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The Influence of the Type of Catalyst on the Polymer Waste Thermodestruction

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Used polymer plastics have high fuel values (approximately 40 MJ/kg for polyolefines). Therefore, they constitute perfect energy materials. Thermodestruction of used products and wastes of polymer plastics on specialized installations seems to be a long-term method to manage this group of wastes in chemical recycling with the destination to obtain fuel ingredients. Application of this technology allows for reduction the quantity of municipal waste. This enables also to obtain the valuable fuel components. In the Department of Environment Chemistry and Technology of Institute of Chemistry at the University of Silesia and in enterprises using the installation for the thermodestruction of used polymer plastics it was studied influence of different catalyst on course of thermodestruction. According to an innovatory technology elaborated in the enterprise called "Speranda-1" Sp. z o.o. the dirty used products of polymer plastics and wastes after melting flow down to the bottom part of the reactor, where they undergo thermal degradation due to a contact with the catalyst.

It was ascertained that type of catalyst influences the course of the primary and secondary destruction processes and is of fundamental importance for capacity of this process and for the composition of the obtained products.

Keywords Catalyst; fuel components; polymer waste; thermo-destruction

Introduction

Used polymer plastics for the sake of its high fuel values (approximately 40 MJ/kg for polyolefines) can constitute perfect energy materials. But their direct combustion is not often accepted. Thermodestruction of used products and wastes of polymer plastics on specialized installations seems to be a long-term method of their management in order to obtain fuel components. Application of thermodestruction technology causes polymer plastics stop being useless and hard degraded wastes

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lingering on rubbish dumps. This enables also to obtain useable product finding application in petrochemical industry [1,2].

In the recent 10 years, intensive research on development of technologies of processing used polymer products into fuel components, directly into fuels and other utility products has been conducted. The said processes may take place in different types of reactors with or without the use of catalysts for selected or unselected used polymer products to obtain different products.

Zeolites (e.g., ZMS) or zeolites modified with metals (e.g., HZSM–5) are the most frequently used catalysts to conduct thermal degradation of polyolefines. Sakata *et al.* [3] found that properties of the products obtained from thermal degradation of polyolefins depend on the acidity of the zeolites used as catalysts. At the same time, Ochoar *et al.* [4] stated that Brönsted acid groups and Lewis acid groups present in the catalysts of polyethylene degradation did not influence the amount of oil fraction obtained. Ding *et al.* [5] stated that the use of HZSM–5 catalysts to degrade HDPE leads to obtaining a liquid fraction containing, in particular, aromatic hydrocarbons, Mordi *et al.* [6] obtained petrol containing, in particular, aliphatic hydrocarbons with carbon chain from C_5 to C_{12} using only HZSM–5 as catalyst. They have proven that activity of zeolites in polymer degradation process depends on the structure and composition of zolites. Sharratt *et al.* [7] conducted pyrolysis of HDPE using HZSM–5 catalyst in the reactor with fluid deposit at a temperature of 350°C and obtained, mainly, gaseous hydrocarbons with carbon chain from C_3 to C_5. Aguado *et al.* [8] analyzed the influence of beta zeolites on degradation of polypropylene, polyethylene with low density and polyethylene with high density. Degradation of HDPE catalyzed at a temperature of 400°C is characterized by high selectivity giving, mainly, hydrocarbons with a carbon chain from C_5 to C_{12} (70% of weight load). At the same time, as a result of catalyzed degradation of LDPE and PP mainly lower hydrocarbons with carbon chain from C_1 to C_4 (64% of weight load) are obtained.

On the basis of literature studies, it may be asserted that using catalysts to thermal destruction of polymer products, mainly zeolites or zeolites modified with metals, does not lead to the same results. No universal, fully efficient installation to thermal degradation of polymer products into fuel components with the use of catalysts has been elaborated to date. The majority of research involved original polymers or used polymer products prepared initially for processing (e.g., washed, cut, etc.).

Therefore technology elaborated in Polish company seems to be a long-term solution for management of used polymer plastics without preliminary preparation. According to an innovatory technology melted plastics are exposed thermodestruction in special construction reactor in the presence of catalyst.

In order to explain the influence of the type of catalyst on the polyolefin thermal destruction process and the quality of products obtained, research on the experimental line in the Department of Environment Chemistry and Technology of the Institute of Chemistry at the University of Silesia and large laboratory line at an enterprise using the industrial installation was carried out.

Materials and Methodology

In the laboratory stand of the line for thermal destruction of polyolefines in the Department of Environment Chemistry and Technology of the Institute of Chemistry at the University of Silesia, the influence of the following catalysts: "Petrochemia

Płock'' production catalyst, catalysts obtained in appropriate form in the Department of Environment Chemistry and Technology [chrome salt (III) and zinc salt (II)], and metallic aluminium on the thermal destruction process was examined. The process was also carried out without the use of catalysts. Each time, approximately 300 g of unpurified used PE, PP products were degradated.

In the large laboratory installation (with reactor with lead deposit), at Speranda-1 Sp. z o.o. thermal destruction of used unpurified polyethylene was conducted with the use of metallic aluminium in the form of flakes and metallic aluminium in the form of dust, bauxite and mixture of bauxite and aluminium in the form of dust as catalysts and also without a catalyst. Each time, approximately 2400 g charge was degradated. The liquid products of thermal destruction were distillated and chromatographic analysis conducted by the Department of Environment Chemistry and Technology. The chromatographic analysis of gaseous and liquid products was conducted using Autosystem XL GC – Turbo Mass chromatograph manufactured by Perkin Elmer using PE 5MS 30 × 0,25 mm × 0,5 μm column.

Results and Discussion

In order to examine the process of thermal destruction of used polyolefin products, chrome salt (III), zinc salt (II) and cadmium salt (II), and bauxite and aluminium in different forms were used as catalysts. For comparison thermal destruction processes were also carried out with catalyst of ''Petrochemia Płock'' production cracking process and without a catalyst.

The results of the laboratory research carried out in the Department of Environment Chemistry and Technology show that the use of a catalyst in the thermal destruction process of used polyethylene does not significantly contribute to an increase in the amount of liquid product (~85% for the process without a catalyst and up to 88.7% for the process with a catalyst) (Table 1). A considerable share of solid remains as a product of thermal degradation process without a catalyst could indicate that the converted polymer contained a filler. However, the results of the research with the use of catalysts show that there was no filler in the used polyethylene subject to the thermal destruction process, since the amount of solid remains after processes accounted for up to 1.3% (Table 1). However, the use of a catalyst contributes to a considerable growth of share of gaseous products which were not condensed in products of the thermal destruction process. Catching them on special sorption columns and chromatographic analysis show that they include ethane, ethylene, propane, propene for the processes with the use of catalysts and methane, ethane, ethene, propane, propene, butane and butane for the processes without a catalyst. The chromatographic analysis of liquid products, use of spectrum library and database supplied by Perkin Elmer showed that these were linear, branched, cyclic, saturated, unsaturated and aromatic hydrocarbons from C4 to C36 (Table 2).

It was observed that the use of ''Petrochemia Płock'' catalysts, zinc salt (II), chrome salt (III) and metal aluminium significantly reduced the share of solid residues after the thermal destruction process (from 8.75% obtained in the process without a catalyst to 0.69% in the process with the use of a catalyst zinc salt (II) with simultaneous increase in the number of liquid products and gaseous products. In the thermal destruction process without a catalyst, the number of gaseous products was the lowest and the amount of solid residues was the highest. It is notable that gaseous

Table 1. The influence of the type of catalyst applied to the thermodegradation process of used polyethylene on quantity of received liquid product, gaseous product and solid residues and maximum temperature of thermodegradation in the laboratory installation

Applied catalyst	Quantity of received liquids [%]	Quantity of received gases [%]	Quantity of received solid residues [%]	Time of thermodegradation process [min]	Maximum temperature of thermodegradation [°C]
Without catalyst	85.05	6.20	8.75	110	265
Catalyst "Petrochemia Płock"	88.70	10.00	1.30	95	270
Salt of zinc(II)	88.58	10.73	0.69	100	258
Salt of chromium(III)	87.52	11.71	0.77	90	270
Metallic aluminum	88.00	11.30	0.70	85	245

Table 2. Exemplary chromatographic analysis of liquid product of thermodestruction of PE, received in the presence of zinc salt as catalyst in the laboratory installation, carried out in accordance with library of spectrum and data base from Perkin Elmer

Time of retention	Formula	Probability of identification [%]	Name of identified compound
1,80	C_5H_{12}	65	2-methylbutane
	C_4H_{10}	74	isobutane
2,24	C_6H_{12}	97	2-methyl-1-penten
	C_6H_{12}	89	1-hexene
3,31	C_8H_{18}	97	4-methylheptane
		96	2,3-dimethylhexane
5,52	C_9H_{18}	97	1,3,5-trimethylcyclohexane
6,53	C_8H_{16}	93	5-methyl-1-heptene
6,62	C_9H_{18}	91	1-etylo-2,4-dimethylcyclohexan
7,71	$C_{12}H_{24}$	83	7-methyl-1-undecene
10,59	$C_{11}H_{24}$	96	2,6-dimethylnonane
10,76	$C_{14}H_{30}$	90	4,6-dimethyldodecane
13,75	$C_{12}H_{24}$	92	5-methyl-3-undecene
15,25	$C_{12}H_{24}$	92	5-methyl-1-undecene
15,43	$C_{14}H_{28}$	95	3-tetradecene
16,55	$C_{12}H_{24}$	88	2,4-dimethyl-1-decene
19,38	$C_{13}H_{28}$	95	3,8-dimethylundecane
	C_4H_{10}	98	4,6-dimethyldodecane
19,68	$C_{10}H_{18}$	76	5,7-dimethyl-1,6-octadiene
23,22	$C_{18}H_{36}$	90	3-octadecene
23,54	$C_{12}H_{24}$	91	7-methyl-1-undecene
23,92	$C_{20}H_{40}$	95	3-eicosene
24,20	$C_{18}H_{36}$	91	5-octadecene, 1-octadecene
27,01	$C_{12}H_{24}$	73	1,2-dimethylcyclohexane
29,75	$C_{20}H_{40}$	94	3-eicosene
33,20	$C_{15}H_{28}$	71	2(1-methylethyl)-cis-1,1′-bicyclohexyl
35,54	$C_{19}H_{38}$	95	1-nonadecene
37,44	$C_{23}H_{46}$	85	11-tricosene
40,71	$C_{20}H_{40}$	86	3,7,11,15-tetramethyl-2-hexadecane
41,51	$C_{23}H_{46}$	83	11-tricosene
42,16	$C_{12}H_{24}$	85	2,3,6,7-trimethyl-4-octene
43,66	$C_{12}H_{24}$	84	1-butyl-2-propylcyclopentane
44,38	$C_{12}H_{24}$	83	2,3,3-trimethyl-4-nonene
	$C_{12}H_{24}$	82	1,4,5-trimethylcyclohexane-1-isopropyl
	$C_{11}H_{22}$	81	1-ethyl-2-propylcyclohexane
45,44	$C_{17}H_{34}$	74	6-cyklohexyl-6-
	$C_{28}H_{56}$	73	cyclohexylundecane, cyklooctacosane
48,19	$C_{27}H_{54}$	82	1,3,5-trimethyl-2-oktadecylcyclohexan
52,33	$C_{26}H_{52}$	83	9-hexacosene
	$C_{27}H_{54}$	82	1,3,5-trimethyl-2-oktadecylcyclohexane

(*Continued*)

Table 2. Continued

Time of retention	Formula	Probability of identification [%]	Name of identified compound
56,22	$C_{17}H_{34}$	85	2,3,4-trimethyl-4-tetradecene
61,28	$C_{27}H_{54}$	83	1,3,5-trimethyl-2-dodecylcyklohexane
	$C_{14}H_{28}$	81	1,2,4,5-tetraethylcyclohexane

products (for example, gaseous fuel) were used in industrial installations, which was difficult under the laboratory conditions. The use of catalysts influenced also the rate of thermal destruction processes. It may be stated that using them shortens the duration of the thermal destruction process by 1/5. The obtained liquid products were separated by distillation and it was found that in the case of thermal destruction carried out with metallic aluminium as a catalyst, the greatest amount of distillate with boiling point of up to 100, 200, 250 and 300°C was obtained (Table 3).

After discussions with users of the technological lines intended for thermal destruction processes of used polymer products (mainly polyolefins) carried out in accordance with the technology elaborated at Speranda-1 [9,10], it was decided to carry out research at large laboratory scale for aluminium, bauxite and mixture of aluminium and bauxite.

The results of the research of thermo-destruction processes of used polyethylene carried out in the large laboratory installation at Speranda-1 Sp. z o.o. with the use of

Table 3. The range of boiling temperature and quantity of obtained distillate for products received from thermodestruction of used PE in presence catalysts in the laboratory installation

	Quantity of distillate (%) for process				
		With catalyst			
Boiling point °C	Without catalyst	Catalyst "Petrochemia Płock"	Salt of zinc(II)	Salt of chromium(III)	Metallic aluminum
Temperature up to 100°C	8.20	9.20	10.10	9.88	10.35
Temperature up to 150°C	18.23	22.75	23.96	23.00	24.18
Temperature up to 200°C	30.95	34.50	33.28	34.18	36.00
Temperature up to 250°C	43.00	52.34	52.00	53.90	56.55
Temperature up to 300°C	62.23	64.75	64.20	65.30	69.90
Temperature above 300°C	37.77	35.25	35.80	34.70	30.10

Table 4. The influence of type of catalyst applied to the thermodegradation process of used polyethylene on quantity of received liquid product, time of process, maximum temperature of thermodegradation and range of distillation temperatures of received liquid product in the large laboratory installation

Applied catalyst	Quantity of received liquids [%]	Time of thermodegrad. process [min]	Maximum temperature of thermodegrad. [°C]	Temperature of beginning of distillation [°C]	Temperature of end of distillation [°C]
Without catalyst	85.19	240	420	24	322
Metallic aluminum in the form of flakes	83.5	210	372	18	329
Metallic aluminum in the form of dust	80.5	200	418	18	314
Bauxite	86.5	180	403	23	319
Metallic aluminum in the form of flakes/bauxite (1:1)	78.4	220	442	20	316

Table 5. The range of boiling temperature and quantity of obtained distillate for products received from thermodestruction of used PE in presence catalysts in the large laboratory installation

	Quantity of distillate (%) for process				
		With catalyst			
Boiling point °C	Without catalyst	Aluminum (flakes)	Aluminum (dust)	Bauxite	Mixture (1:1) bauxite/ aluminum (flakes)
Temperature up to 100°C	7.47	10.12	9.20	10.06	8.24
Temperature up to 150°C	17.65	22.10	19.40	25.10	18.26
Temperature up to 200°C	30.18	35.77	33.44	36.47	29.71
Temperature up to 250°C	45.00	55.44	47.20	58.90	42.13
Temperature up to 300°C	64.67	69.78	63.73	70.10	66.69
Temperature above 300°C	35.33	30.22	36.27	29.90	33.31

different catalysts show that the type of catalyst influences the duration of the thermal destruction of the same amounts of used polyethylene, efficiency of the thermal destruction process and ranges of boiling points of obtained liquid products (Tables 4 and 5).

It was found that the thermal destruction of used polyethylene carried out with the use of bauxite as catalyst took 3 hours (the shortest) and that the greatest amount of liquid product was obtained (up to 87%). The thermo-destruction process carried out without a catalyst was the longest (4 hours). In this case, it was found that the process with catalyst (bauxite) was by ¼ shorter than the process without a catalyst. The lowest amount of liquid product was obtained when using mixture of aluminium in the form of dust and bauxite in a ratio of 1:1 as a catalyst of the thermal destruction process. It accounted for 78.4%.

In the case of products of destruction with the use of bauxite, approximately 60% of distillate with boiling point of up to 250°C, and only 42% of distillate within the same temperature range for the product of thermal destruction with the use of mixture of aluminium in the form of dust and bauxite in a ratio of 1:1 was obtained. The amount of distillate with boiling point of up to 250°C for the product of thermal destruction without a catalyst accounted for 45%.

The above results may indicate that the best catalyst of thermal destruction of polyolefin from among those examined in the large laboratory installation is bauxite. Its use increases the efficiency of liquid products which do not solidify at the surrounding temperature, which is a property desired by refineries. At the same time, using bauxite shortens duration of the thermal destruction process, which results in energy saving.

The results of the research allowed using bauxite as a catalyst in industrial installations. However, if strongly polluted and damp polyolefin waste is subject to the thermal destruction process, the said catalyst quickly deactivates (high purchase costs). The used catalyst removed from the device along with pollution constitutes a solid waste which must be managed. Thus, additional costs arise.

Conclusion

It was ascertained that type of catalyst using to thermodestruction process of used polyolefines influences its course and is of fundamental importance for the composition of the obtained products. It was noticed that the thermal destruction of used polyolefines with the use of analyzed catalysts took place quicker for the same mass, with different efficiencies of the main liquid products. The properties of liquid products obtained as a result of the thermal destruction of used polyolefines are similar to the properties of fuels.

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