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(54) Method for processing industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, to produce petroleum products for use as motor oil components and chemical raw materials

(57) The invention relates to a process involving thermolysis, in particular thermocatalytic liquefaction, of a starting material containing industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, by treating the starting material with a catalyst and an initiator comprising at least one metal hydride in the presence of a hydrogen donor at elevated temperature and pressure, preferably at a temperature of 200-400 °C and a pressure of 3-7 MPa.

EP 2 937 403 A1

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Description

[0001] The present invention relates to the chemical processing of a starting material containing industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, to produce petroleum products, in particular liquid petroleum products for use as motor oil components or as raw materials in the basic organic, petrochemical and biochemical synthesis industries, the production of anode paste for electrothermal and electrochemical enterprises, water-, heat- and sound-insulating materials, and bituminous concrete for road making.

[0002] The chemical processing of industrial and domestic organic wastes, in particular plastic and/or rubber-containing waste materials, is an extremely pressing problem, caused by the continuous increase of these wastes (e.g. scrap tires from automobile, aircraft and other vehicles and various industrial and domestic organic wastes, such as polyethylene, polypropylene, polystyrene, polyisobutylene, nylon, polyester, polyvinylchloride, etc.) on the one hand and the lack of efficient methods for processing such materials on the other. Since rubber is a product originating from petroleum it would be highly desirable to have a process that allows for ecologically clean comprehensive chemical processing of plastic and/or rubber-containing materials with the object of producing liquid petroleum products for use as boiler fuel, components of high-octane motor fuels, raw materials for the petrochemical, organic and biochemical synthesis industries, production of water-, heat- and sound-insulating materials, bituminous concrete for road making, carbon-graphite materials and anode paste for electrothermal and electrochemical plants.

[0003] In particular, such recycling of organic waste, in particular plastic and/or rubber-containing waste, would make it possible substantially to expand the hydrocarbon raw material base, which has been suffering an acute shortage in recent years due to the significant reduction in reserves of natural oil and the rates of exploration, production and subsequent high refining.

[0004] Researchers have therefore been trying to resolve the ecological problem of comprehensive and non-hazardous utilization of industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, in order to reduce the consumption of hydrocarbon raw materials produced from crude oil, lignite and hard coals, oil shales and natural bitumens.

[0005] US 4,175,211 discloses a method for processing plastic and/or rubber-containing wastes - scrap automobile tires - which comprises grinding the latter to 4-0.75 mm, mixing with petroleum products, and heating the resultant mass in a reactor at 65-370 °C for a time sufficient for the material to dissolve. The method involves catalytic cracking of the resultant solution in a reactor at a temperature of not lower than 450 °C and under elevated pressure, discharging the product from the reactor and subsequently distilling it to produce gaseous products, a gasoline fraction, and light and heavy oils.

[0006] The method of US 4,175,211 is characterized by its multi-stage nature and the complexity of the process. Said method also requires grinding the scrap tires, which is extremely challenging, particularly when metal cord is present; using a specific catalyst and periodically regenerating this, and employing high temperatures and pressure, which results in the formation of significant amounts of low-molecular gaseous products and also of high-molecular asphaltenic hydrocarbons due to condensation reaction.

[0007] US 3,895,059 discloses a method for the preparation of liquid products from rubber-containing wastes by heating these wastes at a temperature above 200 °C in a hydrocarbon liquid for a time ensuring conversion of the rubber into a viscous oil-like product. Then, the latter is treated with an alkylation catalyst (H_2SO_4, S_2Cl_2) after addition of an aliphatic aldehyde or ketone thereto. The resultant resin is added to rubber mixtures in tire production.

[0008] The above method is also characterized by a multi-stage nature, the need to use sulfuric acid and sulfur monochloride, which can induce deep condensation reactions, and densification, which complicates the formation of low-molecular liquid products. Furthermore, the fields of application of the resultant product are restricted and specific.

[0009] SU 1613455 discloses a method for processing rubber-containing wastes by stirring a solution of plastic and/or rubber-containing wastes with a concentration of 10-80 wt.% in a hydrocarbon medium at a temperature of 290-380 °C and distilling off low-boiling fractions. The hydrocarbon medium employed is the product of propane deasphaltation of oil tar containing 2.4-5.9 wt.% of asphaltenes. Low-boiling fractions with a boiling point of 230-310 °C are distilled off continuously during the entire stirring process.

[0010] Disadvantages of the method of SU 1613455 relate primarily to limitations regarding the content of asphaltenes in the hydrocarbon medium. This condition is difficult to meet, since the crude oils produced in recent years and the products of their refining have usually a high content of asphaltenes and tarry and organosulfur compounds. Consequently, numerous cycles of extraction of the aforesaid compounds are required to reduce their content in the hydrocarbon medium. Furthermore, the yield of light fractions with a boiling point of up to 230 °C is below 40 wt.%.

[0011] US 3,896,059 discloses a method for processing rubber-containing wastes involving heat-treatment of the wastes in a hydrocarbon solvent at 204-427 °C for 0.1-50 hours, followed by treating the hot dissolution product thus obtained with an alkylation catalyst (a Lewis acid) or a condensation catalyst (0.1-20 wt.% of the product) at 16-149 °C for 0.5-50 hours.

[0012] Drawbacks of the above method are its complexity and multiple stages, and most importantly the limited use of the resultant final product, which is preferably added to rubber mixtures in tire production.

[0013] SU 1289872 discloses a method for processing scrap tires and various rubber-containing wastes by heat-treating a mixture of a previously prepared rubber powder and a plasticizer (shale oil or anthracene oil), first at 190-220 °C and then at 240-260 °C. The product obtained in this process is mixed with bitumen and a structuring agent (polyethylene wax, sulfur, etc.).

[0014] Said process is multi-stage and requires prior grinding of the starting material to particles of less than 1 mm, which is impracticable when recycling tires which contain metal cords and metallic parts. Also, the method of SU 1289872 does not provide for the production of boiler and motor fuel or carbon black as the resultant product is a rubber-bitumen composition containing carbon black and mineral components of the rubber (kaolin, talc, oxides of zinc and titanium, etc.), which restricts the usability of the resultant product.

[0015] RU 2,153,415 discloses a method for recycling scrap automobile tires and rubber-containing goods. In said method, the starting material is heat-treated with petroleum products at 260-290 °C until the rubber is fully dissolved. The resultant rubber-bitumen composition is poured off while the residue of carbon black, mineral components and metal cord remains in a specially perforated basket. The resultant rubber-bitumen composition is used as a material for damp-proofing and roofing work, and for the manufacture of bituminous concrete.

[0016] Disadvantages of said method are its low selectivity and its focus solely on the preparation of a rubber-bitumen mixture - which has limited use. Further problems arise from the difficulty of separating the heavy products which have formed from the carbon black and metal cord.

[0017] RU 2,109,770 discloses a method for processing rubber-containing wastes by processing the wastes at 270-420 °C and a pressure of 1-6 MPa in a hydrocarbon solvent and in the presence of rare-earth metals (REM). REM-based intermetallic compounds or titanium hydride are used in an amount of 0.5-10.0 wt.% of the reaction mixture. The method provides for thermal liquefaction with a 2:1-4:1 weight ratio of hydrocarbon solvent and wastes.

[0018] However, the method is characterized by a low hydrogen potential utilization coefficient of the components of the solvent, which demands repeated use thereof in the process, continuous separation of the initial material from the liquid products of thermal liquefaction and also maintenance of an elevated pressure in the reaction apparatus. A further disadvantage is the use of (liquid) synthetic rubber production wastes as the hydrocarbon solvent, as these are not always available in the required amount.

[0019] RF Patent No. 2110535 discloses a method for processing rubber-containing and also organic industrial and domestic wastes into chemical raw materials and motor fuel components, which is performed in a manner similar to that of RU 2109770 described above. In this method, one or more alkylbenzenes (toluene, xylenes, ethylbenzenes, diethyl-, dimethyl- and tetramethyl-benzenes) are employed as a hydrogen-donor solvent, these being the basis of "crude benzene" - the product of high-temperature coking of hard coals.

[0020] Significant disadvantages of the above method are the use of REM, intermetallic compounds based on neodymium, lanthanum, cerium and aluminum, and also hydrides of titanium and calcium, which are materials in fairly short supply. There is further the difficulty of subsequently recovering these metals from the mass of carbon black and high-tar heavy hydrocarbon residues. Also, there is the problem of high pressure in the reaction apparatus as a consequence of the low degree of utilization of hydrogen from the composition, and the impossibility of processing starting materials differing in chemical composition.

[0021] RF Patent No. 2167168 discloses a method for processing organic wastes involving thermal liquefaction of the wastes at a temperature above 270 °C and at elevated pressure of at least 6 MPa in alkylbenzene. Further steps involve separation of the liquid fraction and distillation thereof. After distillation, the liquid fraction with a boiling point above 210 °C is re-added to the reaction mixture for subsequent thermal cracking to produce kerosene and solar oil fractions.

[0022] A significant disadvantage of said method is its inefficiency in production of a high-octane gasoline fraction due to the removal of the liquid fraction with a boiling point of less than 200 °C from the reaction mixture. Since the most active chain extension initiators of radical reactions are contained in the up to 200 °C fraction, they are also removed from the reaction mixture, leading to a deceleration of the process as a whole and impeding the production of a high-octane gasoline fraction.

[0023] RF Patent No. 2272826 discloses a method for processing plastic and/or rubber-containing wastes through thermocatalytic liquefaction of the wastes at elevated temperature and pressure. The process is performed in the presence of a solvent, which is a mixture of hydrogen-donor hydrocarbons comprising alkylbenzenes and tetraline. The latter has a low induction period value, which allows the process to be performed at 200-320 °C. Metal containing phthalocyanines and dimethylglyoximates are used as the catalyst.

[0024] One disadvantage of said method is the use of catalytic systems based on various metals which are not readily available and have limited solubility in the solvent employed. Further problems arise from the liberation of hydrocyanic acid and dicyanogen during thermolysis of phthalocyanines, as these products need to be neutralized. In addition, regeneration of the catalyst is difficult and the production of tetraline, which is required in order to reduce the induction effect, is limited at the present time. Difficulties also arise in the separation of the carbon black from individual metals and compounds formed due to the neutralizers. Furthermore, a significant amount of the paraffinic-naphthenic oil fraction boiling in the temperature range 230-280 °C is required, which requires that an initial oil rectification section be created.

[0025] The problem solved by the present invention is therefore to provide a process that allows for a safe, simplified, ecologically clean comprehensive chemical processing of a variety of industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, in order to obtain high quality liquid petroleum products that can be utilized as motor fuel components and chemical raw materials.

[0026] Said object is achieved by the process according to claim 1, involving thermolysis, in particular thermocatalytic liquefaction, of a starting material containing industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes. The process of the present invention involves treating the starting material with a catalyst and an initiator comprising at least one metal hydride, optionally in the presence of a hydrogen donor, at elevated temperature and pressure, preferably at a temperature of 200-400 °C and a pressure of 3-7 MPa.

[0027] According to the present invention, the catalyst comprises one or more metal carboxylate salt(s), wherein the carboxylate anion A of each metal carboxylate salt is independently of one another selected from the group consisting of anions of saturated C1-C20 carboxylic acids, and the metallic cation M of each metal carboxylate salt is independently of one another selected from the group consisting of cations of titanium (Ti), aluminum (Al), germanium (Ge), zirconium (Zr), iron (Fe), cobalt (Co), nickel (Ni), chromium (Cr), molybdenum (Mo), manganese (Mn), lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), dysprosium (Dy). The general formula of the metal carboxylate salt is

$$[(M^{n+})(A^{-})_n],$$

with the number n being the degree of oxidation. For instance, if the catalyst comprises a metal carboxylate salt of which the metallic cation M is iron (II), the number of n is 2.

[0028] If the catalyst comprises more than one metal carboxylate salt (different from one another), each metal carboxylate salt preferably contains the same type of carboxylate anion A but a different metallic cation M.

[0029] The process of the present invention has the advantage that a wide variety of industrial and organic domestic wastes, in particular plastic and/or rubber-containing wastes, can be utilized as starting material. For instance, scrap tires, industrial rubber goods, polyethylene, polypropylene, polystyrene, polyisobutylene, polyester, (e.g. kapron, lavsan, enant), polyamide (e.g. nylon), polyvinylchloride, phenolformaldehyde (e.g. novolac resins) etc., can be processed according to the present invention for the preparation of liquid petroleum products. The latter can subsequently be rectified to give liquid product fractions with boiling points ranges of i) up to 200 °C, ii) 200-320 °C and iii) above 320 °C. These fractions can be used as high-octane components of motor fuel and as chemical starting materials for basic organic, biochemical and petrochemical synthesis.

[0030] It is to be noted that the term "starting material" as used in the present application encompasses both, materials containing only one single kind of organic waste as well as material mixtures containing two or more different kinds of organic materials, in particular rubber materials. Also, the term "waste" is to be understood as materials that are disposed goods, independent of their origin. Thus, "waste" as used in the present application encompasses not only trash materials but also new materials, which have been overproduced or are defective in any way.

[0031] An important benefit of the process of the present invention is the use of metal salts of saturated carboxylic acids as catalyst as they are readily soluble in the reaction mixture, forming a homogeneous solution, which provides high availability of the catalyst to the starting material. Thus, the process of the present invention has the advantage of a high uniformity of catalyst distribution in the reaction mixture.

[0032] Also, it has surprisingly been found that thermolysis of the catalyst results in the formation of nano-size free metal particles. These metal nano-particles exhibit high activity and selectivity in reactions of hydrogenation, dehydrogenation, hydrodealkylation, isomerization and cyclization in the course of the process of thermal liquefaction of the starting material. In particular, it is assumed that by means of the highly active nano-size free metal particles, atomic hydrogen is readily detached from the starting material and/or the hydrogen donor and the metal hydride and transferred to radical products, which are formed in the course of thermal decomposition of the starting material.

[0033] In addition, it has been found that carbon monoxide (CO) is liberated during the thermolysis of the catalyst used in the process of the present invention in accordance with the principle of the oxosynthesis reaction. Carbon monoxide is an efficient hydrogen carrier of hydrogen from the starting material and/or the hydrogen donor and the metal hydride to the radical products. As such, the process of the present invention allows for enhancement of the hydrogen donor potential of the reactants and, thanks to this more efficient utilization of hydrogen, it is possible to avoid the use of molecular hydrogen (H_2 gas) under high pressure.

[0034] Furthermore, the initiator comprising at least one metal hydride as used in the process of the present invention acts as a donor of atomic hydrogen and makes it possible to substantially reduce the induction period of the process of thermolysis of the starting material. This is because, during the process of the present invention, the initiator readily undergoes thermolysis, which results in liberation of atomic hydrogen. Thanks to this hydrogen liberation, the process induction effect and consequently the process temperature can be significantly reduced. Also, the liberated atomic hydrogen is available for recombination of radical products formed during thermolysis of the starting material. As such, the productivity of the reaction apparatus is improved and the economic parameters of the process as a whole can be enhanced.

[0035] Overall, the process of the present invention provides a simplified way for thermolysis of a plastic and/or rubber-containing starting material of complex chemical composition, while allowing for an increased process selectivity and productivity with simultaneous improvement in explosion and fire safety and ecological cleanness. Further benefits are elimination of dependence on the nature of the hydrogen donor and the composition of the starting material, as well as an increase in yield of liquid products in relation to their qualitative and quantitative composition. In particular, the process of the present invention allows for obtaining liquid petroleum products with a low content of oxygen-, nitrogen- and sulfur-containing unsaturated compounds.

[0036] In addition, as will be explained in more detail further below, the process of the present invention helps to resolve serious ecological problems caused by the need to recycle industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, allows to lower the prime cost of the products obtained, and to improve the economic parameters of the process as a whole.

[0037] As regards the catalyst, it is preferred that the carboxylate anion A of each metal carboxylate salt is independently of one another selected from the group consisting of anions of saturated C1-C10 carboxylic acids.

[0038] It is further preferred that the catalyst comprises a mixture of at least two metal carboxylate salts different from one another. In particular, the catalyst comprises at least two different metal carboxylate salts, which contain the same type of carboxylate anion A but a different metallic cation M.

[0039] In a further preferred embodiment, the catalyst comprises at least three different metal carboxylate salts, which preferably contain the same type of carboxylate anion A but metallic cations M1, M2 and M3. For instance, it is preferred that the catalyst comprises a first metal carboxylate salt $[(M1^{n+})(A^-)_n]$, a second metal carboxylate salt $[(M2^{n+})(A^-)_n]$ a third metal carboxylate salt $[(M3^{n+})(A^-)_n]$. A specific example would be a catalyst comprising a mixture of iron(II) or iron(III) formate, dysprosium(III) laurate and cerium(III) stearate.

[0040] Concerning the initiator used in the process of the present invention it is preferred that the initiator comprises at least one metal hydride comprising a metallic cation selected from cations of the group consisting of lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), francium (Fr), copper (Cu), silver (Ag), gold (Au), beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radium (Ra), zinc (Zn), cadmium (Cd), mercury (Hg), titanium (Ti), zirconium (Zr), hafnium (Hf), rutherfordium (Rf), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). More preferably, the at least one metal hydride comprising a metallic cation selected from cations of the group consisting of Li, Na, K, Cu, Ag, Mg, Ca, Sr, Zn, Ti, Zr, Si, Sn and Pb. It is also preferred to use a cation mixture comprising two or more cations of the metals listed above.

[0041] In a preferred embodiment, the at least one metal hydride comprises a metallic cation selected from cations of the group consisting of Ca, Na, K, Ba and Ti. Thermolysis of these hydrides in the process of the thermolysis reaction of the starting material results in the release of atomic hydrogen, which is then available for recombination with radical products formed during the reaction. In addition, the hydroxides, which are often formed as recombination products, can act then as neutralizers in the process of the present invention, as will be explained further below.

[0042] If the catalytic reaction according to the present invention is performed in the presence of water, the metallic cation is preferably a cation selected from cations of the group consisting of Zn, Cd, Hg, Ti, Zr, Hf, Si, Ge, Sn and Pb. These hydrides have the advantage that they are not negatively affected by the presence of water, whereby Ti, Zr and Hf are particularly preferred.

[0043] With regard to the hydrogen donor, this does not necessarily have to be an additional material added to the reaction mixture but the hydrogen donor may also be already present in the starting material. For instance, the starting material may comprise polycyclic arenes, which are efficient carriers of hydrogen to the radical products of thermolysis of hydrocarbons. If the nature of the starting material requires it, an additional hydrogen donor is added to the reaction mixture. As such, the process of the present invention avoids dependence on the chemical composition of the starting material.

[0044] Preferably, the hydrogen donor also acts as a solvent for the catalytic reaction. In a preferred embodiment, the hydrogen donor is derived from crude oil and preferably comprises crude paraffinic-naphthenic oil. Paraffinic-naphthenic oil, especially the 230-280 °C fraction thereof, is generally characterized by a high content of isoalkanes, cycloalkanes and low-molecular polycyclic arenes, which are efficient carriers of atomic hydrogen and are available in large quantities. In a particularly preferred embodiment, the hydrogen donor essentially consists of crude oil, in particular crude paraffinic-naphthenic oil. Thus, in contrast to methods of the state of the art, which often require a significant amount of a paraffinic-naphthenic oil fraction boiling in the temperature range of 230-280 °C, the process of the present invention allows for using crude oil as the hydrogen donor. Thus, there is no need for prior deasphaltation and rectification of a crude oil in order to obtain a 230-280 °C fraction thereof. This significantly simplifies the process technology as a whole.

[0045] In a preferred embodiment, the starting material and the hydrogen donor are used in a weight ratio of 1:2-1:5.

This weight ratio is particularly effective for the production of liquid petroleum products with a high octane number and minimum sulfur content.

[0046] With regard to the catalyst, the catalyst and the hydrogen donor are preferably used in a weight ratio of 1:50-1:200.

[0047] It is further preferred that the metal hydride and the hydrogen donor are used in a weight ratio of 1:50-1:200.

[0048] It is further preferred that the starting material is further treated with a neutralizer comprising at least one metal oxide or hydroxide, wherein the metallic cation is selected form the group consisting of cations of lithium (Li), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba). These oxides or hydroxides may also be formed as an intermediate product during thermolysis of the metal hydride used as an initiator. For instance, if hydrides of sodium, calcium, potassium, barium and/or titanium are used as an initiator in the process of the present invention, thermolysis of these hydrides themselves leads to the liberation of atomic hydrogen for recombination with radical products formed during thermolysis of the starting material, while the hydroxides formed in this recombination process can act as neutralizers. Thus, the neutralizer may be added to the starting material or it may also be formed in situ during the reaction process, in particular during thermolysis of the metal hydride. If a neutralizer is added, it is preferred that the neutralizer and the starting material are used in a weight ratio of 1:10-1:40.

[0049] The use of a neutralizer comprising at least one metal oxide or hydroxide as indicated above allows for neutralizing hydrogen sulfide and sulfur (IV) oxides that may be present in the starting material. Thus, the presence of the neutralizer further reduces limitations with respect to the chemical composition of the starting material being processed. Consequently, the process of the present invention is more generally applicable and not dependent on the chemical composition of the wastes. For instance, the process of the present invention, thus, permits simultaneous processing of starting materials differing in composition, particularly waste materials comprising a mixture of rubber and plastics (such as polyethylene, polypropylene, polystyrene, polyisobutylene, polyamide, polyester, polyvinylchloride, etc.), into liquid petroleum products.

[0050] The presence of the neutralizer makes it further possible to significantly reduce the corrosion loading on the metal of the reaction apparatus, which helps to increase the service life of the process equipment. In addition, the neutralizer is further used for binding gaseous compounds, which are liberated during thermolysis of the starting material (e.g. hydrogen sulfide, carbon disulfide, hydrogen cyanide and hydrogen chloride) into solid products. The binding of these gaseous compounds allows for reducing the pressure in the reaction apparatus and to produce a pyrolysis gas which is virtually free of these gaseous substances. As a result, the process of the present invention can avoid ecological problems associated with the need to purify the pyrolysis gas and makes it possible to improve the economic parameters of the process as a whole.

[0051] The solid products that result from the binding of gaseous compounds to the neutralizer can subsequently easily be separated from the desired liquid petroleum products, e.g. by magnetic separation, filtration, etc. The solid products are determined by the nature of the starting material and often contain metal cord, carbon black and other solid inclusions. The carbon black can be used as a filler for industrial rubber goods, and - after particular treatment - for the production of anode paste used in electrothermal and electrochemical plants.

[0052] The liquid products separated from the above-mentioned solid products can be rectified to give the target product fractions with boiling points ranges of i) up to 200 °C, ii) 200-320 °C and iii) above 320 °C. These fractions can be used as high-octane components of motor fuel and as chemical starting materials for basic organic, biochemical and petrochemical synthesis plants.

General Example:

[0053] A starting material containing a mixture of industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes (e.g. scrap tires, industrial rubber goods, polyethylene, polystyrene, polypropylene, polyisobutylene, synthetic rubber, polyvinylchloride, polyamide (e.g. nylon), kapron, enant, lavsan, etc.) is charged into a rotary autoclave (2-liter).

[0054] To the starting material (SM), the following components are added:

- a hydrogen donor (HD) in the form of paraffinic-naphthenic oil, in a SM:HD weight ratio of 1:2-1:5;
- an initiator (I) selected from the group of hydrides of sodium, potassium, calcium, barium and titanium in an I:HD weight ratio of 1:50-1:200;
- a catalyst (Cat) in the form of saturated C1-C20 carboxylic acid salts of metals from the group of aluminum, germanium, tin, manganese, titanium, iron, cobalt, nickel, chromium, molybdenum, lanthanum, cerium, neodymium, samarium and dysprosium in a Cat:HD weight ratio of 1:50-1:200; and

- a neutralizer (N) of oxides and hydroxides of alkali and alkaline earth metals in a N:SM weight ratio of 1:10-1:40.

[0055] The process of thermolysis, in particular thermocatalytic liquefaction, of the starting material is performed at a temperature of 200-320 °C and a pressure of 3-7 MPa (these values being determined by the nature of the starting material).

[0056] The catalyst comprises - and preferably consists of - at least one metal carboxylate salt. The general formula of the metal carboxylate salt is $[(M^{n+})(A^-)_n]$, whereby the number n is the degree of oxidation. For instance, if the catalyst comprises a metal carboxylate salt of which the metallic cation M is Ce(III) and the carboxylate anion A is laurate $[C_{12}H_{23}O_2]^-$, then the number of n is 3.

[0057] Without wanting to be bound by the theory, it is assumed that, at operating temperature, thermolysis of the catalyst and of the hydrocarbon chains of the starting material (and optionally the hydrogen donor) occurs first. This thermolysis reaction results in formation of nano-sized metal particles and carbon monoxide as products of catalyst thermolysis, as well as in formation of radical products of the starting material. If the catalyst is iron(II) formate, thermolysis reaction of the catalyst is as follows:

$$(HCOO)_2Fe \rightarrow Fe\ (\text{nano particles}) + CO + H_2O + CO_2$$

[0058] By means of the highly active nano-sized metal particles, atomic hydrogen is readily detached from polycyclic arenes (e.g. naphthenes and hydroaromatic components) of the starting material and/or the hydrogen donor - and transferred to radical products. Further atomic hydrogen is supplied by the metal hydride type initiator and hydrogen transfer to radical products is intensified by hydrogen carriers of the polycyclic arenes and carbon monoxide.

[0059] Overall, it is assumed that the uniformity of distribution of the catalyst in the reaction mass and the presence of nano-sized metal particles, carbon monoxide, hydrides of active metals and low-molecular polycyclic arenes in the reaction zone is responsible for the high waste thermal liquefaction process rate, the low temperature and pressure values, as well as the high degree of hydrogen utilization of hydrogen donor components and the gaseous phase.

[0060] The present invention therefore provides a process that allows for deep thermolysis of industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, to obtain liquid petroleum products with a low content of oxygen-, nitrogen- and sulfur-containing and also unsaturated compounds in high yield.

[0061] As also evidenced by the experimental data given in table 1 below, in particular, the yield of the up to 200 °C fraction of the liquid products, which is enriched in cycloalkanes, isoalkanes, hydroaromatic and aromatic hydrocarbons, can be particularly increased by the process of the present invention. In addition, said up to 200 °C fraction can be obtained with a low content of sulfur, preferably below 0.040 wt.% and a high octane number, preferably above 80.

Table 1

No.	Process Temp. [°C]	Process time [min.]	Weight ratio of SM:HD	Weight ratio of I:HD	Weight ratio of Cat:HD	Weight ratio of N:SM	**Yield* of LP**	**Yield* of up to 200 °C fraction of LP**	**Yield* of 200-320 °C fraction of LP**	**Sulfur content in up to 200 °C fraction of LP**	**Octane Number of up to 200 °C fraction of LP**
1	320	90	1:2.0	1:50	1:50	1:40	**68.3**	**61.5**	**21.0**	**0.040**	**67.2**
2	280	120	1:2.0	1:50	1:50	1:40	**78.9**	**69.5**	**15.5**	**0.040**	**68.3**
3	280	120	1:5.0	1:100	1:100	1:10	**80.9**	**68.5**	**16.5**	**0.030**	**84.2**
4	280	60	1:3.0	1:200	1:200	1:20	**83.5**	**72.5**	**17.5**	**0.020**	**66.8**
5	280	60	1:5.0	1:200	1:200	1:20	**88.3**	**76.2**	**12.2**	**0.025**	**81.4**
7	360	60	1:5.0	1:200	1:200	1:20	**92.0**	**82.5**	**9.5**	**0.025**	**70.2**
6	320	90	1:3.0	1:50	1:50	1:20	**90.2**	**84.2**	**7.8**	**0.025**	**77.2**
8	360	60	1:3.0	1:200	1:200	1:20	**96.0**	**86.0**	**9.0**	**0.015**	**79.3**
9	360	120	1:5.0	1:100	1:100	1:10	**97.5**	**88.5**	**7.5**	**0.010**	**87.5**

Abbreviations: SM = starting material; HD = hydrogen donor; I = process initiator; N = neutralizer; Cat = catalyst; LP = liquid products

[*] The yield of the liquid products is calculated in wt.% of the starting material.

Specific Example (No. 8 in the table)

[0062] 300 g of industrial rubber goods, 900 g of paraffinic-naphthenic oil, 4.5 g of calcium hydride, 4.5 g of cerium(III) formate, and 15 g of a neutralizer comprising calcium dihydroxide or sodium hydroxide, are charged into a rotary autoclave (2 liter). The process is performed at 360 °C and a pressure of 5 MPa for 60 min. The yield of liquid products is 96 wt.% of the organic substance of the wastes; the content of the up to 200 °C fraction is 86 wt.% of the liquid products; and that of the 200 to 320 °C fraction is 9 wt.%, while the content of sulfur in the up to 200 °C fraction is 0.015 wt.%.

Claims

1. A process for thermolysis of industrial and domestic organic wastes, in particular plastic and/or rubber-containing wastes, used as starting material by treating the starting material with a catalyst and an initiator, optionally in the presence of a hydrogen donor, at elevated temperature and pressure,
   the catalyst comprising one or more metal carboxylate salt(s),
   wherein the carboxylate anion A of each metal carboxylate salt is independently of one another selected from the group consisting of anions of saturated C1-C20 carboxylic acids,
   and the metallic cation M of each metal carboxylate salt is independently of one another selected from the group consisting of cations of aluminum, germanium, tin, titanium, chromium, molybdenum, manganese, iron, nickel, cobalt, lanthanum, cerium, neodymium, samarium and dysprosium,
   and the initiator comprising at least one metal hydride.

2. The process as claimed in claim 1, wherein the thermolysis is performed at a temperature of 200-400 °C, preferably 280-380 °C, and a pressure of 3-7 MPa.

3. The process as claimed in claim 1 or 2, wherein the catalyst comprises a mixture of at least two different metal carboxylate salts.

4. The process as claimed in one of the preceding claims, wherein the catalyst comprises a mixture of at least three different metal carboxylate salts.

5. The process as claimed in one of the preceding claims, wherein the at least one metal hydride comprises a metallic cation selected from the group consisting of lithium, sodium, potassium, copper, silver, magnesium, calcium, barium, zinc, titanium, zirconium, silicon, tin and lead.

6. The process as claimed in claim 5, wherein the at least one metal hydride comprises a metallic cation selected from the group consisting of cations of sodium, potassium, calcium, barium and titanium.

7. The process as claimed in one of the preceding claims, wherein the hydrogen donor is derived from crude oil and preferably comprises paraffinic-naphthenic oil.

8. The process as claimed in one of the preceding claims, wherein the hydrogen donor and the starting material are used in a weight ratio of 1:2-1:5, preferably 1:3-1:5.

9. The process as claimed in one of the preceding claims, wherein the catalyst and the hydrogen donor are used in a weight ratio of 1:50-1:200.

10. The process as claimed in one of the preceding claims, wherein the initiator and the hydrogen donor are used in a weight ratio of 1:50-1:200.

11. The process as claimed in one of the preceding claims, wherein the starting material is further treated with a neutralizer comprising a metal oxide or metal hydroxide, wherein the metallic cation is selected from the group consisting of cations of lithium, sodium, potassium, magnesium, calcium, strontium and barium.

12. The process as claimed in claim 11, wherein the neutralizer and the starting material are used in a weight ratio of 1:10-1:40, preferably 1:10-20.

13. The process as claimed in one of the preceding claims, wherein the octane number is increased, preferably over 80.

14. The process as claimed in one of the preceding claims, wherein the thermolysis is performed in the absence of H_2 gas.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 18 7755

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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TECHNICAL FIELDS SEARCHED (IPC)

C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	16 September 2015	Gzil, Piotr

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EPO FORM 1503 03.82 (P04C01)

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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