Degradation of polyolefine wastes into liquid fuels

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Abstract In Poland, the consumption of polymers like polyethylene, polypropylene and polystyrene amounts is nearly one million tons per year. Most of the products made of these polymers becomes wastes in short time. Polymers are very resistant to biodegradation, therefore technologies of their transformation into useful materials should be developed. In our Institute, the technology of catalytic cracking of polyolefines into liquid fuels is studied. Experiments are concentrated on the selection of proper catalyst and on the construction of continuously operated installation for cracking of polyolefine wastes. Experiments on the selection of catalyst were performed in a laboratory scale batch reactor. A big laboratory installation with a yield of ca. 1 kg/h of liquid products was tested with positive results and plans are to construct a pilot plant installation with a yield of 30 kg/h of liquid products. The products of catalytic cracking are separated in a distillation column into gas, gasoline, light oil and heavy oil fractions. The gas is used for heating the reactor. The heavy oil fraction is recycled to the reactor and the gasoline and light oil fractions are the final products. The gasoline fraction can be used as a component of motor gasoline and the light oil fraction can be used as a component of diesel fuel or as a heating oil.

Key words fuel • polyolefins • degradation of plastics • cracking of polyolefins

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Introduction

Plastics have found a wide range of application in housing, agriculture, packaging, piping and construction. This is the reason of a big an increase in their production and increase of their content in solid wastes.

60% to 70% of plastic wastes are polyolefines and polystyrene. The high resistance of plastics against chemical and biological degradation makes a serious ecological problem with these wastes. Small economical effectiveness of mechanical recycling of polyolefine wastes and the worse quality of recycled granulates results that only about 11% of them is recycled. Most of the polyolefine wastes up to 64% are deposed in landfills and about 22% is fired for energy recovery. Landfiling of plastics is the worst method of their reduction because of the emission of gaseous pollutants, water pollution and, in addition, the waste occupies a big area of land. Incineration allows to recovery energy, but recently it is strongly questioned because of the emission of dangerous pollutants. Recently, a lot of works is devoted to the catalytic method of destruction of plastic wastes especially polyolefines and polystyrene into gas or liquid hydrocarbons which may be used in chemical synthesis or as fuels. The methods of transformation of polyolefine wastes into liquid fuels by thermal or catalytic cracking were reported in many

papers [1–8]. The reports present laboratory works on the degradation of pure polyethylene or polypropylene with the use of different catalysts. Both, catalytic and thermal degradation give as a product gases, liquids and coke. Most valuable products are liquid hydrocarbons. The main aim of the tests with catalytic cracking is to select such a catalyst which gives as low as possible amounts of coke and gases. Limited amounts of gases may be used in the installation for heating. The coke makes more problems because it forms deposits on the walls of the reactor and reduces heat transfer from heating medium to melted wastes. Standards for motor fuels provides limits for the content of olefins and aromatics. The content of aromatics in liquid products of cracking usually is low, but the content of olefins usually is above the limits. The high content of olefins reduces the stability of fuel. This is a reason for looking for new catalysts giving less olefins. The process of cracking consists of the chain cracking primer reactions and the secondary radical ones. For example, the number of reactions for thermal decomposition of n-hexane is 218 [2]. Decomposition of a very long chain of polymers and reactions of decomposition of impurities and additives makes unpredictive the number of possible reactions. But experiments show that the type of catalyst has an influence on the amount of coke and the content of aromatics and olefins. Another problem is the stability of a catalyst. Coke deposes on catalysts and reduces its activity and changes its selectivity. This is one group of problems. There are still three other groups of problems:
– preparation of wastes for decomposition,
– construction of apparatus,
– separation of liquid products of decomposition.

Preparation of wastes for decomposition

Preparation of wastes for decomposition depends on the way of introducing the wastes into the reactor. Three loading devices for this purpose are used:
– extruder,
– piston,
– sluice.

Polyolefine wastes for an extruder should be grinded to particles of size 4 to 10 mm. Wastes should be clean and dry. The wastes are melted in the extruder and there are no problems with the emission of gases from the reactor by a loading device. But the high cost of the extruder, costs of fine grinding and cleaning of wastes make this method expensive.

Loading the wastes by a piston or a press allows to use much bigger particles of waste size from few centimeters to ca. two meters for a foil. Normal impurities of wastes does not affect the work of this loading device. The proper length of loading device tube prevents the emission of gases from the reactor. The piston loading device is designed and constructed together with an installation and this is the most popular loading system in new plants.

The sluice allows to introduce to the reactor bigger particles or whole elements of plastic wastes, but wastes are not pressed and contain a lot of air, which oxidizes part of the hydrocarbons in the reactor. For reduction the oxidation and emission of hydrocarbons, the inert gas, usually nitrogen, should be blowed into sluice. However, some gases from the reactor can pass into atmosphere by sluice. This needs better ventilation and increased emission of hydrocarbons into atmosphere. The sluice loading device is not applied in new designed installations.

Construction of apparatus

In the earlier installations batch or semi-batch reactors were used. The batch reactor consists of a big vessel loaded with polyolefine and polystyrene wastes with heating and vapour condensation systems. The fully loaded reactor was heated. The wastes were melted and at 350°C to 450°C decomposed. The volatile products of decomposition were condensed as a final product. The heat transfer to solid plastics, because of their porous structure, is very low and the mass of wastes and batch reactor is high. Those are the reasons why the time of heating of the reactor to the temperature of decomposition is long. The reactor after decomposition of all wastes has to be cooled what need also some time. Finally, the effective time of work in comparison to the time of the whole cycle is low. The work cycle in the semi-batch reactor is much longer and heating and cooling times can be reduced, because usually the volume of semi-batch reactor in comparison to batch reactor is smaller. The semi-batch reactor can operate until the deposits of coke inside the reactor are too big, which reduce the heat transfer from heating medium to melted wastes. Deposits of coke on the inside walls of the reactor are very difficult to remove.

Continuous flow tank reactors have inside on the heating surfaces, scraping devices to avoid the formation of thick layer of coke. The coke is continuously removed from the reactor by a screw conveyor.

There are a few solutions of scraping devices presented in Fig. 1. In the first solution (a) the device is in the form of an inclined tubular reactor [9] with a spiral band conveyor rotating inside the tube. This conveyor transports the coke to the top of the reactor. From the top end of the reactor, the coke falls to container. In the second solution (b), the bottom of the reactor has a wave shape. Inside of the half pipe screw conveyors rotate, which prevent the deposition of coke on the walls and mix the wastes with those melted. The coke is withdrawn by a special device to the tank.

In the third solution (c), the reactor has a flat bottom with a layer of liquid metal, usually lead, on it. Inside moves a special conveyor which immerses the introduced wastes under the surface of melted metal. Impurities like coke, sand etc. flow on the surface of liquid metal and have no contact with heating surface. Heat transfer from the walls of the reactor to liquid metal is good. The coke and impurities are withdrawn periodically, usually after one month of operation or continuously. Other types of reactors like a fluidized bed reactor or a rotary kiln reactor were also tested in the pilot plant installations, but they were not applied on industrial scale.
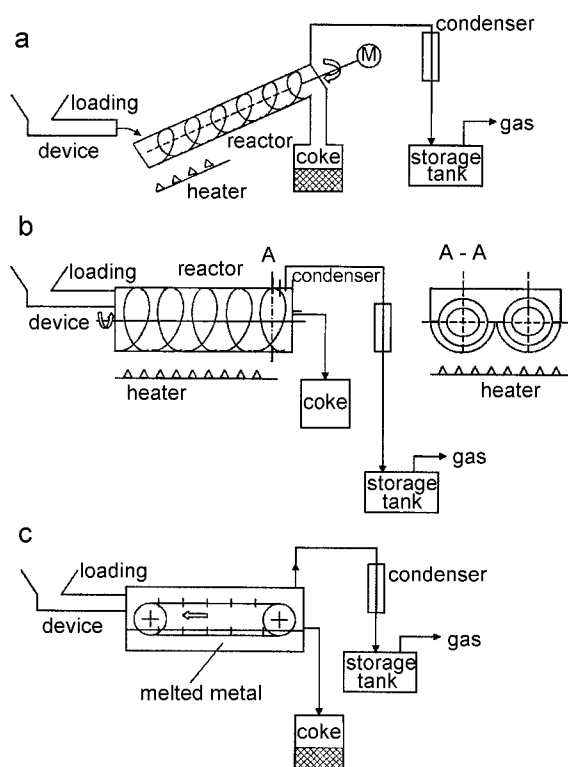
Fig. 1. Schemes of apparatus for plastic waste decomposition.

Fig. 2. Scheme of laboratory apparatus for testing of catalysts.

Separation of the liquid product of decomposition

The hydrocarbons, liquid in the temperature range −20°C to 0°C are most valuable products of the decomposition of polyolefine wastes. Products of decomposition leave the reactor in the gas phase and are condensed. Gases are separated after condensation and are used for heating in the installation. Condensed products contain gasoline, light oil and heavy oil fractions. Usually, the content of heavy oil fraction is big and the freezing point temperature of the mixture of the fractions is about 35°C. It is a solid product at ambient temperature. Such product can be used in a refinery, where it is processed with petrol oil. Mixed product should be stored in heated tanks to prevent its solidification. There are also problems with a long distance transport of the liquid product. Separation of these fractions *in situ* allows to obtain most valuable gasoline and light oil fractions with low freezing points. The heavy oil fraction was used again as a reactor feed for decomposition.

Our works have three main tasks:
– checking catalysts and their stability,
– testing new constructions of apparatus,
– separation from products most valuable gasoline and light oil fractions.

Experimental section

Checking of the catalysts

A 2 l batch reactor was applied in the experiments of checking catalysts (Fig. 2). Gaseous products of cracking of polyolefine wastes were separated in a distillation column. Reflux from the distillation column was returned to the reactor. Uncondensed gases from the column were combusted in a laboratory burner. From the column, 5 side distillates were taken. The freezing point temperature, viscosity, density and normal distillation curve for each distillate were determined. Temperatures were measured 20 mm above the bottom of the reactor, on the top of the reactor in the gas phase and in five levels in the distillation column at the points of distillate withdrawal.

Flow rate of the uncondensed gases was measured in part of the experiments. In experiments ca. 800 g of polyolefine wastes and ca. 200 g of a catalyst were used. The ratio of wastes to catalyst in all experiments was as 5 to 1.

List of experiments, used catalysts and selected results of experiments are presented in Table 1.

Content of gasoline, light oil and heavy oil fractions were determined on the basis of results of normal distillation. Gasoline fraction distilled below 200°C, light oil fraction between 200°C and 350°C and heavy oil fraction above 350°C.

Results of fractionation of distillates by the normal distillation for experiment 9 are presented in Table 2 as an example.

In Table 3, properties of gasoline fraction are presented and for comparison requirements of the standard for motor gasoline.

In Table 4, properties of light oil fraction are presented and for comparison requirements of the standards for diesel oil and heating oil. From Table 3, it follows that the gasoline fraction properties are close to the requirements of the standard for motor gasoline

Table 1. List of experiments and selected results

Exp. no.	Catalyst	Kind of waste	Cracking temperature [°C]	Amount of fractions [%]			
				gas	gasoline	light oil	heavy oil
1	Without catalyst	PE	420 to 448	–	14.0	36.0	50.0
2	Without catalyst	PE	400 to 420	10.2	17.0	43.8	29.0
3	Catalyst from Orlen, used	PE	390 to 415	–	32.2	42.0	25.8
4	Catalyst from Orlen, used	PP	350 to 365	–	31.0	52.2	16.8
5	Catalyst from Orlen, used	PE (41%) PP (38%) PS (21%)	310 to 420	–	44.3	42.1	13.6
6	Catalyst from Orlen, fresh	PE	420 to 460	18.6	14.8	21.7	33.0
7	Molecular sieves 4A, balls	PE	400 to 440	16.0	13.9	48.1	22.0
8	Molecular sieves 4A, balls	PE	380 to 425	–	25.6	53.1	21.3
9	Molecular sieves 4A, balls	PE	420 to 440	14.3	15.9	39.9	29.9

Table 2. Properties of distillates in experiment 9

| Fraction	% of distillates	Density [g/cm^3]	Freezing point temp. [°C]	% of fraction related to sum of distillates		
				gasoline	light oil	heavy oil
1	37.4	0.781 (50°C)	21	2.2	44.3	53.5
2	15.1	0.796 (20°C)	9	15.0	46.3	38.7
3	23.1	0.793 (20°C)	3	15.9	50.8	33.3
4	14.2	0.782 (20°C)	< –15	20.5	74.3	5.2
5	10.1	0.720 (20°C)	< –15	88.9	9.2	1.9

Amount of gases 14.3% of charge.

and it can be used as a component for its preparation. Results presented in Table 4 show that the light oil fraction can be used as a heating oil or as a component of diesel oil.

Testing new constructions of apparatus

The experiments on the construction of a reactor we began with the use of a tubular continuous flow catalytic reactor. As a loading device was the sluice. The results of tests were negative and, finally we constructed the installation presented in Fig. 3.

A continuous flow tank reactor was applied. The wastes were introduced by a tube a with piston to the separate part of the reactor, where they were melted. Melted wastes flowed down to the reactor. Gases from the reactor flow to the distillation column. A reflux from the distillation column flowed down to the reactor. Uncondensed gases from the top of the column were burned under the reactor. The five side distillates were taken from the column. In experiments, temperatures at points marked in Fig. 3, mass of introduced wastes and mass of collected distillates were measured. For distillates, freezing points temperature, viscosity, density and normal distillation curve were determined. Productivity of the installation was ca. 1 kg/h of distillates. Gases from the combustion of natural gas were used as a heating medium. Temperature of the catalyst layer
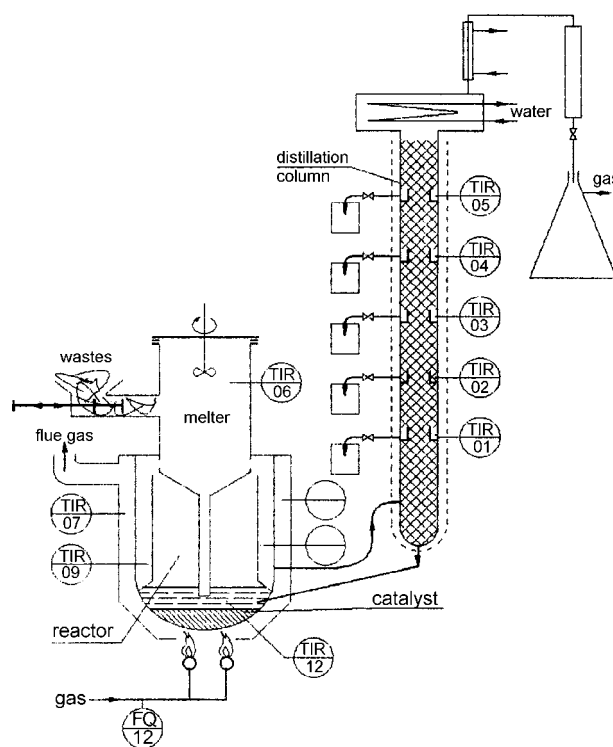
Fig. 3. Scheme of a big laboratory installation for catalytic cracking of polyolefine wastes.

Table 3. Comparison properties of gasoline fraction with requirements for gasoline motor fuel

	% of charge	Sulphur content [mg/kg]	Octane number research	Density [kg/m³]	Distillation [%]					Content of olefins [%]	Content of aromatics [%]
					to 70°C	to 100°C	to 150°C	end of distillat. [°C]	residue after distillat.		
Gasoline fraction	20–26	10–55	75–92	736–747	0–4.1	1.3–21.1	41–81.5	236–270	1.3–1.5	40–66	12–17
Standard requirements PN-EN 228:2003	–	150	95	720–775	20–48	46–71	min. 75	max. 210	max. 2	max. 18	max. 42

Table 4. Comparison properties of light oil fraction with requirements for diesel oil and heating oil

|	% of charge	Sulphur content [mg/kg]	Cetane index	Density [kg/m³]	Distillation [%]			Ignition temperature [°C]	Viscosity [mm²/s]
					to 250°C	to 350°C	to 95% dist. at a temp. of		
Oil fraction	39–49	11–21	61–71	796–809	13–47	89–97	337–370	69–71	2.9
Standard requirements for diesel oil PN-EN 590:2002	–	max. 350	over 46	820–845	max. 65	min. 85	max. 360	over 65	2.0–4.5 at 40°C
Standard requirements for heating oil EKOTERM	–	max. 2000	–	below 860	max. 65	min. 85	–	56	below 6.00 at 20°C
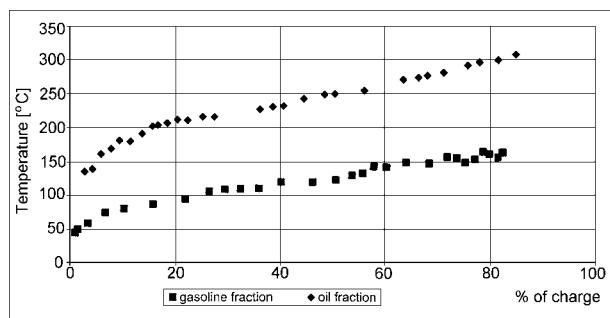
Fig. 4. Distillation curves for gasoline and light oil fractions.

inside of the reactor was controlled manually by changing the amount of burned gas.

Separation of most valuable gasoline and light oil fractions from cracking products

The efficiency of normal distillation is about one theoretical plate. It is too low for good separation of gasoline and light oil fractions. A better separation of both fractions were performed in a periodic distillation column. The distillation curves for both fractions are presented in Fig. 4.

The temperatures of distillates were measured at the top of the column. The efficiency of the column was estimated as 11 theoretical plates. Distillations were finished when the temperature in the boiler was 350°C in case of the oil fraction, or the distillation rate decreased in case of the gasoline fraction.

The distillates from the oil fraction contain about 15% hydrocarbons with the boiling temperature below 200°C. About 15% of this fraction remained in the column as a hold-up and in the boiler as a heavy oil fraction with the boiling temperature above 350°C. End of distillation was at a temperature of 308°C in the head of the column. Temperature of the end distillation of the gasoline fraction was 164°C. 18% of charge remainded in the column as a hold-up and in the boiler. Generally, the distillates are more volatile than the feed fraction. The freezing point temperature for the light oil fraction before distillation was −2°C and after distillation it was reduced to −12°C.

Conclusions

1. The laboratory batch reactor with the distillation column used in the work is very suitable for evaluation of cracking catalysts and products.
2. Freezing point temperatures and standard distillation curves are very useful parameters for primary evaluation of the cracking products.

3. Separation of vapour products in the distillation column is running quite well.
4. Products of the reaction contain some very fine mist beside gas and vapours.
5. Temperature is a very sensitive process parameter. With increasing temperature the distillates contain more heavy products and the rate of cracking increases.
6. The content of sulphur and aromatics in the products is very low and other parameters are relatively close to the standard requirements for gasoline 95 and diesel oil. This makes the products valuable components of gasoline and diesel oil.
7. The fresh catalyst showed a different activity, but after one to two hours its activity became similar because of the deposition of coke on the surface of the catalyst.
8. Construction of a big laboratory installation allows to crack the polyolefine wastes continuously and safety.
9. The distillates contain some non-volatile hydrocarbons which can be removed by additional distillation.
10. Storage of the distillates during a few months does not change their colour or consistence.

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