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DESCRIPTION

The invention concerns a pyrolysis process for the fractionated recovery of valuable substances and energy from free-flowing, cross-linked organic compounds of high molecular weight, in particular granules of used tires, sealing profiles and other plastic materials, in the sense of a feedstock recycling into gaseous, liquid and solid recyclates, as well as an apparatus for carrying out the process.

The feedstock recycling of wastes and residual materials is gaining increasing importance due to the increasing scarcity and the rising cost of raw materials, in particular fossil fuels, associated therewith. The development of new energy sources and processes, especially of renewable energies, is being given increasing attention and support. Currently experiencing increasing interest here is pyrolysis technology, which specially focuses on the utilization of renewable bio resources for example wood, agricultural waste, or also rapeseed, maize and other types of cereals.

According to the prior art, pyrolysis processes are classified in continuous and discontinuous processes. According to the configuration of the appliances and technologies, the classification is made into

- rotary kiln processes and other rotating appliances
- fluidized bed or fluid bed processes
- entrained-bed process
- shaft and vertical reactor process.

Furthermore, the classification of the so-far known pyrolysis processes is made into

- low temperature
- medium temperature (and)
- high temperature processes,

wherein the processes are furthermore differentiated depending on the operating pressures.

Despite the very rapid technical and technological development, a great demand for innovative further developments and links to already available basic processes and technologies continues to exist. The employment of appliances and equipment proven in

practice here is of steadily rising significance because synergy effects are to be expected here.

WO 00/64997 A1 discloses a process and an apparatus for converting plastic waste
5 material into combustible hydrocarbons, including a thermal separation at about 450°C and ambient pressure of the plastic waste material, as well as its liquefaction and subsequent conversion into gaseous hydrocarbons.

EP 1 052 279 A1 likewise describes an apparatus for converting plastic waste materials,
10 in which a gas component is separated from a liquid polymer phase.

Pyrolysis processes for used tires are known from US 4,740,270 A, US 4,648, 328 A and WO 00/55385 A1.

15 US 4,313,011 A describes a process for obtaining hydrocarbons from plants.

In DE 196 20 378 A1, a pyrolysis reactor, in particular for the conversion of waste fats, is described.

20 DE 197 07 306 A1 concerns a process for the obtaining of micro-waxes, paraffins and oils from waste plastics or waste plastic mixtures.

The object of the invention is to develop an energy self-sufficient, continuously operating multi-stage pyrolysis method and a corresponding apparatus for carrying out the
25 pyrolysis according to the preamble.

According to the invention, this object is achieved in that

- the organic compounds pass through a vertical, multi-stage pyrolysis reactor from the top to the bottom, wherein they are pyrolyzed by
30 process temperatures that can be set to different values in the temperature range from 300 to 1,200°C and different residence times, and in a separation region the pyrolysis vapor that is drawn off by means of negative pressure is conveyed into a multi-stage

condensation tower, wherein the condensation of the pyrolysis vapor phases into pyrolysis oils takes place in the respective condensation stages in mixed phases at various product-related temperatures and below the normal atmospheric pressure,

- 5
- the organic compounds pass through a pretreatment stage upstream of the pyrolysis reactor, wherein they are preheated with pyrolysis oils from the condensation stages, being depolymerized at the surface and therefore becoming tacky as a result, and are dusted with a powdered catalyst mixture so that the added mixed catalyst powder can stick thereto, said mixed catalyst powder having a targeted effect on the subsequent cracking process in terms of product formation,
- 10
- the energy-rich permanent gas generated during the process is converted in an electrical energy generating unit to electrical energy and thermal energy.

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While the organic compounds pass through the individual pyrolysis stages of the reactor, various pyrolysis reactions take place.

The products generated by this process concern oil mixtures with low, medium and high boiling points, a low-molecular-weight permanent gas and a pyrolysis coke which closely resembles petroleum coke in its physical and chemical properties.

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Due to the fact that the organic compounds pass through a pretreatment stage upstream of the pyrolysis reactor, wherein they are preheated with pyrolysis oils from the condensation stages, thereby being depolymerized at the surface and therefore becoming tacky as a result and are dusted with a powdered catalyst mixture, the added mixed catalyst powder can stick thereto, said mixed catalyst powder having a targeted effect on the subsequent cracking process in terms of product formation.

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The electrical and thermal energy generated here ensures the self-sufficient energy supply of the pyrolysis process.

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On the one hand, the catalyst mixture causes the releasing sulfur to be bound at the point of origin of the pyrolysis vapors and, on the other hand, the cracking process to be initiated in a targeted manner.

- 5 A preferred embodiment of the invention is that the thermal energy needed for the pyrolysis process is generated by electrical energy generated in the apparatus itself from an electrical energy generating unit, preferably by way of electrical heating elements, by microwave magnetrons or by the combustion of the permanent gas formed during the process.

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A classic thermal energy generation is likewise possible by combustion of the permanent gas resulting from the process, but is not sought primarily.

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The heating of the organic compounds occurring indirectly by way of the outer wall of the internal tube of the pyrolysis reactor has proven to be advantageous.

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In an apparatus for carrying out the process according to the invention, it is expedient that a vertical, multi-stage pyrolysis reactor is provided, through which organic compounds can pass from top to bottom, and in which different process temperatures from 300 to 1,200°C can be incrementally set, in that a separation region is provided, which comprises means for drawing off pyrolysis vapor by means of negative pressure and for conveying the pyrolysis vapor into a multi-stage condensation tower, in that a pretreatment stage having means for preheating the organic compounds with pyrolysis oils from the condensation stages and having means for dusting with a powdered catalyst mixture is arranged upstream of the pyrolysis reactor, and in that an electrical energy generating unit is provided for converting the energy-rich permanent gas generated during the process into electrical energy and thermal energy.

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A preferred embodiment of the invention is that the resulting pyrolysis vapor mixture is selected and, in a product-oriented manner, is condensed rapidly and in a targeted manner in a multi-stage injection condensation tower to avoid a renewed formation of long-chained hydrocarbon compounds.

It is within the scope of the invention that a vertical pressure vessel with a minimum nominal pressure of PN 16 is used as the pyrolysis reactor, the shape of which vessel can preferably be designed cylindrical, but alternatively also oval or in a cuboid shape and consists of multiple pyrolysis zones arranged one above the other.

5

In this context, it is advantageous that means for the indirect electrical heating of the internal tube of the pyrolysis reactor are provided and that a slot system is provided on the cylindrical surface of the internal installations to suck away the resulting pyrolysis vapors by means of negative pressure.

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Likewise within the scope of the invention is that concentrically arranged internal installations are located in the interior of the pyrolysis reactor, which installations on the one hand guide the granule flow and on the other hand make the discharge of the pyrolysis vapors out of the reactor possible.

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It has proven to be advantageous that the outer shell of the reactor is formed from H II boiler plate or other materials, the internal shell and the installations as well as the vapor-venting tube are fabricated from a heat-resistant material like e.g. 1.4828, AVESTA 253, 353 MA, Nicrofer 45 TV or similar materials, so that operating temperatures of up to

20 1,200°C can be reached.

Furthermore within the scope of the invention is that the granule ingress and egress occurs by way of a clocked lock system which has automatically controllable and regulatable inerting devices and that the throughput, in the pyrolysis reactor, is regulated

25 by way of the freely selectable clock frequency of the lock system.

It is furthermore within the scope of the invention that each pyrolysis module is assigned an injection condensation unit, which consists of at least two, preferably three to four, individual stages (8, 9, 10), which are spatially connected to each other and can

30 preferably be arranged one on top of one another, but can also be arranged next to each other and in which the pyrolysis vapor mixtures are selected and condensed.

It has proven to be advantageous that an external heat exchanger, a circulation / injection pump, a vacuum generator, as well as tubing lines with corresponding fittings are assigned to each condensation stage.

- 5 It is within the scope of the invention that the condensation stages are preferably designed circularly and concentrically arranged spiral injection nozzles, or selectively tangential nozzles, guide tubes and demisters, are located in the interior.

Designing the first condensation stage from two aggregates, a horizontal lower container
10 and a condenser having a fluid jet vacuum pump and a guide tube integrated into the interior standing vertically on said container has proven to be particularly advantageous.

It is likewise within the scope of the invention that each pyrolysis module consisting of pretreatment, pyrolysis, condensation, fatty-substance treatment, oil and gas treatment
15 stage, is assigned an energy generating unit.

For example, this energy generating unit consists of a gas engine with a coupled alternating current generator, a heat recovery apparatus, as well as diverse regulating and control devices which make the self-sufficient energy supply of the pyrolysis module
20 possible.

Also in the scope of the invention is that exhaust gases forming from the combustion of the permanent gas in gas engine pass through an exhaust gas purification stage, consisting of a soot and fine particulate matter particle filter, catalyst and muffler, so that said gases
25 definitely comply with the presently required EU emissions norms.

It is also within the scope of the invention that the continuously operating pyrolysis process functions in a waste-free manner, and all resulting products are recyclable materials and not waste.

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In summary, a self-sufficient, multi-stage, continuously operating medium temperature pyrolysis process and an apparatus of modular construction are created in the scope of the invention, which make it possible, in the sense of a feedstock recycling, to recover

gaseous, liquid or solid recyclates for the rubber, plastics or petroleum industry from pourable, cross-linked organic compounds of high molecular weights, in particular granules of used tires, sealing profiles and other plastic materials.

- 5 An exemplary embodiment of the invention is subsequently described by means of illustrations and tables.

Shown are in:

- 10 Fig. 1 a block circuit diagram

- As is apparent from Fig. 1, the organic compounds, which are granules of rubber or plastic material in the illustrated example, pass through a storing device 1, a metering device 2 and a pretreatment stage 3 in the apparatus according to the invention. The
- 15 granulate ingress and egress preferably occurs by way of a clocked rotary valve which has automatically controllable and regulatable inerting devices, wherein the flow rate and the residence time in the pyrolysis reactor is regulated by way of the clock frequency or by way of a speed regulation of the lock system.
- 20 In the pretreatment stage 3, the granulates are preheated with pyrolysis oil from the condensation stages of the plant, thereby depolymerized at the granule surface and therefore becoming tacky as a result, so that a mixed catalyst powder added in the pretreatment stage 3 can stick to the granule surface.
- 25 The granules subsequently pass through a vertical, multi-stage pyrolysis reactor 4 gravimetrically from the top to the bottom, wherein they can be heated to individually regulatable process temperatures from 300 to 1,200°C, preferably by way of electrical heating elements or also by microwave magnetrons, in the different pyrolysis zones arranged one above the other. It is possible to control the pyrolysis product division, that
- 30 is the resulting percentages by mass of coke, oil and permanent gas, within defined limits, by way of a temperature and negative pressure regulation.

Since explosive gas mixtures form in the pyrolysis, the pyrolysis reactor is preferably designed as a pressure vessel in a nominal pressure stage PN 16, wherein other nominal pressure stages can also result from the product of nominal pressure x volume content.

- 5 The granules form a uniform packed bed in the upper part of the pyrolysis reactor 4, which bed is intensively mixed, however, in the gravimetric passage through internal installations in the reactor stages, so that a nearly uniform temperature profile forms in the fixed bed. The internal installations are further configured such that slot systems are located on their cylindrical surface, which systems on the one hand make the suctioning-
10 off of the resulting pyrolysis vapors possible by means of vacuum pumps and, on the other hand, prevent the intrusion of granules or of abraded material into the vapor ventilation line.

- The solid, carbon and filler material rich pyrolysis coke produced in the pyrolysis reactor
15 4 is continuously drawn off in the lower part, in the separation region 5 (separation of pyrolysis solid materials from pyrolysis vapor), by way of an inerteable locking system. The pyrolysis coke, in the present form, as an absorbent with a BET surface of 80-120m²/g, is preferably drawn off towards the pyrolysis coke storage 7 by way of a cooling apparatus 6. Alternative uses are employment as blast furnace coke in the steel industry
20 or use as filler material for tire production or sealing and insulation material production.

- The pyrolysis vapor drawn off by means of negative pressure in the separation region 5 (11) is conveyed into the multi-stage condensation tower 8,9,10. The condensation of the pyrolysis vapor phases takes place in the respective condensation stages in mixed phases
25 at various product-related temperatures and below the normal atmospheric pressure.

- In the first condensation stage 8, the condensation of the heavy oil fractions takes place by way of the injection of a part of the return flow of the second stage 9 in the countercurrent process.

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The condensation stages 9 and 10 operate according to the same principle of return-flow injection by means of high-pressure spiral nozzles. A selective and product-oriented breakdown of the pyrolysis oils takes place analogously to a rectification plant by way

of the catalyst mixture, the selected operating temperatures and pressures, the reflux ratio as well as the residence times in the condensation tower. In the head section of the condensation stage 10, heat exchange surfaces are installed, which effect a precondensation of the remaining pyrolysis vapor. The separation of the permanent gases from the light oil takes place in the separation device 11 connected thereto. For safety reasons, a downstream cooling device 12 ensures the keeping of a maximum permanent gas temperature of 40°C. An intermediate storing of the gas in a container 13 takes place in order to be able to compensate for volume and heating value fluctuations of the permanent gas owing to the technology. The pyrolysis oil fractions from the first condensation stage 8 are transferred into a storage 16 by way of a cooling means 15, those fractions from the second condensation stage 9 into a storage 18 by way of a cooling means 17, and those fractions from the third condensation stage 10 into a storage 20 by way of a cooling means 19.

The further utilization of the permanent gas occurs in a combined heating and power unit 14. The energy supply required for the pyrolysis process that takes place endothermically preferably results by way of a combined heat and power unit 14 configured as a commercially available gas engine / alternating current generator for reasons of cost, wherein the utilization of a gas engine would be possible in principle if a construction size fitting the requirements is available.

Furthermore, a process control system 21 to control the apparatus and the process, as well as an operating and support materials supply 22 is provided.

With the apparatus according to the invention can be created (with the respective amounts of the total resulting pyrolysis products and the lower heating value) the following pyrolysis products can be obtained

pyrolysis coke	30 52	wt. %	H _u	23 30,000 kJ / kg
pyrolysis oils	30 50	wt. %	H _u	3646,000 kJ / kg
pyrolysis gas	8 30	wt. %	H _u	3845,800 kJ / Nm ³

e.g. from free-flowing granules of old tires, the typical composition of which is as follows:

	natural rubber	14 42	wt. %
5	synthetic rubber	18 26	wt. %
	reclaimed rubber	 5	wt. %
	filler materials (soot + silicon compound)	28 44	wt. %
	plasticizer		
		3 4	wt. %
10	cross-linking agent		
		 1.5	wt. %
	dispersant agent	 1.2	wt. %
	anti-aging agent	 1.2	wt. %
	light protection waxes	 1	wt. %
15	vulcanization accelerators	 1	wt. %
	other materials	 3	wt. %

In a pilot plant, the following composition of pyrolysis products was determined:

pyrolysis coke	ca.	38	wt. %
pyrolysis oils	ca.	50	wt. %
pyrolysis gas	ca.	12	wt. %

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wherein the pyrolysis gas (permanent gas) had the following composition:

methane	ca.	30	vol. %
hydrogen	ca.	16	vol. %
butadiene 1, 3	ca.	8	vol. %
ethene	ca.	6	vol. %
ethane	ca.	5	vol. %
carbon dioxide	ca.	4.6	vol. %
carbon monoxide	ca.	3	vol. %
butane	ca.	2.5	vol. %

propane	ca.	2	vol. %
propene	ca.	2	vol. %
hydrogen sulfide	ca.	0.4	vol. %

fraction of other remaining compound:

lower heating value H_u ca. 44,800 kJ /Nm³

The raw pyrolysis oil had the following composition:

	benzene		10	wt. %
5	xylene		8	wt. %
	toluene	0.5	5	wt. %
	styrene	1	5	wt. %
	C ₅ compounds	1	5	wt. %
	ethylbenzene	0.5	4	wt. %
10	naphthalene	0.5	5	wt. %
	indane / indene	0.5	3	wt. %

The apparatus according to the invention is of modular construction, so that it can easily be adapted to the capacitive requirements and expanded, without production losses arising.

PATENTKRAV

1. Pyrolysefremgangsmåde til fraktioneret genudvinding af værdifulde substanser og energi fra fritstrømmende, tværbundne organiske forbindelser med høj molekylvægt, især granulat af brugte dæk, forseglingsprofiler og andet plastmateriale, med henblik på en råstofmæssig genanvendelse i gasformig, flydende og fast recyclet, **kendetegnet ved, at**

- de organiske forbindelser passerer igennem en vertikal, flertrinspyrolysereaktor (4) fra toppen til bunden, hvor disse pyroliseres ved procestemperaturer, som kan indstilles til forskellige værdier i temperaturområdet fra 300 til 1200°C og forskellige opholdstider, og i et separationsområde (5) føres pyrolysedampene, som udtrækkes ved hjælp af negativ tryk, til et flertrinskondensationstårn (8, 9, 10), hvori kondenseringen af pyrolysedampfaserne til pyrolyseolier finder sted i de respektive kondensationstrin (8, 9, 10) i blandede faser ved forskellige, produktrelaterede temperaturer og under det normale atmosfæriske tryk,
- de organiske forbindelser passerer igennem et forbehandlingstrin (3) opstrøms for pyrolysereaktoren (4), hvori de forvarmes med pyrolyseolier fra kondensationstrinnene (8, 9, 10), depolymeriseres ved overfladen og derfor bliver klæbrige som et resultat, og pudres med en pulverformet katalysatorblanding, således at det tilførte blandede katalysatorpulver kan hæfte dertil, idet det blandede katalysatorpulver har en målrettet virkning på den efterfølgende crackingproces med henblik på produktdannelse,
- den energirige permanente gas, som genereres under processen, konverteres i en elektrisk energigenereringsenhed (14) til elektrisk energi og til termisk energi.

2. Pyrolysefremgangsmåde ifølge krav 1, **kendetegnet ved, at** den termiske energi, som kræves for pyrolyseprocessen, genereres ved af elektrisk energi genereret i selve apparaturet fra en elektrisk energigenererende enhed (14), fortrinsvis ved hjælp af elektriske varmeelementer, ved hjælp af mikrobølgemagnetroner eller ved forbrænding af den permanente gas dannet under processen.

3. Apparat til udøvelse af fremgangsmåden ifølge krav 1 eller krav 2, **kendetegnet ved, at** en vertikal, flertrinspyrolysereaktor (4) er tilvejebragt, igennem hvilken organiske forbindelser kan føres fra toppen til bunden, og i hvilken forskellige procestemperaturer fra 300 til 1200°C kan indstilles inkrementalt, at et separationsområde (5) er tilvejebragt,

som omfatter organer til at ekstrahere pyrolysedampe ved hjælp af undertryk og til at fremføre pyrolysedampene til et flertrinskondensationstårn (8, 9, 10), at et forbehandlingstrin (3) med organer til forvarmning af de organiske forbindelser med pyrolyseolier fra kondensationstrinnene (8, 9, 10) og med organer til at pudre med en pulverformet katalyseblanding er anbragt opstrøms for pyrolysereaktoren (4), og at en elektrisk energigenererende enhed (14) er tilvejebragt til at konvertere den energirige permanente gas, som genereres under processen, til elektrisk energi og termisk energi.

4. Apparatur ifølge krav 3, **kendetegnet ved, at** organer til den indirekte opvarmning af det indvendige rør i pyrolysereaktoren (4) er tilvejebragt, og at, for at bortsuge de resulterende pyrolysedampe ved hjælp af undertryk, er et slidssystem tilvejebragt på den cylindriske overflade af de indvendige installationer.

5. Apparatur ifølge krav 3, **kendetegnet ved, at** et første kondensationstrin (8) består af to enheder, en horisontal nedre beholder og en vertikal kondensator, som står derpå, som har en væskestrålevakuumindretning integreret i det indre og et føringsrør.

6. Apparatur ifølge krav 3, **kendetegnet ved, at** hvert pyrolysemodul er knyttet til en injektionskondensationsenhed, som består af i det mindste to, fortrinsvis tre til fire, individuelle trin (8, 9, 10), som er rumligt forbundet med hinanden og som fortrinsvis kan være anbragt ovenpå hinanden, men også kan være anbragt ved siden af hinanden, og i hvilke pyrolysedampblandingerne udvælges og kondenseres.

