(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 155 367 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.03.2023 Bulletin 2023/13

(21) Application number: **21382854.4**

(22) Date of filing: **23.09.2021**

(51) International Patent Classification (IPC):
C10B 53/07 *(2006.01)* ***C10G 1/10*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C10B 53/07; C10G 1/10

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

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(54) PYROLYSIS PROCESS ACTIVATED BY NANOCARBON-BASED METAL FREE REAGENTS TO OBTAIN SYNTHETIC FUELS FROM PLASTIC WASTE

(57) The present invention provides a pyrolysis process activated by nanocarbon-based metal free reagents to obtain synthetic fuels from plastic waste. The process of the present invention comprising the steps of: i) adding a feedstock of plastic waste and a nanocarbon-based metal free reagent to a pyrolysis reactor at room temperature and atmospheric pressure; ii) increasing the reactor temperature up to 500°C, a pressure between 1-20 bar during a period of time between 1-3 hours for a thermal decomposition; iii) separating the gases generated in the reactor in different fractionating columns, obtaining thereby different fractions; iv) cooling the gas fractions obtained in the step iii) in a condenser obtaining a liquid fraction; and v) extracting the resulting liquid fraction as the final product; and wherein the nanoparticle carbon-based metal free reagent is selected from the group consisting of graphene, carbon nanotubes, carbon nanowires or combinations thereof.

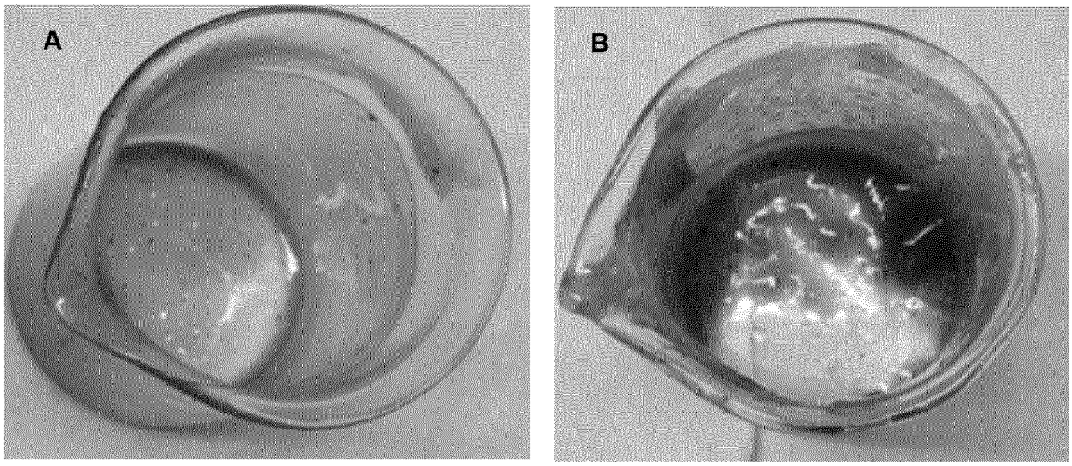

FIG. 1

EP 4 155 367 A1

Description

FIELD OF THE INVENTION

[0001] The field of the invention relates to a pyrolysis process for obtaining synthetic fuels and from plastic waste, more specifically, relates to a pyrolysis process activated by nanocarbon-based metal free reagent for converting plastic waste into oil and synthetic fuels in the absence of catalysts.

BACKGROUND ART

[0002] Around six trillion tons of plastic waste have been generated worldwide in the last 50 years. It has been observed that 90% of the waste accumulated by the municipal corporation is plastic waste. This garbage is recycled, however about 80 percent of it sits in landfills or in the natural environment, where it damages wildlife, filters out harmful chemicals, and emits harmful gases.

[0003] Therefore, there is a need for increased recycling of this type of waste. The three main purposes of recycled plastic are direct reuse, use as a raw material for the manufacture of new products and its conversion as fuel or as new chemical products.

[0004] Processes for treating plastic waste to obtain fuels and other value-added chemicals are known in the state of the art.

[0005] US4038100A discloses a pyrolysis process to obtain petrochemical solid products from plastic waste, specifically rubber tires. Particularly, the invention provides a process for recycling rubber, especially scrap rubber such as tires, by separating the rubber into its components, and using these components as natural resources for the production of other articles. The plastic waste is fed into the reactor together a heat-carrying solid which can be selected between metal or ceramic solids. However, this process is focused on obtaining solid products, not liquid products. In addition, the heat-carrying must be treated to eliminate it from the final product, which makes the process more expensive and there is a risk of contamination of the final product.

[0006] US20170313945A1 discloses a pyrolysis process to transform waste (including plastics) from different sources into high-quality carbon, which can be used or sold as a solid fuel. The process comprising: a) drying the waste by submitting said waste to a pressure of at least 3 bar, and a temperature of at least 250°C.; b) releasing the water vapor out of the reactor, and; c) carbonizing at least partially the waste by maintaining said waste during a period of time of at least 5 minutes to a pressure of at least 3 bar, and a temperature of at least 250° C., thereby obtaining carbon; and d) optionally separating non-organic material from the obtained carbon. However, the process requires a sorting and treatment of the waste prior to the process, so the process is expensive and complex. Furthermore, this process is focused on obtaining solid products, not liquid products.

[0007] US2007083068A1 describes a method of recycling a plastic to produce the hydrocarbons which can be used as gasoline for vehicles. The method comprising decomposing the plastic in the presence of a metallocene catalyst thereby forming hydrocarbons. As in the previous document, the method includes the step of processing the plastic with physical and/or chemical treatments. This type of treatment makes the process more expensive. Furthermore, the use of this type of catalysts has the disadvantage that the metals in its composition contaminate the products and/or sub-products.

[0008] WO2013187787 discloses a continuous process of pyrolysis of plastic waste and/or rubber waste and/or organic waste, comprising subjecting these components to a thermal decomposition in a pyrolytic reactor without any access to air, at a temperature of 200 to 850°C, under atmospheric pressure or elevated pressure or reduced pressure, characterized in that, into the pyrolytic reactor chamber, a composition of chemical modifier is dosed, which comprises 10 to 30% by weight of water, 20 to 80% by weight of at least one aliphatic alcohol, 5 to 15% by weight of carbamide or its derivatives, and 5 to 15% by weight of monoacetylferrocene.

[0009] WO2014040634A1 describes a method and apparatus for recycling plastic wastes. Plastic wastes which for at least 80 wt% contain a polymer or a mixture of polymers from a group including polymethyl methacrylate, polypropylene, polyethylene, polystyrene, polyethylene terephthalate and/or polytetrafluoroethylene, are recycled using the following steps: (i) heating the plastic wastes to a temperature at which they are flowable; (ii) pyrolyzing the flowable plastics together with a catalyst and/or an adsorber and withdrawing the resulting gases; (iii) condensing the gases. The catalyst used was a zeolite and the adsorbent consist of calcium oxide and / or magnesium oxide.

[0010] WO2015128033A1 relates to a process for converting mixed waste plastic (MWP) into valuable petrochemicals, comprising feeding mixed waste plastic (MWP) to a pyrolysis reactor, converting said MWP into a gaseous stream and a liquid stream, and further processing said gaseous stream into valuable petrochemicals, said process further comprising the steps of: i) feeding said liquid stream, together with a hydrocracker feed, to a hydrocracking unit; ii) converting said liquid stream, together with said hydrocracker feed, through hydrocracking into at least one gaseous stream and a liquid stream: iii) further processing said at least one gaseous stream into valuable petrochemicals. In this process, hydroc-

racking catalysts are used, which are commercially available hydrocracking catalysts such as Co-Mo / Ni-Mo on alumina, among others.

[0011] WO2017103010A1 discloses a process for converting waste plastic into gases, liquid fuels and waxes by catalytic cracking. The process comprises the steps of introducing waste plastic and a catalyst within a reactor; allowing at least a portion of the waste plastic to be converted to gases, liquid fuels and waxes within the reactor; and removing a product stream containing said gases, liquid fuels and waxes from the reactor. The process uses a zeolite-type catalyst and/or an amorphous-type catalyst (silica, alumina, kaolin or a mixture).

[0012] JPH08337782 describes the conversion of a heavy oil into a light oil, reutilizing waste plastics without hydrogen and catalyst by mixing a heavy oil with waste plastics and heat-treating the mixture at a specific temperature in a non-oxidizing atmosphere. The process consists of the addition of a heavy oil consisting of a petroleum-based heavy oil or a coal-based heavy oil mixed with plastic waste and the mixture is heat-treated at 350-460°C in a non-oxidizing atmosphere such as nitrogen, argon, helium or hydrocarbon gas. The heat-treatment is carried out under a pressure between atmospheric pressure and 50 atm for 10-40 min. After separation and cooling of the gases, the resulting liquid phase is obtained.

[0013] In the method described in JPH08337782, catalyst addition is not necessary. However, not totally exclude the addition of a catalyst. Catalyst can be added to promote the decomposition and reaction in the heat treatment. For example: silica, alumina catalysts, transition metal-based catalysts, noble metal catalyst, metal compound or natural minerals.

[0014] Furthermore, the raw materials include a heavy oil consisting of a petroleum-based heavy oil or a coal-based heavy oil, not only plastic waste.

[0015] Despite the fact that there are a lot of processes, they involve the use of catalysts, which makes the process more expensive, can generate waste and also generates environmental damage from the use of the catalysts themselves. In addition, the processes are less efficient, since, apart from the cost associated with the catalysts, longer times and higher temperatures are required and lower yields are obtained.

[0016] The present invention solves the technical problems present in the state of the art and mentioned above.

SUMMARY OF INVENTION

[0017] In view of the problems of the state of the art, the main object of the present invention is to provide a process of pyrolysis for converting plastic waste into synthetic fuels, particularly based on the use of nanocarbon-based metal free reagents, instead of using catalysts, which allows the use of lower temperatures and pressures than those described in the state of the art, achieving better results.

[0018] Furthermore, in the present invention it is not necessary to use non-oxidizing atmospheres, since the process of the present invention works directly with air. It reduces the process cost and avoids the use of strategic gases such as helium or argon.

[0019] The process of the present invention is an advanced pyrolysis, since the energy required for the degradation of plastics or polymers in which the C-C and C-H bonds are broken is less than the required in the usual reactions, which translates into a lower reaction temperature. This has some advantages such as that the energy accumulated in the fuel or/and gas obtained is greater than the necessary in the process and is a more economically pyrolysis process.

[0020] The present invention solves the problems that exist in the state of the art by means of an advanced pyrolysis process activated by nanocarbon-based metal free reagent in which catalysts are not used to obtain high-quality fuels and second-life products from plastic waste.

[0021] It should be noted that, in the present invention, plastic waste does not need pre-treatment, thus constituting an advantage for recycling and a lower cost of the process.

[0022] As used herein, the term *"synthetic fuel"* and its plural have the meaning commonly attributed in the state of the art, this is, a liquid or gaseous fuel derived from a source such as coal, shale oil, tar sands, or biomass.

[0023] In a first aspect of the invention, the present invention provides a pyrolysis process activated by nanocarbon-based metal free reagents to obtain synthetic fuels from plastic waste, comprising the following steps:

i) adding a feedstock of plastic waste and a nanocarbon-based metal free reagent to a pyrolysis reactor at room temperature and atmospheric pressure;

ii) increasing the reactor temperature up to 500°C, a pressure between 1-20 bar during a period of time between 1-3 hours for a thermal decomposition;

iii) separating the gases generated in the reactor in different fractionating columns, obtaining thereby different fractions;

iv) cooling the gas fractions obtained in the step iii) in a condenser obtaining a liquid fraction; and

v) extracting the resulting liquid fraction as the final product;

wherein the nanoparticle carbon-based metal free reagent is selected from the group consisting of graphene, carbon nanotubes, carbon nanowires or combinations thereof.

[0024] The pyrolysis process of the present invention achieves yields greater than 80% of the liquid fraction. The resulting liquid fraction includes synthetic fuels such as pyrolysis oils, paraffins or naphthas.

[0025] The plastic waste and the nanocarbon-based metal free reagent can be introduced within the reactor simultaneously or subsequently.

[0026] The nanocarbon-based metal free reagents have a very large specific surface, which represents a very large active surface. Due to this, the interaction between the intermediate products of the gas and liquid phases is superior in the presence of nanocarbon-based metal free reagents. The reaction is activated as it would in the presence of a catalyst. However, unlike catalysts, these nanocarbon-based metal free reagents are integrated into the final product. In the present invention, during steps ii) and iii), the nanocarbon-based metal free reagents are integrated into the final products without leaving additional residues and controlling the size of the final compounds obtained.

[0027] Therefore, the use of said nanocarbon-based metal free reagents in the process of the present invention allows using lower temperature ranges than those described in the state of the art and obtaining higher liquid fraction yields.

[0028] In summary, the use of the nanocarbon-based metal free reagents has several advantages such as the absence of additional solid residues, optimization of the process, environmentally friendly (absence of metals), and a low cost (compared to catalysts).

[0029] In another aspect of the invention, the feedstock of plastic waste comprises at least one polymer selected from the group comprising high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyethylene (PET), nylon and polypropylene (PP) or combinations thereof.

[0030] In another aspect of the invention, the nanocarbon-based metal free reagents have a size equal to or less than 250 nm in one or more of its axes, preferably a size equal to or less than 150 nm in one or more of its axes.

[0031] The temperature increases in the reactor (step ii)) can be carried out directly or by at least 3-steps process with stationary temperatures.

[0032] In another aspect of the invention, the temperature increases in the reactor of step ii) is carried out by at least 3 steps process with stationary temperatures at 70-110 °C, 150-280 °C and 250-500 °C, respectively.

[0033] In another aspect of the invention, the temperature increases in the reactor of step ii) is carried out by at least 3 steps process with stationary temperatures at 70-110 °C, 150-420 °C and 420-500 °C, respectively.

[0034] In the present invention, thermal decomposition (step ii)) is carried out at low temperature (<500°C, preferably between 50-500°C) and at controlled pressure (1-20 bar, preferably between 1-16 bar). These optimized reaction conditions allow a controlled polymeric degradation in which there is a rearrangement of the atoms that permits to control the size of the final compounds obtained using nanocarbon-based metal free reagents that are integrated into the reaction products without generating additional residues.

[0035] Typically, the decrease in reaction temperature is achieved through the use of catalysts, but it supposes an additional cost for the process and an environmental problem since these catalysts include metals that can be heavy or toxic. In addition, there is the problem of recovering and/or treating them once their useful life has ended and they remain together with the solid waste.

BRIEF DESCRIPTION OF DRAWINGS

[0036] The following figures are described below. These illustrate the exemplary embodiments and are not limiting their scope.

[0037] Figure 1 shows the fraction of wax obtained for the pyrolysis process of the present invention using nanoparticle carbon-based metal free reagents (A) and without using said reagents (B).

DESCRIPTION OF EMBODIMENTS

[0038] The skilled person is aware of suitable apparatus and equipment for carrying out the process in accordance with the present invention and will select the suitable system based on his professional experience, so that no further extensive details need to be given here.

Example 1. Pyrolysis process of the present invention using a mixture of polyethylene (PET) and PE and carbon nanotubes as reagents.

[0039] Initially, a mixture of 200 g of plastic waste having a composition of 25-30% by weight of PET, 55-65 % by weight of PE (LDPE and HDPE mixed), <10% impurities and humidity and approximately 0,1 g of carbon nanotubes, synthesized by methods known in the state of the art, were added to a pyrolysis reactor. The addition was carried out at room temperature and atmospheric pressure.

[0040] Subsequently, the temperature of the reactor was increased up to 500°C and the pressure was fixed below 16 bar, producing a thermal decomposition of the mixture of the plastic waste and the carbon nanotubes. In this example, the temperature increases in the reactor were carried out by a 3-step process with stationary temperatures at 70-110 °C, 150-280 °C and 250-500 °C, respectively.

[0041] Afterwards, the different phases of the gases generated into a fractionating column were separated. Attached to this fractionating column there was placed a condenser.

[0042] Finally, the gases were cooled in the condenser and the resulting liquid fraction was stored.

[0043] The products obtained were a 90% by weight of a liquid fraction that includes synthetic fuels such as pyrolysis oil, fuels, paraffins or naphthas, 3% by weight of a non-condensable gaseous fraction and 7% by weight of solid waste.

Example 2. Comparative tests of the pyrolysis process of the present invention using nanoparticle carbon-based metal free reagents and without using said reagents

[0044] To carry out this example, 9 mixtures of plastic waste with different compositions were used:

Plastic waste Mixture N°	Composition of the mixture (%wt. of the mixture)
1	100% PS
2	100% HDPE
3	55% LDPE/25%PS/20%PET
4	80%LDPE/20%PP
5	55% LDPE/25% PS/20% PET
6	55% LDPE/25% PS/20% PET
7	100% PP
8	100% LDPE
9	85% LDPE

[0045] The process described below was performed for the 9 plastic waste mixtures.

[0046] Initially, 200 g of a plastic waste mixture and approximately 0,1 g of carbon nanotubes, synthesized by methods known in the state of the art, were added to a pyrolysis reactor. The addition was carried out at room temperature and atmospheric pressure.

[0047] Subsequently, the temperature of the reactor was increased up to 500°C and the pressure was fixed below 16 bar, producing a thermal decomposition of the mixture of the plastic waste and the carbon nanotubes. In this example, the temperature increases in the reactor were carried out by a 3-step process with stationary temperatures at 70-110 °C, 150-420 °C and 420-500 °C, respectively.

[0048] Afterwards, the different phases of the gases generated into a fractionating column were separated. Attached to this fractionating column there was placed a condenser.

[0049] Finally, the gases were cooled in the condenser and the resulting liquid fraction was stored. The process was repeated for the 9 mixtures but without the addition of the carbon nanotubes, which act as reagents.

[0050] Table 1 shows the yield values obtained. Thanks to the addition of said nanocarbon-based metal free reagents in the first step of the process, the yield of the liquid phase obtained increased between 2 and 9%, compared to the pyrolysis process in which said reagents were not used.

Table 1. Yield improvement of liquid phase (%wt. of the organic liquid phase) with and without nanocarbon-based metal free reagents

	With nanocarbon-based metal free reagent	Without nanocarbon-based metal free reagent	
Plastic waste Mixture N°	Yield (%wt. of the liquid phase)	Yield (%wt. of the liquid phase)	Yield improvement (%wt. of the liquid phase)
1	51,20	49,30	1,9
2	59,18	50,70	8,48

(continued)

	With nanocarbon-based metal free reagent	Without nanocarbon-based metal free reagent	
Plastic waste Mixture N°	**Yield (%wt. of the liquid phase)**	**Yield (%wt. of the liquid phase)**	**Yield improvement (%wt. of the liquid phase)**
3	29,59	17,90	11,69
4	70.53	61,23	9,30
5	26,76	20,86	5,90
6	20,65	18.01	2,64
7	84,63	80,49	4,14
8	41,52	37,56	3,96
9	68,06	59,06	9,00

[0051] Furthermore, the kinematic viscosity was measured, at 40 °C according to ASTM D445 standard, for the fraction of wax obtained under the same reaction conditions with and without reagents. As can be seen in Figure 1, a lower fraction of wax was obtained using the reagents, it is obtained a product with that has a lower kinematic viscosity. Measured with reagent 1.4 $\times 10^{-6}$ m^2/s. and without reagent 2.4 $\times 10^{-6}$ m^2/s.

[0052] This result reflects that the use of said reagents in this pyrolysis process gives rise to a high quality and improved fluidity, which is an advantage because it produces less waste, and this results in less damage to the equipment and engines.

Claims

1. Pyrolysis process activated by nanocarbon-based metal free reagents to obtain synthetic fuels from plastic waste, comprising the following steps:

   i) adding a feedstock of plastic waste and a nanocarbon-based metal free reagent to a pyrolysis reactor at room temperature and atmospheric pressure;
   ii) increasing the reactor temperature up to 500°C, a pressure between 1-20 bar during a period of time between 1-3 hours for a thermal decomposition;
   iii) separating the gases generated in the reactor in different fractionating columns, obtaining thereby different fractions;
   iv) cooling the gas fractions obtained in the step iii) in a condenser obtaining a liquid fraction; and
   v) extracting the resulting liquid fraction as the final product; and

   wherein the nanoparticle carbon-based metal free reagent is selected from the group consisting of graphene, carbon nanotubes, carbon nanowires or combinations thereof.

2. The pyrolysis process according claim 1, wherein the feedstock of plastic waste comprises at least one polymer selected from the group comprising high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyethylene (PET), nylon and polypropylene (PP) or combinations thereof.

3. The pyrolysis process according claim 1 or 2, wherein the nanocarbon-based metal free reagent has a size equal to or less than 250 nm in one or more of its axes.

4. The pyrolysis process according claim 1 or 2, wherein the nanocarbon-based metal free reagent has a size equal to or less than 150 nm in one or more of its axes.

5. Pyrolysis process according to any one of claims 1 to 4, wherein the temperature increases in the reactor of step ii) is carried out by at least 3-steps process with stationary temperatures at 70-110 °C, 150-280 °C and 250-500 °C, respectively.

6. Pyrolysis process according to any one of claims 1 to 4, wherein the temperature increases in the reactor of step ii) is carried out by at least 3-steps process with stationary temperatures at 70-110 °C, 150-420 °C and 420-500 °C, respectively.

7. Pyrolysis process according to any one of the preceding claims, wherein the pressure of step ii) is between 1-16 bar.

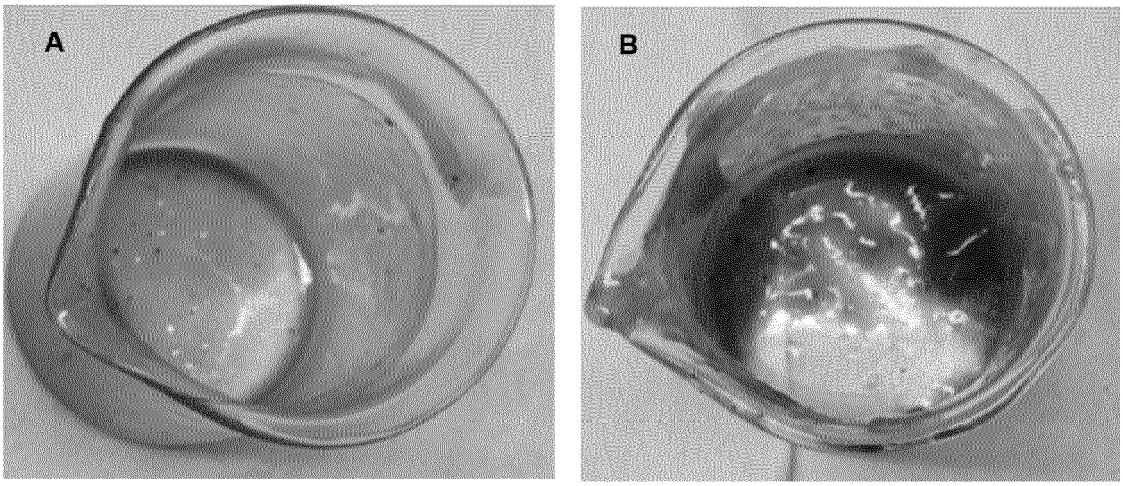

FIG. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 21 38 2854

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Place of search	Date of completion of the search	Examiner
The Hague	14 March 2022	Bertin, Séverine

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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