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(54) **PROCESS AND DEVICE FOR GASIFICATION OF CRUDE GLYCEROL**

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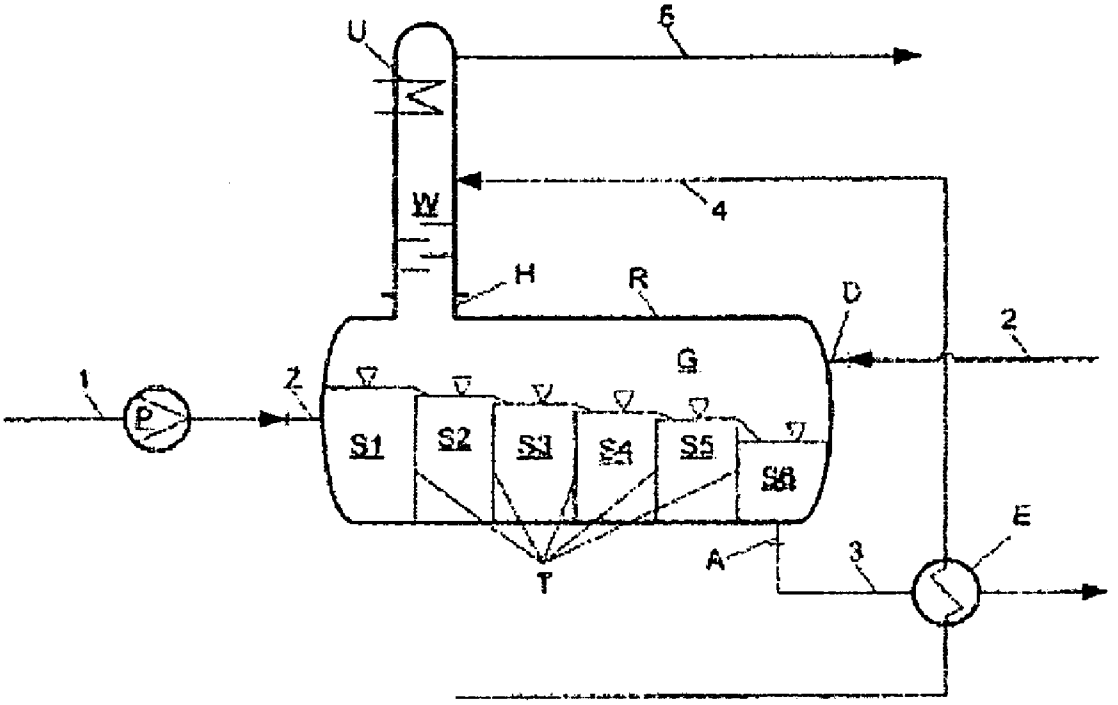
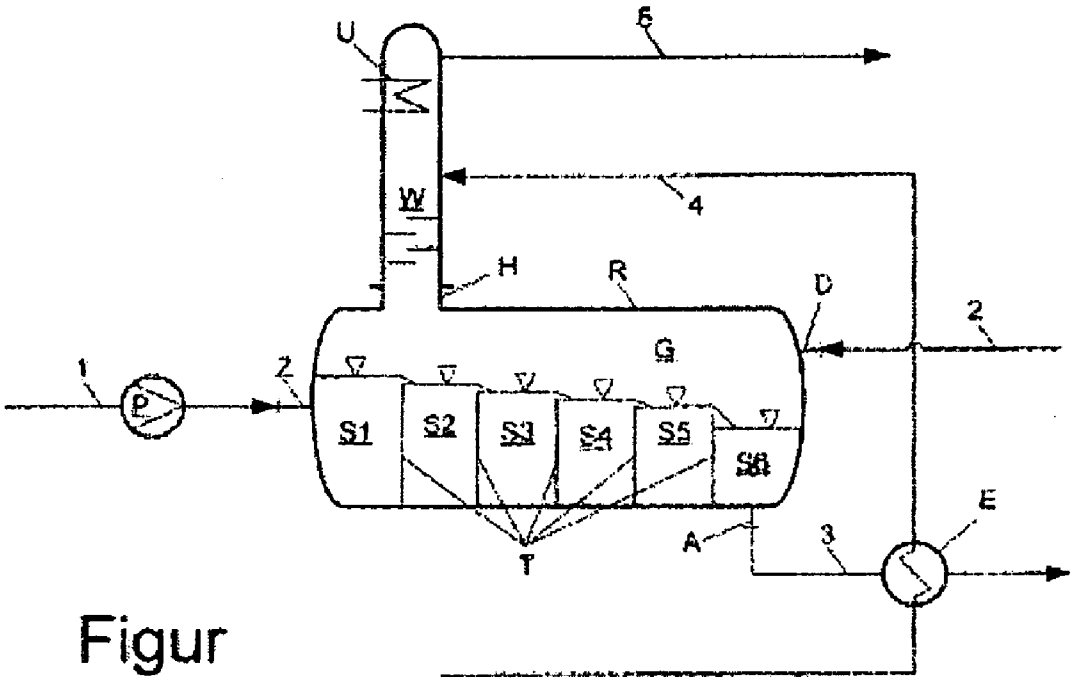
(57) **ABSTRACT**

The invention relates to a process as well as a device for continuous thermal decomposition (pyrolysis) of a mixture of substances (crude glycerol) (**1**) that contains glycerol, salts and water, whereby the crude glycerol (**1**) is heated in a reactor (pyrolysis reactor) (R) to a temperature (pyrolysis temperature) of more than 100° C. The pyrolysis of the crude glycerol (**1**) is performed at a pressure (pyrolysis pressure) that is higher than the vapor pressure of the water, present in the pyrolysis reactor (R), at pyrolysis temperature, and salts and other higher-boiling substances together with water are drawn off continuously from the pyrolysis reactor (R) as waste water (**3**).





Figur

PROCESS AND DEVICE FOR GASIFICATION OF CRUDE GLYCEROL

[0001] The invention relates to a process for continuous thermal decomposition (pyrolysis) of a mixture of substances (crude glycerol) that contains glycerol, salts and water, whereby the crude glycerol is heated in a reactor (pyrolysis reactor) to a temperature (pyrolysis temperature) of more than 100° C., as well as a device for performing the process.

[0002] In an attempt to reduce the input of carbon dioxide into the Earth's atmosphere or at least not allow it to increase further, and as alternatives to the shrinking crude oil and natural gas reserves, energy sources from renewable raw materials will be increasingly produced in the future. According to an EU guideline, at least 5.75% of the fuel requirement is to be covered by such energy sources in the European Union by 2010. In this connection, biodiesel, which is already now added at a concentration of up to five percent to diesel fuel available to German gas stations, plays a tremendous role.

[0003] Biodiesel is a standardized fuel that is obtained primarily from rapeseed oil, but also from other vegetable oils and fats. Vegetable oils and fats consist of triglycerides, i.e., compounds in which three fatty acids are bonded to glycerol. As a result of this chemical structure, vegetable oils and fats are viscous to solid at normal ambient temperatures, i.e., they have a much higher viscosity than the fuels for which a current diesel engine is designed. Thus, vegetable oils and fats behave differently in the injection process, and also the combustion of vegetable oils and fats runs less cleanly. These drawbacks can be compensated only incompletely by powered interventions - such as, for example, the preheating of the vegetable oil.

[0004] Biodiesel is produced from vegetable oils and fats by replacement of glycerol with methanol. The viscosity of biodiesel corresponds to the commercially available diesel fuel, and thus it can easily be burned even in non-modified diesel engines.

[0005] The glycerol that is separated from vegetable oils and fats during biodiesel production is not obtained in pure form, but instead the glycerol accumulates as part of a mixture of substances which, in addition to glycerol, contains larger amounts of contaminants. Such a mixture of substances, for example, so-called crude glycerol, has a glycerol content of 80-85%, but, moreover, also contains water and salts in still larger amounts as well as residual substances from the production process. According to prior art processes, crude glycerol is purified in expensive process steps by vacuum distillation, deodorization, and filtration to the extent that the purified glycerol satisfies the strict requirements of the European Pharmacopeion and can be purchased with a purity of at least 99.5% as a pharmaglycerol in the pharmaceutical industry. At present, the entire amount of glycerol accumulating in biodiesel production can be used in this way. However, with the foreseeable expansion of biodiesel production, this will become increasingly difficult in the future, such that still other methods of use of the crude glycerol must be sought.

[0006] In several patent applications filed with the German Patent and Trademark Office (1020060178888.2, 102006020985.0, 102006051262.6, 102006056641.6), the disclosures of which are hereby incorporated by reference in the entirety, alternative processes for using crude glycerol are proposed, in which the crude glycerol is reacted by thermal decomposition (pyrolysis) to form a gaseous pyrolysis product (pyrolysis gas). While in one of these patent applications (102006056641.6), the glycerol is separated from the crude glycerol before pyrolysis, for example by vacuum distillation, the other patent applications describe processes in which the crude glycerol is fed to a pyrolysis without preliminary treatment.

[0007] To decompose glycerol thermally, the glycerol is fed to a reactor (pyrolysis reactor) according to the prior art and heated to temperatures of more than 100° C., optionally in the presence of acids or Lewis acids. Under these conditions, pure glycerol, for examples glycerol separated from crude glycerol, is reacted without residue in pyrolysis gas. Water contained in the pyrolysis reactor is evaporated and conveyed together with the pyrolysis gas discharged from the pyrolysis reactor. However, if untreated crude glycerol is reacted in this way, higher-boiling substances, in particular salts, remain as residues in the pyrolysis reactor.

[0008] So as not to impair the functionality of the pyrolysis reactor (e.g., by forming deposits), the residues must be removed. For this purpose, either the pyrolysis reactor is shut down and purified at intervals, or the higher-boiling substances are drawn off continuously from the pyrolysis reactor during the pyrolysis process together with a portion of the glycerol. Separation of the glycerol from the crude glycerol, purification of the pyrolysis reactor itself, and the associated unit shut-down as well as loss of glycerol in a continuous removal of the residues produce high costs and considerably impair the economic efficiency of the described types of crude glycerol use.

[0009] Therefore, an aspect of this invention is to provide a process of the type described above, as well as an apparatus for performing the process, by which the problems and/or disadvantages of the prior art in the pyrolysis of crude glycerol are overcome.

[0010] In the process according to the invention, pyrolysis of the crude glycerol is performed at a pressure (pyrolysis pressure) that is higher than the vapor pressure of the water present in the pyrolysis reactor at the pyrolysis temperature, and salts and other higher-boiling substances together with water are drawn off continuously from the pyrolysis reactor as waste water.

[0011] Higher-boiling substances are defined as those substances that do not pass into the gaseous state under the conditions prevailing in pyrolysis, but rather accumulate as residues. Higher-boiling substances, such as salts, can already be contained in the crude glycerol fed to the pyrolysis reactor, or are formed only during pyrolysis.

[0012] The idea on which the invention is based is to produce residues that accumulate during the pyrolysis of crude glycerol in a flowable and sufficiently viscous form. By providing the residues in such a form, the residues can be continuously drawn off or removed from the pyrolysis reactor—even during the pyrolysis process and without shutting down the unit—and without loss of valuable glycerol from the pyrolysis reactor. In accordance with the invention, this is achieved by performing pyrolysis at a pressure that is higher than the vapor pressure of the water, contained in the pyrolysis reactor, at pyrolysis temperature. The liquid water thus also represents a residue, in which other residues are present in dissolved form (e.g., salts) or suspended form (e.g., carbon black).

[0013] In performing the process according to the invention, at least a portion of the water present in the pyrolysis reactor unavoidably changes into the gas phase and is drawn off from the pyrolysis reactor with the pyrolysis gas. To avoid the accumulation of the residues formed during the pyrolysis as a result of this water loss—with a viscosity by which their continuous removal from the pyrolysis reactor is prevented, an embodiment of the process according to the invention

provides for the addition of water to ensures that the water content of the crude glycerol is raised to a value that is high enough to produce residues from pyrolysis in a sufficiently viscous form.

[0014] The pyrolysis temperature, together with the dwell time, is decisive for the achievable crude glycerol conversion: the higher the temperature, the greater the conversion. Pyrolysis temperatures of more than 290° C. have proven suitable. Since water cannot be heated higher than up to 373° C., it is proposed to perform processes according to the invention at pyrolysis temperatures of between 290 and 370° C., preferably between 290 and 340° C., and especially preferably between 290 and 310° C.

[0015] To be able to perform the pyrolysis of pure glycerol more effectively, acids and/or Lewis acids (subsequently referred to only as acids) are fed to the pyrolysis reactor according to the prior art, so that the pyrolysis of glycerol is carried out in direct contact with these acids. The acids, which are liquids or solids (e.g., Al_2O_3), act as catalysts in this connection and are not consumed. Since it is to be expected that acids also have an effectiveness-increasing effect on pyrolysis of crude glycerol, it is proposed according to the invention that acids be fed to the pyrolysis reactor so that the pyrolysis of the crude glycerol is also carried out in direct contact with these acids. The acids, in particular liquid acids, are drawn off from the pyrolysis reactor with the waste water and, therefore, must be continuously replaced by fresh acids. To keep operating costs low and to avoid problems in disposal of waste water, the acids are separated from the waste water in a suitable way and fed again (recycled) to the pyrolysis reactor.

[0016] One purpose of using crude glycerol as a feed to a pyrolysis reactor is to cleave the glycerol—contained in the crude glycerol—completely into hydrogen and carbon monoxide and produce a pyrolysis gas that can be used in the chemical industry as synthesis gas for the production of a number of products. Because of the relatively low pyrolysis temperatures, in which the process according to the invention is performed, the pyrolysis gas produced contains, in addition to hydrogen and carbon monoxide, long-chain hydrocarbons. However, these long-chain hydrocarbons must be cleaved in additional process steps. A further development of the process according to the invention, therefore, is to superheated the pyrolysis gas produced in the pyrolysis reactor, i.e., heated to a temperature that is higher than the pyrolysis temperature in order to cleave long-chain hydrocarbons contained in the pyrolysis gas into hydrogen and carbon monoxide.

[0017] To remove entrained particles, for example, carbon black, from the pyrolysis gas before further treatment, in particular before superheating, according to another embodiment of the process according to the invention the pyrolysis gas is subjected to a gas scrubbing, which is suitably a water scrubber. The charged washing water is preferably introduced into the pyrolysis reactor, from which it is drawn off again with the waste water.

[0018] In accordance with another aspect of the process according to the invention, energy required for pyrolysis is introduced indirectly into the pyrolysis reactor via heating surfaces. As experience has shown, there is a risk of the heating surfaces carbonizing in this type of energy introduction. To eliminate this risk or to at least reduce it, according to another aspect of the process according to the invention the energy required for pyrolysis is introduced with high-pressure vapor into the pyrolysis reactor and is transferred to the mixture of substances (crude glycerol mixture) that is to be decomposed thermally by direct contact. Process variants ensure that the high-pressure vapor is introduced into the gas chamber of the pyrolysis reactor, i.e., into the pyrolysis gas, and/or into the mixture of substances (crude glycerol mixture) that is to be decomposed thermally.

[0019] The invention also relates to an apparatus for thermal decomposition (pyrolysis) of a mixture of substances (crude glycerol) that contains glycerol, salts and water, the apparatus comprising a reactor (pyrolysis reactor) with a feed device (crude glycerol feed) for the feeding of crude glycerol, and a discharge device (gas discharge) for discharging a gaseous pyrolysis product (pyrolysis gas), wherein the crude glycerol can be heated to a temperature (pyrolysis temperature) of more than 100° C. in the reactor.

[0020] According to an aspect of the invention, the pyrolysis reactor is designed as a pressure vessel, in which the crude glycerol is gasifiable at a pressure (pyrolysis pressure) that is higher than the vapor pressure of the water, present in the pyrolysis reactor, at pyrolysis temperature, and in that it has a second discharge device (waste water discharge), via which salts and other higher-boiling substances together with water can be drawn off continuously from the pyrolysis reactor as waste water.

[0021] The device according to the invention is designed so that the crude glycerol can be run through the pyrolysis reactor at a dwell time that is long enough to react the entire amount of glycerol fed with the crude glycerol and convert it into pyrolysis gas.

[0022] In a suitable way, the pyrolysis reactor is equipped with suitable built-in components, between the crude glycerol feed and the waste water discharge, that ensure a sufficiently narrow dwell-time distribution and thus prevent a premature glycerol removal with the waste water.

[0023] To cleave long-chain components of the pyrolysis gas and for conversion into hydrogen and carbon monoxide, an embodiment of the apparatus according to the invention provides a means for superheating pyrolysis gas (superheater), into which pyrolysis gas formed in the pyrolysis reactor can be introduced, and in which the pyrolysis gas can be heated to a temperature higher than the pyrolysis temperature.

[0024] A variant of the apparatus according to the invention provides heating surfaces, arranged inside and/or outside of the pyrolysis reactor, via which energy required for pyrolysis can be introduced by indirect heating into the pyrolysis reactor and can be transferred to the mixture of substances (crude glycerol mixture) to be decomposed thermally. Another variant of the apparatus according to the invention is equipped with at least one feed device for high-pressure vapor, via which energy required for pyrolysis can be introduced via high-pressure vapor into the pyrolysis reactor and can be transferred directly to the mixture of substances (crude glycerol mixture) to be decomposed thermally. In a suitable way, the feed device for high-pressure vapor is designed as pipe connections or lances, via which the high-pressure vapor can be introduced directly into the mixture of substances (crude glycerol mixture) to be decomposed, or into the gas chamber of the pyrolysis reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] The invention and further details, such as features and attendant advantages, of the invention are explained in more detail below on the basis of exemplary embodiments which are diagrammatically depicted in the drawing, and wherein:

[0026] FIG. **1** shows an embodiment of the device according to the invention.

DETAILED DESCRIPTION OF THE DRAWINGS

[0027] In the embodiment of FIG. **1**, a pyrolysis gas is produced by pyrolysis of crude glycerol in a pyrolysis reactor designed as a horizontal pipe. The pyrolysis gas is subsequently subjected to water scrubbing and superheating to form a hydrogen- and carbon monoxide-rich gas.

[0028] The pump P suctions off crude glycerol **1** and conveys it with pyrolysis pressure into the pyrolysis reactor R via the crude glycerol feed Z. The pyrolysis reactor R is designed essentially as a horizontal pipe and is embodied with the compressive strength and temperature stability necessary for the process. The interior chamber of the pyrolysis reactor R has built-in components T that, in this respect, ensure that the crude glycerol remains in the pyrolysis reactor R with a uniform dwell time that is long enough to completely thermally decompose the glycerol present in the crude glycerol. Via line **2** and the pipe sockets D, high-pressure vapor is introduced into the gas chamber G of the pyrolysis reactor R. The high-pressure condenses on the surfaces of the mixture of substances, i.e., S**1**-S**6** (the mixture primarily being made up of crude glycerol), and releases a majority of the energy stored therein to the mixture of substances S**1**-S**6**, thereby heating the latter to a pyrolysis temperature of about 300° C. At this temperature, the glycerol molecules contained in the crude glycerol **1** decompose, and a pyrolysis gas is formed that is further conveyed via the gas discharge H into the gas scrubbing unit W (e.g., a water scrubber). The pyrolysis pressure that prevails in the pyrolysis reactor R prevents evaporation of the water portion in the mixture of substances S**1**-S**6**. With progressive pyrolysis, the glycerol content in the mixture of substances S**1**-S**6** is reduced, and salts and other higher-boiling substances accumulate in the water. The free-flowing mixture of substances S**6**, which accomplishes the removal of waste water A, is ultimately free of glycerol to a large extent and is drawn off via line **3** from the pyrolysis reactor R.

[0029] Undesirable solids (e.g., carbon black) are also extracted from the pyrolysis reactor R with the pyrolysis gas. To separate these solids, the pyrolysis gas in the gas scrubbing unit W is subjected to gas scrubbing with water **4**, which is heated in the heat exchanger E from the hot waste water **3**. The washing water that is charged in the gas scrubbing unit W flows downward into the mixture of substances S**1**-S**6** that is to be decomposed, and is drawn off with the waste water **3** from the pyrolysis reactor R. In connection to the gas scrubbing unit W, the purified pyrolysis gas is introduced into the superheater U and is further heated there to the starting temperature of a reformer (not shown) that is arranged downstream. Long-chain components that are present in the pyrolysis gas decompose at this temperature and are converted into hydrogen (H_2) and carbon monoxide (CO). The gas produced in superheater U, which in addition to H_2 and CO primarily contains water and carbon dioxide, is drawn off via line **5** and fed to, for example, a separating device (not shown) to produce an H_2 product and a CO product.

[0030] From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

[0031] The entire disclosure of all applications, patents and publications, cited above and below, and of corresponding German Application No. 102007045360.6, filed Sep. 22, 2007, is hereby incorporated by reference.

1. A process for continuous thermal decomposition of a crude glycerol mixture containing glycerol, salts and water, comprising:

heating said crude glycerol mixture (**1**) in a pyrolysis reactor (R) to a pyrolysis temperature of more than 100° C., wherein pyrolysis of the crude glycerol mixture (**1**) is performed at a pyrolysis pressure that is higher than the vapor pressure of water present in said pyrolysis reactor (R), at said pyrolysis temperature, and

withdrawing continuously salts and other higher-boiling substances, together with water, from the pyrolysis reactor (R) as waste water (**3**).

2. A process according to claim **1**, wherein said process is performed at a pyrolysis temperature of 290° C.-370° C.

3. A process according to claim **1**, wherein said process is performed at a pyrolysis temperature of 290° C.-340° C.

4. A process according to claim **1**, wherein said process is performed at a pyrolysis temperature of 290° C.-310° C.

5. A process according to claim **1**, wherein said crude glycerol mixture (**1**) is thermally decomposed in the presence of acids and/or Lewis acids.

6. A process according to claim **1**, wherein the heat required for the pyrolysis is introduced into the pyrolysis reactor (R) by indirect heating via heating surfaces and/or by direct heating via high-pressure vapor (**2**).

7. A process according to claim **1**, wherein a pyrolysis gas, produced by pyrolysis of crude glycerol mixture in said pyrolysis reactor (**1**) is superheated to cleave long-chain compounds contained therein and thereby form hydrogen and/or carbon monoxide.

8. An apparatus for thermal decomposition of a crude glycerol mixture (**1**) containing glycerol, salts and water, said apparatus comprising:

a pyrolysis reactor (R) having a feed inlet (Z) for feeding of a crude glycerol mixture, a gas discharge outlet (H) for discharging a gaseous pyrolysis product, means for heating the crude glycerol mixture (**1**) to a pyrolysis temperature of more than 100° C.,

wherein said pyrolysis reactor (R) is a pressure vessel, in which a crude glycerol mixture (**1**) is gasifiable at a pressure higher than the vapor pressure of water present in the pyrolysis reactor, at the pyrolysis temperature, and

wherein said pyrolysis reactor (R) has a second discharge outlet for discharging waste water (A), via which salts and other higher-boiling substances together with water can be drawn off continuously from pyrolysis reactor (R) as waste water (**3**).

9. An apparatus according to claim **8**, wherein between the crude glycerol feed inlet (Z) and the second discharge outlet for discharging waste water (A), the pyrolysis reactor further comprises built-in components (T) that ensure a sufficiently long dwell-time of crude glycerol (**1**) in the pyrolysis reactor (R) to avoid premature removal of glycerol with the waste water (**3**).

10. An apparatus according to claim **8**, wherein said apparatus further comprises a device for superheating (U) the pyrolysis gas, in which pyrolysis gas can be heated to a temperature higher than the pyrolysis temperature.

11. An apparatus according to claim **8**, wherein said apparatus further comprises a feed means for introducing high-pressure vapor (D) into the pyrolysis reactor (R), whereby energy required for pyrolysis can be introduced into the pyrolysis reactor (R) via high-pressure vapor.

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