A METHOD FOR TRANSFORMATION OF POLYOLEFINE WASTES INTO HYDROCARBONS AND A PLANT FOR CARRYING THEREOF

FIELD OF THE INVENTION

The subject of the invention is a catalytic method for transformation of polyolefine wastes into hydrocarbon products, e.q. gasoline, diesel oil and crude oil, and a plant for carrying thereof.

BACKGROUND OF THE INVENTION

The development of the production of polyolefines and their use in almost every line of life causes a consequent increase of related wastes, collected in the dumps, where they take big space relatively to their weight.

A chemical resistance of polyolefines makes them stable for hundreds years, while they do not yield to destruction, being particularly burdensome contamination of the environment. A problem of making polyolefine wastes productive is at present the matter of a special priority and is a very important element of a natural environment protection.

The hitherto used methods, such as combustion and gasification are generating more problems than they solve.

Till now they are the most expensive methods of utilisation of plastic wastes and all probes of making they less expensive result with an ecological catastrophe. The said situation causes, the countries taking care of ecology do not allow a combustion of plastic wastes.

There are known some methods of a thermical decomposition of polyolefines to hydrocarbons in the range of temperatures between 650-850^{0}C. Also there are disclosed the methods combining a high-temperature pyrolysis with consequent catalytic conversion of pyrolytic products to gasoline, diesel oil and crude oil. In the known methods catalysts were used in a form of zeolites, as it has been described in the patent US No.4 016 218. The most popular is the use of zeolite

ZMS-5 hydrogen form, as known from the patent US 3 702 886. The use of other zeolites, e.q. ZMS-11 (US 3709979), ZMS-12 (US 3832449), ZMS-23 (US 4076842), ZMS-35 (US 4016245) and ZMS-48 (US 4375573) is also disclosed. In known and used methods catalysts in a form of zeolites with metal atoms, e.q. platinum are applied also.

The basic imperfection of zeolite-type catalysts is their sensitivity to hydrochloride, which causes destruction of a catalyst in concentrations above 200 ppm in a product. Considering the fact, plastic wastes always contain poly/vinyl chloride/, the application of expensive zeolite-type catalysts is economically disadvantegeous.

The American patent description No US 4 584 421 and European patent application NO. 0276081 A2 disclose a thermical decomposition of polyolefines and a catalytical process of products conversion using zeolites.

However in that method also chlorine containing polymers have to be selected and separated, which operation makes the whole process unprofitable.

The German patent publication No. DE-A-196 41 743 relates to a method of converting polyolefine waste into hydrocarbons, where the polyolefine waste is treated at temperatures of 180-620^{0}C, preferably 300-450^{0}C in the presence of a heavy metal silicate used as a catalyst in amount of up tp 30% by weight, based on the polyolefine waste.

The methods specified above enabled obtaining hydrocarbons with the yield of 60-94%, and the obtained hydrocarbons comprised mainly chains up to C_{39}. Besides the above a product contained a big share of gaseous substances, which caused a frequent breaks of a process and forced cleaning of the reactor, disturbing and interrupting a continuous operation between the maintenance overhauls. The reactors used in the known methods for carrying the reaction had usually a shape of typical chemical reactor in a form of a cylindrical tank, provided with a dosing system, heating system and a low-speed mixer, preventing deposition of the reaction mixture.

An analysis of the information material concerning a prior art allowed a conclusion, that an ideal technological solution is a method of polyolefine

decomposition at low temperatures in one-step process, carried in a liquid phase of molten polymer, while the used catalyst is hydrochloride - resistant and not expensive.

The subject-matter of the invention is the plant to polyolefines waste conversion into liquid hydrocarbons.

Nowadays the utilization of objects made of plastics is an ecologic problem. The known plant to objects' made of plastics utilization comprises the reactor, the raw material dosage system, the condenser of product, the buffer tank and the distillation column. The reactor in form of vertical tank is equipped with the hatch, the raw material receiving connection pipe, the control system and the heating system. The heating system consists of heating tubes which are placed on the tank`s surface or within the tank. Such a heating system caused the sinter and coke formation.

SUMMARY OF THE INVENTION

The above aim is reached in the method according to the invention, using cements as a catalyst. Moreover, it has been found, heavy metals resonates are resistant to hydrochlorine and are the ideal catalysts for breaking C-C bonds in polyolefine chains at low temperatures.

A process of the transformation of polyolefine wastes to liquid hydrocarbons is carried out in a plant according to the invention, comprising at least one reactor in a shape of vertical tank, provided with an inlet charging hole, connected to a polyolefine raw material and catalyst dosing device, combustion gases outlet pipe, product receiving pipe, mixer and sieve membrane and a heating system in a form of a combustion chamber surrounding a tank from below and the said chamber is heated with at least one burner, supplied with reaction products, and in the combustion chamber, symetrically distributed on a tank circumference, preferably in some rows, heating pipes are located, which pass throughout inside of the tank above the level of an upper edge of a mixer and which are led out through sieve membrane to the combustion gases outlet chamber. The plant comprises also a condenser for a product condensation, a raw product buffer tank and a distillation column. Products of the reaction coming out from the

reactor through an outlet pipe are cooled and condensed and then are directed to a buffer tank, heated up to 40^0C.

The preferable regulation of a process is achieved, when a buffer tank is provided with a level sensor, included into a raw material dosing device automatic regulation system, ensuring keeping a level of a reactor content at the same range.

From a buffer tank a product is directed to a distillation column, where fractions of various boiling temperatures are separated.

The introduction of heating pipes above the upper wedge of a mixer enables more efficient mixing, especially of a bottom zone, an uniform distribution of a catalyst in a reaction mass and remarkably decreases formation of agglomerates and coke.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

Figure 1 is a schematic view of the apparatus of the present invention.

Figure 2 is a side, partially cutaway view of the apparatus of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a method according to the invention the disintegrated polyolefine raw material is subjected in a reactor to the progressive heating to the temperature below 600^0C together with a catalyst chosen from a group comprising cements, heavy metal resinates combinations thereof with heavy metal silicates, where a catalyst is used in amount below 30% b.w., preferably in amount of 5-10% b.w., calculating on a weight of the polyolefine raw material. The reaction has a particularly preferable course at the temperatures in the range between 300-450^0C. Preferably, chromium Cr^{3+}, iron Fe^{3+}, nickel Ni^{2+}, cobalt Co^{2+}, manganese Mn^{2+}, cadmium Cd^{2+}, copper Cu^{2+}, zinc Zn^{2+} and Pb^{2+} resinates are used as the admixture to the said cement. A catalyst can contain a mixture of two or more resinates. Using cement with the admixture of chromium and/or nickel resinate in amount of up to 20% bow., calculating for the weight of

cement results with a particularly preferable course of reaction with a yield close to a theoretical.

Preferably, if the catalyst is deposited on aluminium oxide Al_2O_3 carrier. The catalyst are also heavy metal silicates.

In a method according to the invention the catalyst can be recycled and used many times.

The method can be carried out in a periodical or continuous process.

Using a method according to the invention, LD and HD polyethylene, poly-propylene, polyisobutylene, and a natural and synthetic caotchouc can be transformed.

A method according to the invention enabled a utilisation of polyolefine wastes, being especially stable contamination of environment, and forming of a fully valuable, ecological product, which is a raw material for the production of desired hydrocarbon materials.

In a result low molecular hydrocarbons of C_4 to C_{20} of a high isomerization degree are produced.

The method according to the invention is presented on the enclosed drawing in from of an exemplary embodiment of the invention.

A plant according to the invention is presented on the enclosed drawing in a form of an exemplary embodiment of the invention.

A process of the transformation of polyolefine wastes to liquid hydrocarbons is carried out in a plant according to the invention, comprising at least one reactor in a shape of vertical tank, provided with an inlet charging hole, connected to a polyolefine raw material and catalyst dosing device, combustion gases outlet pipe, product receiving pipe, mixer and sieve membrane and a heating system in a form of a combustion chamber surrounding a tank from below and the said chamber is heated with at least one burner, supplied with reaction products, and in the combustion chamber, symetrically distributed on a tank circumference, preferably in some rows, heating pipes are located, which pass throughout inside of the tank above the level of an upper edge of a mixer and which are led out through sieve membrane to the combustion gases outlet chamber. The plant comprises also a condenser for a product condensation, a raw product buffer

tank and a distillation column. Products of the reaction coming out from the reactor through an outlet pipe are cooled and condensed and then are directed to a buffer tank, heated up to 40^0C.

The preferable regulation of a process is achieved, when a buffer tank is provided with a level sensor, included into a raw material dosing device automatic regulation system, ensuring keeping a level of a reactor content at the same range.

From a buffer tank a product is directed to a distillation column, where fractions of various boiling temperatures are separated.

The introduction of heating pipes above the upper wedge of a mixer enables more efficient mixing, especially of a bottom zone, an uniform distribution of a catalyst in a reaction mass and remarkably decreases formation of agglomerates and coke.

A plant according to the invention is presented on the enclosed drawing in a form of an exemplary embodiment of the invention.

A plant comprises one reactor 1 according to the invention, in a shape of vertical tank, provided with an inlet charging hole 2, connected to a polyolefine raw material and catalyst dosing device 3, combustion gases outlet pipe 4, product receiving pipe 5, mixer 6 and a sieve membrane 7 and a heating system in a form of a combustion chamber 8 surrounding a reactor 1 from below and the said combustion chamber 8 is heated with at least one burner 9 supplied with reaction products, and in the combustion chamber 8, symetrically distributed on a reactor 1 circumference, preferably in some rows, heating pipes 10 are located, which pass throughout inside of the reactor 1 above the level of an upper edge of a mixer 6 and which are led out through a sieve membrane 7 to the combustion gases outlet chamber. The plant comprises also a condenser 11 for a product condensation, a raw product buffer tank 12 and a distillation column 13.

The reaction products, coming out from the reactor 1 through a product receiving pipe, are directed to a condenser 11 wherein they are cooled and condensed and then directed to the buffer tank 12, which is heated to 40^0C.

A buffer tank 12 is provided with a level sensor, included into a raw material dosing device 3 automatic regulation system, ensuring keeping a level of a

reactor 1 content at the same range, which is for achieving the preferable regulation of a process.

From the buffer tank 12 raw product is directed to the distillation column 13, where fractions of different boiling temperatures are separated.

Example 1. In the reactor according to the invention, provided with a mixer, worm dosing unit, outlet pipe for receiving a distillation product, connected to a water cooler 11, 180 kg of agglomerated polyethylene and polypropylene (1:1) foil wastes were placed. 15 kgs of white Portland cement were added into the reactor and a content was heated up to melting. After melting a content a mixer was put on and it was heated up to 350^0C and then kept in that temperature till a moment, the formation of a product was stopped. After a condensation of all the product in a buffer tank 179 kgs of a viscous oil were obtained, which properties are shown in Table 1a and 1b.

Table 1a

Physical properties of a product

Property	Value
Density [g/cm^3]	0,786
Ignition temperature [^{0}C]	20
Viscosity at 80^0C [mm^2/s]	1,51
Calorific value [kJ/kg]	42 120

Table 1b.

Elementary analysis of a product

Component	Content (%)
carbon	85,51
hydrogen	14,13
sulphur	none
nitrogen	traces
chlorine	none
metals	traces

Example 2. To the reactor provided with a mixer, a worm dosing unit and an outlet pipe for receiving a distillation product 15 kgs of a Portland cement and 150 kgs of polyolefine wastes in a form of cut milk product containers, canisters and motor-oil bottles were added. A content of the reactor was heated up till melted and then a mixer was operated. The reaction mixture was heated up to 390^{0}C and kept in this temperature, still stirring. A product distilling from a reaction mixture was condensed in a condenser /water cooler/. As a product 148 kgs of a yellowish-brown mass were obtained, which solidified after some time. The resulted mass was subjected to a distillation, which course is given in Table 2.

Table 2

A course of distillation of the raw product

fraction volume (% b.v.)	start	5	7,5	10	20	30	40	50	60	70	80	90
temperature (°C)	48	77	100	115	153	186	224	265	325	365	372	375

Example 3. To the reactor provided with a mixer, distillate receiving pipe and a heating system 150 kgs of cut polyethylene wastes and 10 kgs of cobalt resinate were added. A content was heated till melted and then a mixer was operated. Still mixing a content of the reactor was lead up to 400°C and a product distilled. A course of the distillation is presented in Table 3.

Table 3

The course of distillation of a raw product

fraction volume (% b.v.)	start	5	10	20	30	40	50	60	70	80	90
temperature	51	72	112	145	172	220	251	354	368	375	382

Example 4. In a reactor provided with a heating-cooling system, a mixer and an outlet pipe 150 kgs of cut polyolefine wastes with 2 kgs of manganese resinate deposited on aluminium oxide, were added. After a temperature of 200^{0}C was reached and a content was melted, a mixer was operated and a reaction mass

was gently heated up to 380^0C, distilling a product. A course of the distillation is presented on Table 4.

Table 4

The course of distillation of a raw product

fraction volume (% b.v.)	start	5	10	20	30	40	50	60	70	80	90
temperature (°C)	45	70	85	115	140	185	195	220	255	285	320

Table 5

Physico-chemical properties of a gasoline-corresponding fraction of catalytic degradation product, resulted in a method according to the invention

Properties	Value	Method of determination
Course of distillation	°C	PN -81/C-040 12
beginning	48	
5% distilled to	73	
10% distilled to	83	
20% distilled to	96	
30 % distilled to	110	
40% distilled to	120	
50% distilled to	126	
60% distilled to	130	
70% distilled to	133	
80% distilled to	137	
90% distilled to	143	
95% distilled to	151	
distillation finish	155	
Density at 20°C [g/cm^3]	0,73	PN -90/C-0404
Vapour pressure [kPa]	29	PN -84/C-4404
Induction period [min]	40	PN-57/C-04040, method A
Sulphur content [%]	none	PN -88/C-04005
Water content [%]	------	PN -81/C-04959
Octane number value	88	PN -82/C-0412
Aqueous extract reaction	neutral	PN -84/C-04064, method B
Element content	traces of Ca, V, Fe, Ni	Rtg

Table 6.

Physico-chemical properties of a Diesel oil-corresponding fraction of catalytic degradation product, resulted in a method according to the invention

Properties	Value[^{0}C]		Method of determination
Course of distillation	N1	N2	PN -81/C-040 12
beginning	190	292	
5% distilled to	200	305	
10% distilled to	203	307	
20% distilled to	210	308	
30 % distilled to	214	309	
40% distilled to	220	310	
50% distilled to	227	311	
60% distilled to	235	313	
70% distilled to	243	315	
80% distilled to	251	317	
90% distilled to	262	322	
95% distilled to	270	327	
distillation finish	273	333	
Density at 20^{0}C [g/cm^3]	0,789	0,813	PN -90/C-0404
Kinematic viscosity at 40^{0}C [mm^2/s]	1,7	5,0	PN -81/C0411
Cloud point [DC]	(-) 45	(-) 2	PN-76/C-04115
Flash point /closed crucible/ [^{0}C]	69	150	PN - 7 5/C-04009
Sulphur content [%]	----	-----	PN -88/C-04005
PCB content [ppm]	----	----	ITN 3794 method
WWA content [ppm]	---	----	ITN 4693 method
Cetane factor	66,5	84,0	PN -85/C-040093
Corrosion	la	la	PN -85/C-040093, method B

Table 7.

Physico-chemical properties of a residue remained after distillation of fuel fractions from a catalytic degradation product, resulted in a method according to the invention

Properties	Value[^{0}C]	Method of determination
temperature> 350^{0}C		
Density at 20^{0}C [g/cm::!]	0,851	PN -90/C-0404
Kinematic viscosity at 60^{0}C [mm^2/s]	5,6	PN -81/C0411
Flash point /opened crucible/ [^{0}C]	224	PN - 75/C-04009
Flow temperature [^{0}C]	46	PN-83/C-04117
Residue after incineration [%]	0,06	PN -82/C-04077
Paraffin content [%]	37,4	PN-91/c-04109
Sulphur content [%]	0,001	PN -88/C-04005
PCB content [ppm]	----	ITN 3794 method
WWA content [ppm]	0,03	ITN 4693 method
benzo-α-pyrene content [ppb]	10	ITN 2693 method
Element content	Fe, Zn, Ti, Ni traces	Rtg
Net calorific value kJ/kg	43500	PN -86/C-04062

Relating to petrochemical products a product obtained in a method according to the invention does not contain any amount of sulphur or heavy metals. This product can be a raw material for the production of gasolines, diesel oil and ecological crude oil.

WHAT IS CLAIMED IS:

1. A method for transformation of polyolefine wastes into hydrocarbons, wherein a broken raw polyolefine material is subjected to a progressive heating to the temperature below 600^0C, a reaction is carried in a range of temperatures between 300-450^0C, with a catalyst in a closed reactor, and a product, after condensation is subjected to a distillation, **characterized in, that** the disintegrated polyolefine raw material is subjected in a reactor together with a catalyst chosen from a group comprising cements and/or heavy metal resonates and mixtures thereof, preferably with the admixture of heavy metal silicates, where a catalyst is used in amount below 30% b.w., preferably in amount of 5-10% b.w., calculating on a weight of the polyolefine raw material.
2. A method according to claim 1, **characterized in, that** at least one catalyst is selected from from a group of chromium Cr^{3+} resinate, iron Fe^{3+} resinate, nickel Ni^{2+} resinate, cobalt Co^{2+} resinate, manganese Mn^{2+} resinate, cadmium Cd^{2+} resinate, copper Cu^{2+} resinate, zinc Zn^{2+} resinate and lead Pb^{2+} resinate.
3. A method according to claim 1, **characterized in, that** a catalyst comprises white cement and/or portland cement and/or puzzolanic cement or a mixture of at least two said substances.
4. A method according to claim 1, **characterized in, that** as a catalyst a mixture containing white cement and chromium Cr^{3+} resinate, preferably with admixture of Cr^{3+} silicate, in amount of up to 20% b.w. calculating to the mass of a cement is used.
5. A method according to claims 1-4, **characterized in, that** a catalyst is deposited on aluminium oxide Al_2O_3.
6. A method according to claims 1-4, **characterized in, that** heavy metal silicates are deposited on aluminium oxide Al_2O_3.
7. A method according to claim 1, **characterized in, that** a process can be run in a periodic or continuous way.

8. A plant for transformation of polyolefine wastes into hydrocarbons, comprising a reactor in a shape of a vertical tank provided with an inlet charging hole, connected to a polyolefine raw material and catalyst dosing device, product vapour receiving pipe, a mixer and a liquid level regulation system and a distillation column, **characterized in, that** a reactor (1) is provided with a heating system in a form of a combustion chamber (8) surrounding a reactor (1) from below and the said chamber (8) is heated with at least one burner (9), supplied with reaction products, and in the combustion chamber, symetrically distributed on a tank circumference, preferably in some rows, heating pipes (10) are located, which pass throughout inside of the reactor (1) above the level of an upper edge of a mixer (6) and which are led out through sieve membrane (7) to the combustion gases outlet chamber.
9. A plant according to claim 8, **characterized in, that** a buffer tank (12) is provided with a level sensor, included into a raw material dosing device (3) automati cregulation system.