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(54) Title: THE METHOD OF OBTAINING LIQUID FUELS FROM POLYOLEFINE WASTES

(57) Abstract

The subject of the invention is the method of obtaining liquid fuels from polyolefine wastes. According to the method, properly disintegrated polyolefines in an amount of 100 parts y weight are heated in the temperatures between 300 °C to 450 °C till the moment of a decay of volatile product forming, in the presence of heavy metals silicates as catalysts, added in amounts of 1–30 parts by weight. As catalyst, the silicates of iron Fe^{3+}, cobalt Co^{2+}, nickel Ni^{2+}, manganium Mn^{2+}, chromium Cr^{3+}, copper Cu^{2+}, zinc Zn^{2+}, cadmium Cd^{2+} and/or their mixtures are used. The catalyst is applied in an amorphic form in an amount from 5 to 10 % by weight, calculated on the mass of the raw material. The catalyst is recycled and used multiply. A process is run in a continous way.

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The method of obtaining liquid fuels from polyolefine wastes

A subject of the invention is the method of obtaining liquid fuels from polyolefine wastes.

Heretofore from the Polish patent description no. 149887 there is known a method of obtaining liquid fuels from atactic polypropylene, according to which raw material is subjected to a thermodegradation process at the temperatures between 180^{0}C to 340^{0}C, introducing air into a reaction system. During the process according to the known method the fractionated reception and condensation of products are kept.

From the European patent application no. 0577279 A1 there is known a method of polymers processing, which base is a thermal decomposition of polyolefines, poly/vinyl chloride/ and poly/ethylene terephtalate/ at the temperatures from 300^{0}C to 600^{0}C in the stream of a hot gas free of oxygene. A process runs in the presence of a catalyst in a form of zeolytic clay, amorphic aluminium silicate, silica, quartz, aluminium, zirconium, ash and calcium oxide.

In the above method the use of a fluidal reactor is necessary. Obtained products are characterised in a broad range of a molecular weight distribution.

From the American patent description no. 4.584.421 there is known a method of decomposition of polyolefines wastes, basing on heating of a melted reaction mass up to the temperatures between 440^{0}C - 470^{0}C in a presence of catalyst. In the mentioned temperatures volatile products are obtained, which are consequently introduced into a catalyst bed of a temperature between 350^{0}C - 470 ^{0}C, after leaving which the hydrocarbons of a narrow range of molecular weight are formed.

The catalyst belongs to the group of compounds, comprising ferrous-aluminium oxide complex, silicic acid - ferrous oxide complex and zeolites.

The products, obtained according to the known methods had a broad scatter of molecular weights.

A method according to the invention bases on heating the disintegrated polyolefin wastes at the temperatures between 180^{0}C to 620^{0}C in a presence of heavy metals silicates as catalyst, which are used in amounts from 1 to 30% by weight, calculating on the mass of polyolefin raw material.

Particularly favourite run of the reaction occurs at the temperatures between 300^0 C to 450^{0}C, using as the catalysts silicates of iron Fe^{3+}, cobalt Co^{2+}, nickel Ni^{2+}, manganium Mn^{2+}, chromium Cr^{3+}, copper Cu^{2+}, cadmium Cd^{2+} which process runs the most favourably with the amount of catalyst between 5 and 10 %.

The applied catalyst, after use can be recycled and reused in the process according to the invention.

The process lead according to the invention can be run in a periodic or continous way, and the raw material comprises used and waste polyethylene, polypropylene, polyisobutylene, polystyrene, natural and synthetic caotchouc.

In a method according to the invention properly disintegrated polyolefine raw material is placed with a determined amount of a catalyst in the heated reactor, provided with a mixer and a cooler. A content of the reactor is melted and then heated up to the temperature in which the process is run according to the invention. Vapours of a product are condensed in a cooler and then separated on a distillation column.

In a result, the low-molecular weight, liquid hydrocarbons of C_4-C_{20} are obtained, having a remarkable isomerization and aromatization grade. Next to the petrochemical products the current product does not contain sulphur and heavy metals and it is a valuable raw material for the production of motor liquid fuels of high octane number and ecological crude oil.

A method according to the invention is an effective way of the utilisation of polyolefine wastes, which are difficult waste and contaminant of the natural environment.

Example no. 1. In the heated reactor, provided with a mixer, inlet pipe and outlet pipe connected with a cooler, and a manhole connected with a

doser, the polyolefin raw material in amount of 180 kgs, composed of the chips of polyethylene foil and cut polypropylene forms was placed. After melting, nickel silicate $Ni(SiO_2)$ was added in amount of 15 kgs, and the content of a reactor was heated up to 380 ^{0}C, which temperature was kept till forming of product vapours was stopped. After a condensation and cooling 175 kgs of an oily product were obtained, which physical characteristics is given in a table no. 1 and results of an elementary analysis are presented in a table no.2.

Examle no. 2. In a cylindrical reactor of 9 m^3 capacity provided with an automatised heating-cooling system, a mixer, an inlet opening connected with a polyethylene raw material dosing system and an inlet opening, connected with a catalyst dosing system and an inlet pipe connected with a cooler the amount of disintegrated postproduction polyethylene wastes was placed, which, when melt, filled 85% of the reactor volume. The amount of 5% of ferrous silicate was added to the melted mass and the content of a reactor was heated up to 390^{0}C, which temperature was kept while a mixer was operating. As the product of a reaction vapourised, the raw material was added through a dozer of polyolefin raw material, keeping the level of filling a reactor at 80 - 85%.

After the vapours are condensed and cooled a product was obtained, which was subjected to a distillation according to ASTM D2892 under an atmospherical pressure in Podbielniak apparatus model Hyper Col series 3800, resulting the following fractions:

- to 170^{0}C	32,3 vol. % /gasoline fraction/,
- from 170^{0}C to 300^{0}C	24,6 vol. % /Diesel oil N-1/,
- from 300^{0}C to 350^{0}C	10,4 vol. % /Diesel oil N-2/,
- residue above 350^{0}C	29,7 vol. %,
- losses	3,0 vol %.

A total content of fuel fraction in a product reaches 67,3vol. %; it is higher than an analogical content in petroleum.

The gasoline fraction had an octane number. 86

Table no. 1 Physical properties of a product

Property	Value
Density [g/cm^2]	0,786
Temperature of igition [^{0}C]	max. 20
Viscosity at 80^{0}C [mm^2/s]	1,51
Calorific value [kJ/kg]	42,12

Table no. 2 The elementary analysis of a product.

Element	Content [%mol]
carbon	85,51
hydrogen	14,13
nitrogen	traces
sulphur	traces
chlorine	0,001
metals	traces

The product of polyolefin degradation, obtained according to a method of the invention was consequently subjected to separation with fractional distillation, which course is given in table no. 3.

Table no. 3 The course of a boiling temperature of a product.

Fraction volume (% obj.)	start point	5	7,5	10	20	30	40	50	60	70	80	90
Temperature (^{0}C)	48	77	100	115	153	186	242	265	325	365	372	375

A fraction of Diesel oil /170^{0}C - 300^{0}C/ showed very good low-temperature properties /a cloud point and cold filter blocking temperature CFPP= (-)45^{0}C/, and also very high cetane number of 65.

The distillation residue has an appearance of a slag wax and it contains mainly higher parafine hydrocarbons. In the distillation tests of this fraction it was found, that over 90% distillates in the range of 350^{0}C-450^{0}C. Simultaneously a possibility of recycling that fraction to the reaction for resulting fuel fraction has been fully confirmed.

The patent claims

1. The method of obtaining liquid fuels from polyolefin wastes, comprising a thermal degradation of polyolefin raw material in the presence of catalysts, containing metal silicates, and then the distillation of resulted products, **characterised in that** the properly disintegrated polyolefines in amount of 100 parts by weight are heated, preferably in the temperatures between 180^{0}C to 620 ^{0}C, till the moment of a decay of volatile product forming, in the presence of heavy metals silicates as catalysts, added in amount of 1 - 30 parts by weight.
2. The method according to the claim no. 1, **characterised in that** the transformation is run at the temperatures range between 300 - 450 ^{0}C.
3. The method according to the claims 1 and 2, **characterised in that** as a catalyst iron Fe^{3+} silicate of is used.
4. The method according to the claims 1 and 2, **characterised in that** as a catalyst cobalt Co^{2+} silicate is used.
5. The method according to the claims 1 and 2, **characterised in that** as a catalyst nickel Ni^{2+} silicate of is used.
6. The method according to the claims 1 and 2, **characterised in that** as a catalyst manganium Mn^{2+} silicate of is used.
7. The method according to the claims 1 and 2, **characterised in that** as a catalyst chromium Cr^{3+} silicate of is used.
8. The method according to the claims 1 and 2, **characterised in that** as a catalyst copper Cu^{2+} silicate of is used.
9. The method according to the claims 1 and 2, **characterised in that** as a catalyst zinc Zn^{2+} silicate of is used.
10. The method according to the claims 1 and 2, **characterised in that** as a catalyst cadmium Cd^{2+} silicate of is used.
11. The method according to one or more above claims, **characterised in that** a catalyst is a mixture of two or more catalysts.

12. The method according to one or more claims from nos 1 to 11, characterized in that the catalyst is used in the amorphic form.

13. The method according to the claim no. 2, **characterised in that** a catalyst is added in amount from 5 to 10 % by weight, calculating on the mass of the raw material.

14. The method according to the claims nos. 1 or 2, **characterised in that** a catalyst is recycled and used multiply.

15. The method according to the claim no. 1, **characterised in that** the process is run in a continous way.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/IB 97/01125

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9405 Derwent Publications Ltd., London, GB; Class A17, AN 94-040118 XP002052121 & JP 05 345 894 A (TOYO SEIKAN KAISHA LTD) see abstract	1,2,4-6
A	EP 0 577 279 A (BP CHEM INT LTD) 5 January 1994 cited in the application	
A	US 4 584 421 A (SAITO KIYOSHI ET AL) 22 April 1986 cited in the application	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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