 32, Vinnytsia, Ukraine

<sup>&</sup>lt;sup>3</sup> Lviv Polytechnic National University, Department of Ecology and Sustainable Environmental Management, Viacheslav Chornovil Institute of Sustainable Development, 12 Bandera St., 79013, Lviv, Ukraine

<sup>&</sup>lt;sup>™</sup> sakalovag@gmail.com

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them are dangerous: brominated/chlorinated flame retardants, plasticizers, dyes, stabilizers, etc. The most common polymer materials used in large EEE are polystyrene (42%), ABS plastic (38%), and polypropylene (10%). The remaining 10% are polyethylene, polyvinyl chloride, and some other polymers. The use of low-temperature pyrolysis of 250-400 °C allows the efficient processing of such polymer waste. The pyrolysis technology of processing ABS plastic is environmentally safe, because the thermal destruction process takes place in a closed volume, and the resulting products: pyrolysis liquid, gas mixture, and pyrocarbon can be effectively used as alternative sources of energy.<sup>10</sup> The thermal decomposition of polymer waste has been studied in many scientific works, but it remains an important object of applied studies on obtaining alternative energy sources.<sup>11-</sup>

<sup>13</sup> For example, the properties of the obtained pyrolysis liquid, depending on the processing temperature, are similar to diesel fuel or kerosene.<sup>11</sup> The main principles of low-temperature pyrolysis of plastic waste are defined in different works.<sup>14,15</sup> However, the practical processing of waste is complicated by the lack of reliable identification of waste, and the need to sort and process the mixture of plastic of unknown origin.

It determined a number of tasks to optimize the technology of pyrolytic processing of plastic waste, taking into account their chemical composition, temperature regime, time, use of a catalyst, and equipment design of the process.

The purpose of this study is to investigate the thermochemical destruction of ABS plastic waste as a component of EEE and to consider the possibility of practical use of the obtained pyrolysis products.

#### 2. Experimental

The studied ABS plastic wastes were extracted as a component of EEE and processed in the form of a crushed homogeneous mass of approximate dimensions of  $5 \times 5 \times 3$  mm. Experimental studies of EEE waste thermal destruction were carried out in a sequencing batch reactor in the absence of air oxygen and a catalyst at the installation, the schematic diagram of which is shown in Fig. 1.



Fig. 1. Basic technological scheme of the experimental and industrial installation for the pyrolysis of polymer waste: 1 –pyrolysis reactor; 2 – electric heating furnace; 3 – chrome-alumel thermal steam; 4, 11 – manometers; 5 – dispenser of plastic waste; 6 – hydraulic seal; 7, 8 – heat exchangers-condensers; 9 – condenser-gas separator; 10 – gas holder; 12 – gas meter; 13 – compressor; F-1...F-3 – pyrolysis liquid fractions

The main part of the given research and industrial installation is the pyrolysis reactor 1, which is placed in the electric heating furnace 2 and is heated by electrons. The steam-gas mixture that is formed in this case passes successively through the hydraulic seal 6 and the cooling system separating it into pyrolysis liquid and gas mixture. The main part of the pyrolysis liquid (F1, F2) is formed in the heat exchangers-condensers 7 and 8, and the additional part – in the condenser-gas separator 9, where the liquid fraction is finally separated from the gas mixture. The latter is collected in the gasholder 10. If

necessary, the gas mixture can be used for the internal needs of the pyrolysis installation or used directly by the consumer. In the latter case, the pyrolysis gas from the gas holder is fed into standard gas cylinders using the compressor 13.

Methods of thermal destruction of ABS plastic. The crushed mass of ABS plastic was weighed (30.0 kg) and poured into reactor 1, an oiled asbestos harness was laid around the perimeter for sealing, the reactor cover was bolted to the main body, and the flange connection to the vapor-gas mixture condensation system. The temperature of the process was automatically regulated by the temperature control unit for the sequential heating of three electrodes mounted in the heat-insulating housing of the heater **2**. The excess pressure in the reactor and the whole system was controlled, respectively, by manometers **4** and **11** (Fig. 1).

For quantitative and qualitative analysis of the obtained pyrolysis liquid (F-1 – F-3, Fig. 1) and establishing the possibility of its practical use as an alternative fuel for internal combustion engines (ICE), its fractional distillation was carried out.

<u>The method of distillation of pyrolysis liquid.</u> 250 cm<sup>3</sup> ( $\rho = 0.898$  g/cm<sup>3</sup>) of pyrolysis liquid of thermal destruction of ABS plastic was loaded into a three-necked flask, a temperature of 150 °C was set on a contact thermometer, which was maintained in the automatic mode with the help of an electric relay. The electric heater was turned on and in the first temperature interval of 40-140 °C, the fraction corresponding to gasoline was selected. Similarly, other fractions were selected, while

increasing the heating temperature interval. The obtained data of the fractional distillation of the pyrolysis liquid of the thermal destruction of PL are shown in Table 1.

Chromatographic analysis of the obtained liquid fractions of pyrolysis processing of ABS plastic waste (Table 1) was carried out using an "Agilent Technologies 7890 A" gas chromatograph (Agilent Technologies, USA) with a flame ionization detector using a quartz capillary column 60 mm long, with an inner diameter of 0.320 mm with a medium-polar cyanopropyl methyl silicone (6% cyanopropyl, 94% methylpolysiloxane) stationary phase DB-624 UI (layer thickness 1.8  $\mu$ m) in the temperature programming mode. Samples with a volume of 0.4–0.6  $\mu$ L were introduced into the column with a microsyringe with a capacity of 10.0  $\mu$ L. Fractions with different temperature ragines. The conditions of gas chromatographic analysis are given in Table 2.

The results of analytical studies were processed using the Chem Station analytical program.

Fraction	Temperature, °C	Distillate characteristics				
		$V, \text{ cm}^3$	<i>m</i> , g	$\rho$ , g/cm <sup>3</sup>	Result, %	
gasoline	40-140	66.8	52.0	0.778	23.17	
naphta	140-180	28.9	23.6	0.817	10.51	
kerosene	180-240	37.2	31.2	0.840	13.90	
diesel	240-250	54.5	47.1	0.865	20.98	
fuel oil	< 350	62.5	61.6	0.986	27.44	
losses	-	-	5.6	-	2.49	
remains in the flask	-	-	3.4	-	1.51	
In total	-		224.45	-	100.0	

Table 1. Results of fractional distillation of pyrolysis liquid of ABS plastic waste thermal destruction

Notes:  $V = 250 \text{ cm}^3$ ; density of pyrolysis liquid  $\rho = 0.898 \text{ g/cm}^3$ .

Table 2. Conditions	for chromatographic	analysis of pyroly	sis liquid fractions	s on a chromatograph	"Agilent
Technologies 7890 A	<b>\</b> "				

	The range of boiling temperatures of fractions			
Analysis parameters	40 – 215 °C	215 – 360 °C		
	Indi	cator		
Column temperature °C	70 °C – 5 m; 70260 °C – heating	210 °C – 40 m; 210260 °C – heating		
Column temperature, C	7°/m; 260 °C − 20 m	5°/m; 260 °C – 30 m		
Evaporator temperature, °C	250	270		
Detector temperature, °C	250			
Carrier gas	Не			
Carrier gas usage (He), cm <sup>3</sup> /m	2.054	1.156		
Usage of additional gas (He), cm <sup>3</sup> /m	25	5.0		
Stream distribution He (flow /	1 / 100	1 / 150		
downthrow)	1 / 100	17130		
Hydrogen consumption, cm <sup>3</sup> /m	3	0		
Air consumption, cm <sup>3</sup> /m	3.	50		

#### 3. Results and Discussion

The pyrolysis liquid was obtained by thermal destruction of ABS plastic waste in a sequencing batch reactor in the temperature range of 250-400 °C for 4.4 hours. The excess pressure in the reactor and technological system was 0.20-0.25 atm. (Fig. 1). At the same time, it should be noted that the steel reactor (St. 5,  $V = 150 \text{ dm}^3$ ) was heated in an electric heating furnace with the help of 220-volt heating elements. The process temperature and excess pressure in the plastic thermal destruction reactor were controlled using, respectively, a temperature control unit (OVEN UKT38 type - 8-channel meter with an emergency alarm), a thermopyrometer (TERA TXA 1-3), and a manometer (DM 05100, radial, 0 -250 mPa, class 1.0). The heating speed was usually determined by the type of polymer mixture that was going to be thermally processed. The amount of electric energy that was spent on heating was determined by the meter (three-phase induction single-tariff electricity meter CA4-1678), and the amount of the gas mixture formed was determined by the membrane gas meter (Metrix UG6). The gas-vapor mixture of thermolysis products of polymeric waste was condensed successively in the heatexchanger-condenser 7 (Fig. 1, F-1 - heavy fraction, usually dark brown), heat-exchanger-condenser 8 (Fig. 1,

F-2 – medium fraction, usually brown or light brown) and condensers-gas separators **9** (Fig. 1, F-3 – light yellow fraction), the composition of which was subjected to chromatographic analysis (Agilent Technologies 7890 A chromatograph, USA). After each experiment, the reactor was cooled to a temperature of 30-35 °C, the lid was disconnected, and the formed pyrocarbon was unloaded manually and weighed on technical electronic scales VTA-60/15-73 (Dnipro Company LLC, Ukraine). The data of the material balance of the thermal destruction of ABS-plastic waste (Table 3) indicate that the formation of pyrolysis liquid is 61.7 wt. %, the gas mixture is 4.2 wt. %, and pyrocarbon is 28.3 wt. %.

The research results showed that the temperature in the pyrolysis zone of ABS plastic has a decisive effect not only on the ratio of the process main products – pyrolysis liquid: gas mixture: pyrocarbon but also on the chemical composition of the first two components. Fig. 2 shows that the majority of the pyrolysis liquid is formed in the temperature range of 250-400 °C in 4.4 hours and makes 61.7 wt. % from the total amount of obtained pyrolysis products. At the same time, at temperatures of 310-315 °C, an inexplicable decrease in the formation of pyrolysis liquid was observed, which, can be explained by the formation of monomers with a more complex structure and the passage of other diverse reactions.

Table 3. Material balance of thermal destruction of ABS plastic waste

Loaded			Resulted			
Name	Mass, kg	Mass fraction, %	Name	Mass, kg	Volume, dm <sup>3</sup>	Mass fraction, %
1. ABS plastic wastes:	30.00	100.0	1. Liquid fraction:	20.06	22.15	66.9
- ABS plastic	28.25	94.1	<ul> <li>pyrolysis liquid<sup>*</sup></li> </ul>	18.51	20.60	61.7
- water	1.75	5.9	- water	1.55	1.55	5.2
			2. Gas mixture <sup>**</sup>	1.26	1775	4.2
			3. Pyrocarbon	8.50	-	28.3
			4. Losses	0.18	-	0.6
Total	30.00	100.0	Total	30.00		100.0

Notes: \*density of pyrolysis liquid  $\rho = 0.898 \text{ g/cm}^3$ ; \*\*for a gas mixture  $\rho = 0.71 \text{ kg/m}^3$ .



Fig. 2. Dependence of pyrolysis liquid yield of ABS plastic waste thermal destruction on temperature

The obtained results indicate that the first stage of pyrolysis of ABS plastic waste is accompanied by heating of the reaction mass and distillation of accompanying water (1.55 dm3) at a temperature of 100 °C. Further thermal destruction of ABS plastic waste is accompanied by the formation of oligomers with a much lower molecular weight and their decomposition into saturated  $C_8 - C_{16}$  hydrocarbons of normal and isomeric structure (Table 4).

The identification of the obtained chromatography of different fractions of the pyrolysis liquid (Table 1) was carried out taking into account the linear retention index of individual chemical compounds, the database of which is located in the Chem Station analytical program, using some reference compounds to identify unknown peaks, as well as taking into account the obtained results of the original works of low-temperature pyrolysis of ABS plastic or its mixtures with other types of polymer waste in the temperature range of 310 - 500 °C.<sup>15</sup> Table 4 shows the chemical composition of various fractions of pyrolysis liquid of thermodestruction of ABS plastic, obtained after its fractional distillation.

According to the chemical composition, the majority of the compounds of the investigated fractions consist of saturated hydrocarbons of normal and isomeric structure. For the gasoline fraction, saturated hydrocarbons make up 94.87 %, for naphtha – 78.27 %, for kerosene – 79.75 %, and for diesel – only 51.02 % of the total mass. In addition, on the chromatograms of the

kerosene and diesel fractions of ABS plastic thermal destruction, the presence of 4.56 and 17.18 wt. % of the original styrene is observed. Based on the chemical composition of individual compounds, the studied liquid fractions differ significantly. The gasoline fraction consists of 83.34 % of  $C_9 - C_{10}$  hydrocarbons; liquefied petroleum gas consists of 61.46 % of hydrocarbons  $C_9 - C_{10}$ ; kerosene – 44.54 % of  $C_{14} - C_{15}$  hydrocarbons of normal and isomeric structure, and only 23.96 % of the diesel fraction are saturated  $C_{10} - C_{15}$  hydrocarbons.

In some works, the possibility of using the obtained pyrolysis products of polymer waste as alternative sources of energy was investigated. For example, the technology of using the obtained pyrocarbon as the part of fuel briquettes was developed by Hlavatska and Ishchenko.<sup>10</sup> In our previous work,<sup>14</sup> gasoline and diesel fractions of pyrolysis liquid of polypropylene waste processing were used as components of liquid fuels for internal combustion engines. Such results correspond to those obtained by us during the pyrolysis of ABS plastic waste. So, if we start from the total mass of 100 kg of computers that are not in use, the amount of ABS plastic there is 46 kg. This amount of ABS plastic during pyrolysis processing ensures the formation of 31.6 dm<sup>3</sup> of pyrolysis liquid, 2720.8 dm<sup>3</sup> of gas mixture, and 13.0 kg of pyrocarbon. Thus, it can be stated that pyrolytic processing of ABS plastic, as a component of EEE waste disposal, is environmentally safe and provides the formation of alternative sources of energy: pyrolysis liquid, gas mixture and pyrocarbon.

Hydrocarbons*	Fractions of pyrolysis liquid, %					
Trydrocaroons	Gasoline**	Naphtha (140-180 °C)	Kerosene (180-240 °C)	Diesel**		
C <sub>8</sub> H <sub>18</sub>	7.83	-	-	2.79		
n-C <sub>9</sub> H <sub>20</sub>	48.11	-	-	-		
iso-C <sub>9</sub> H <sub>20</sub>	18.01	3.94	-	-		
$n-C_{10}H_{22}$	13.26	7.69	3.06	3.63		
iso-C <sub>10</sub> H <sub>22</sub>	3.96	22.99	11.48	4.79		
n-C <sub>11</sub> H <sub>24</sub>	3.70	7.98	4.07	4.88		
iso-C <sub>11</sub> H <sub>24</sub>	-	22.80	2.97	-		
$C_{12}H_{26}$	-	3.19	4.57	-		
$n-C_{13}H_{28}$	-	2.82	3.16	-		
iso-C <sub>13</sub> H <sub>28</sub>	-	-	3.53	-		
$n-C_{14}H_{30}$	-	3.37	12.84	-		
iso-C <sub>14</sub> H <sub>30</sub>	-	2.63	∑ <b>24</b> .51	-		
n-C <sub>15</sub> H <sub>32</sub>	-	0.86	4.05	8.49		
iso-C <sub>15</sub> H <sub>32</sub>	-	-	3.14	2.17		
C <sub>16</sub> H <sub>34</sub>	-	-	2.37	-		
C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	-	-	4.56	17.18		

Table 4. Chemical composition of liquid products of thermal destruction of ABS plastic waste

Notes: \*only the peaks of chemical compounds were taken into account, the part of which in the total area exceeded 2 %; \*\*fractions obtained during distillation according to ITS 2177-99.

#### 4. Conclusions

The expediency of pyrolytic processing of ABS plastic as a component of waste disposal of electronic and electrical equipment is substantiated.

The pyrolysis technology of processing ABS plastic with the production of pyrolysis liquid, gas mixture and pyrocarbon was developed.

It was established that low-temperature pyrolysis of ABS plastic in the temperature range of 250-400 °C for 4.4 hours provides the output of pyrolysis liquid 61.7 % by mass, gas mixture 4.2 % by mass. and pyrocarbon 28.3 % by mass.

The perspective and environmental friendliness of the use of pyrolytic processing of ABS plastic is shown, which improves the ecological state of the environment and allows to reduce the use of fossil (oil, gas, coal) energy sources.

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#### ПІРОЛІЗНА ПЕРЕРОБКА ПОЛІМЕРНИХ СКЛАДОВИХ ВІДХОДІВ ЕЛЕКТРОННОЇ ПРОДУКЦІЇ

Анотація. Показана й обтрунтована доцільність переробки АБС-пластику як складової відходів електронного й електричного обладнання методом низькотемпературного піролізу й отримання альтернативних джерел енергії: піролізної рідини, газової суміші та пірокарбону. Проаналізовано основні компоненти відходів електронного й електричного обладнання, які складаються з пластику і вогнетривких оксидів, а також сполук міді та заліза. Приведено склад дорогоцінних, токсичних, малопоширених, основних металів і пластикових відходів. Показано, що відходи електронного й електричного обладнання є цінною вторинною сировиною та потребують окремих екологічно чистих технологій переробки. Досліджена термодеструкція АБС-пластику як складової відходів електронного й електричного обладнання на технологічній установці періодичної дії за відсутності кисню повітря та каталізатора кислотного типу. Дистиляцією піролізної рідини отримано бензинову, лігроїнову, керосинову, дизельну фракції та проведено дослідження їхнього якісного та кількісного складу методом газової хроматографії. Встановлено, що переважна більшість сполук у різних фракціях є насиченими вуглеводнями С8-С16 нормальної й ізомерної будови.

Ключові слова: відходи електронного й електричного обладнання, АБС-пластик, піроліз, технологія, хроматографічний аналіз, альтернативна енергетика.