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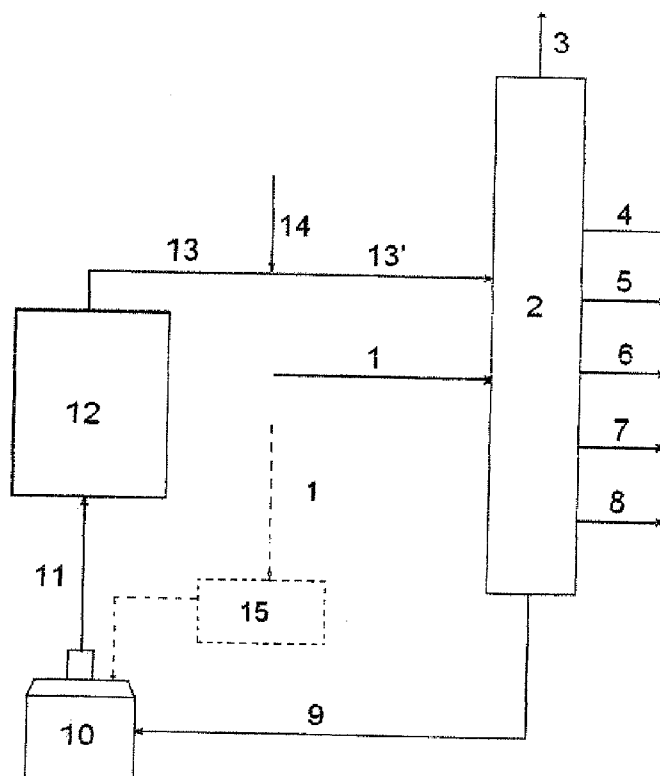
(19) **United States**(12) **Patent Application Publication**
PORTILHO et al.(10) **Pub. No.: US 2010/0024283 A1**(43) **Pub. Date: Feb. 4, 2010**(54) **PROCESS FOR PRODUCTION OF BIO-OIL
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Publication Classification(51) **Int. Cl.**
C10L 1/18 (2006.01)(52) **U.S. Cl.** **44/307**(57) **ABSTRACT**

A process is described for production of Bio-Oil by delayed coking with modified feedstock, in which the feed of the conventional coke unit envisages, in addition to the usual fresh feed of hydrocarbon (vacuum residue, atmospheric residue etc.), the feeding of a biomass for coprocessing. Said biomass can be selected from the group comprising sugar cane straw, sugar cane bagasse, castor seed cake, coconut shells, rice husks, raw soya, castor seed, canola, oil palm, and cottonseed oils, and oils and fats of animal origin, which can be used separately, or as mixtures thereof in any proportions.

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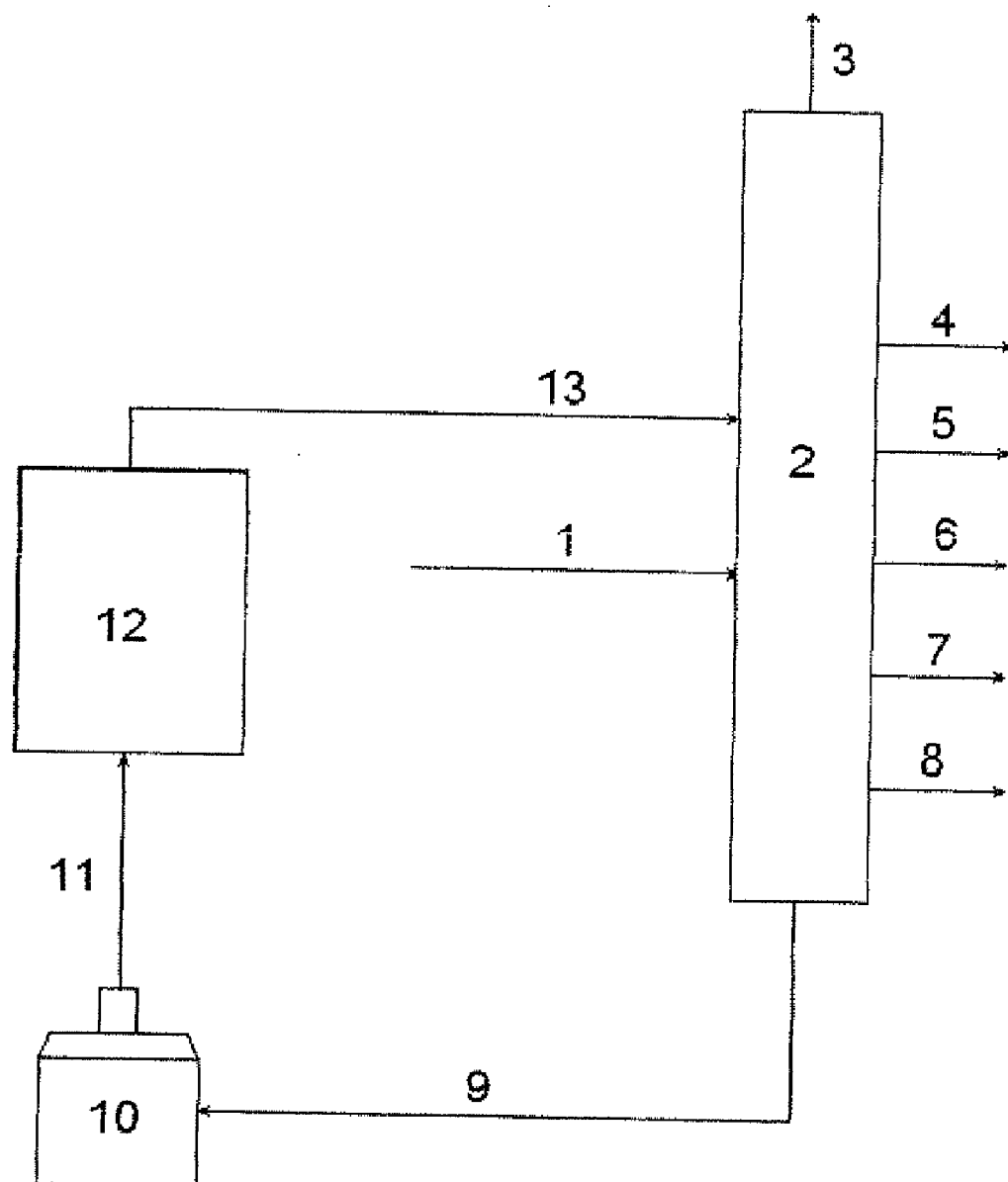


FIG. 1

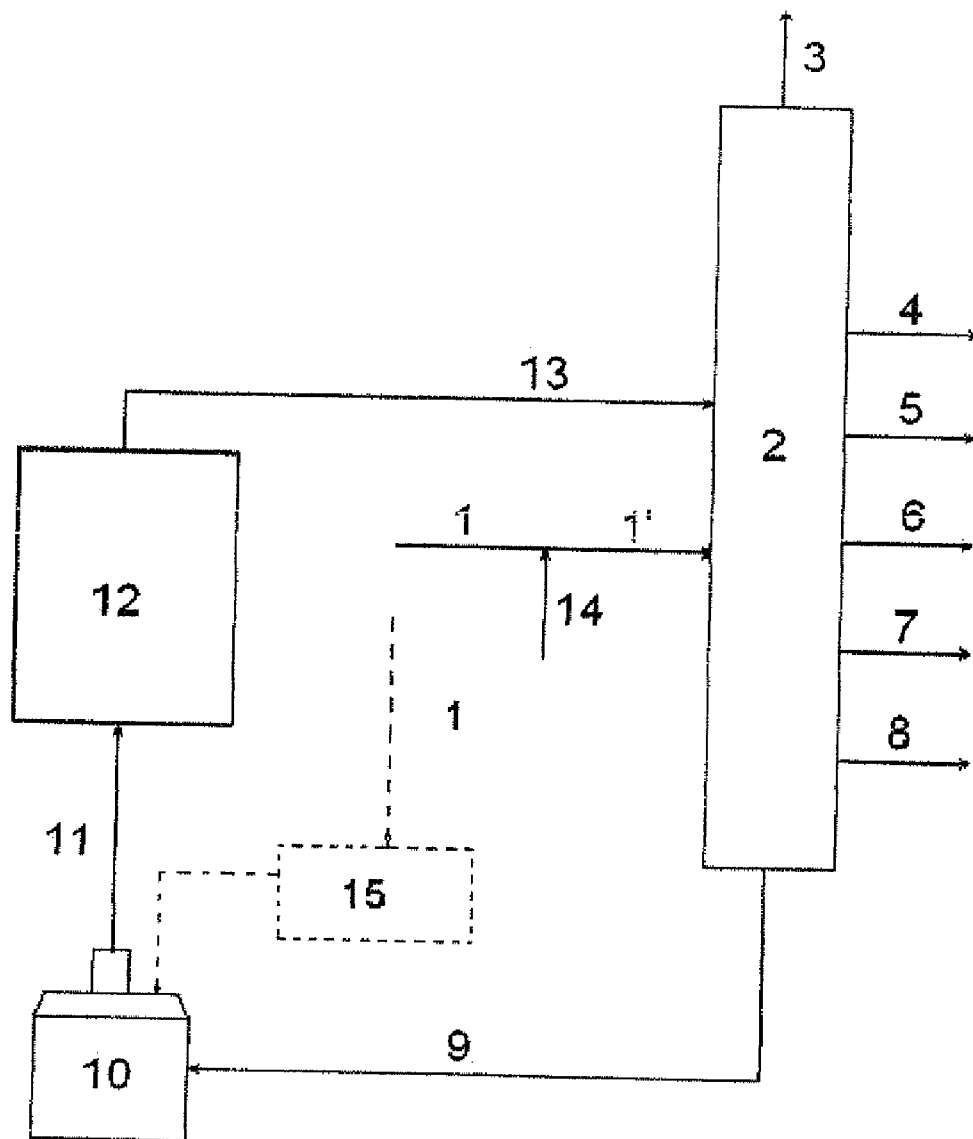


FIG. 2

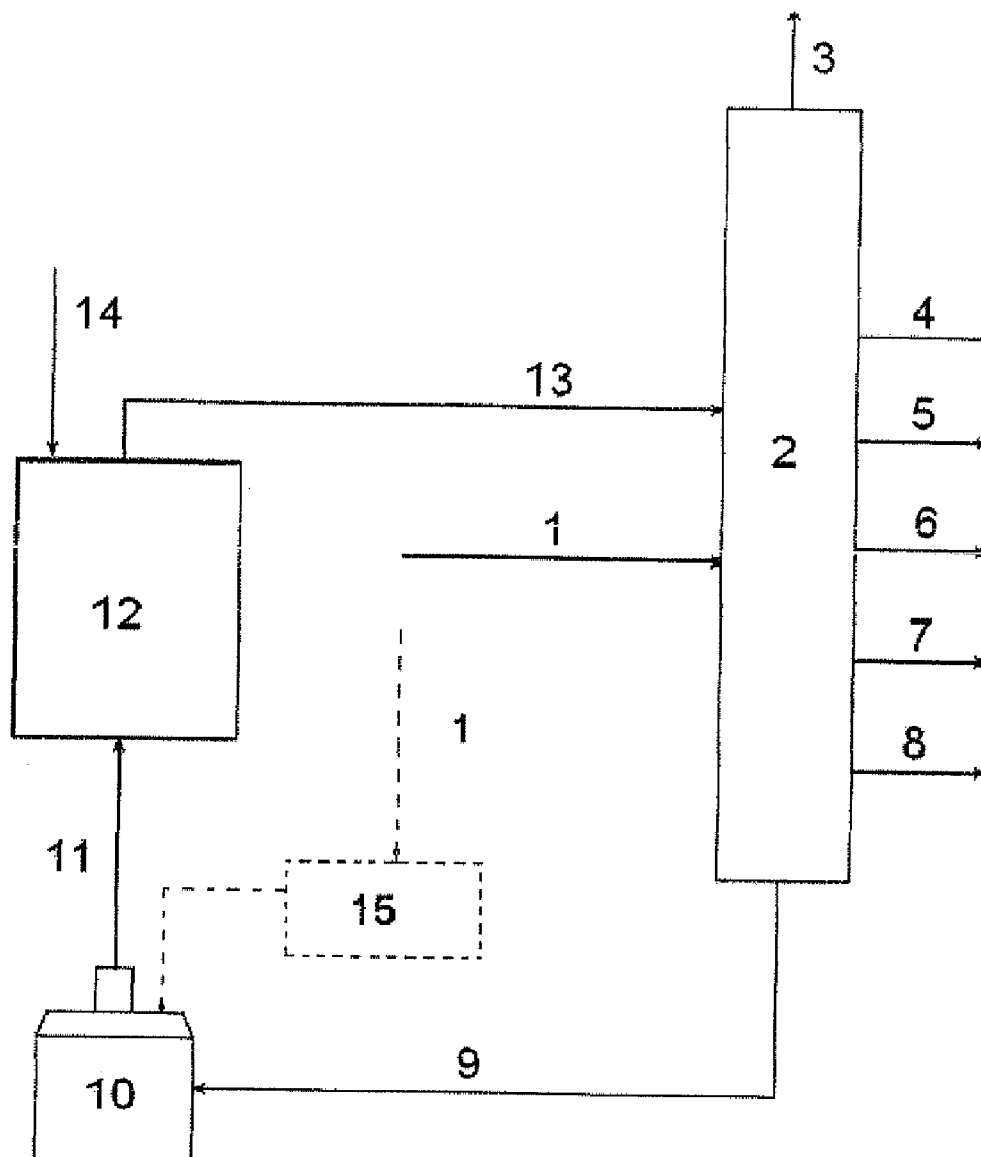


FIG. 3

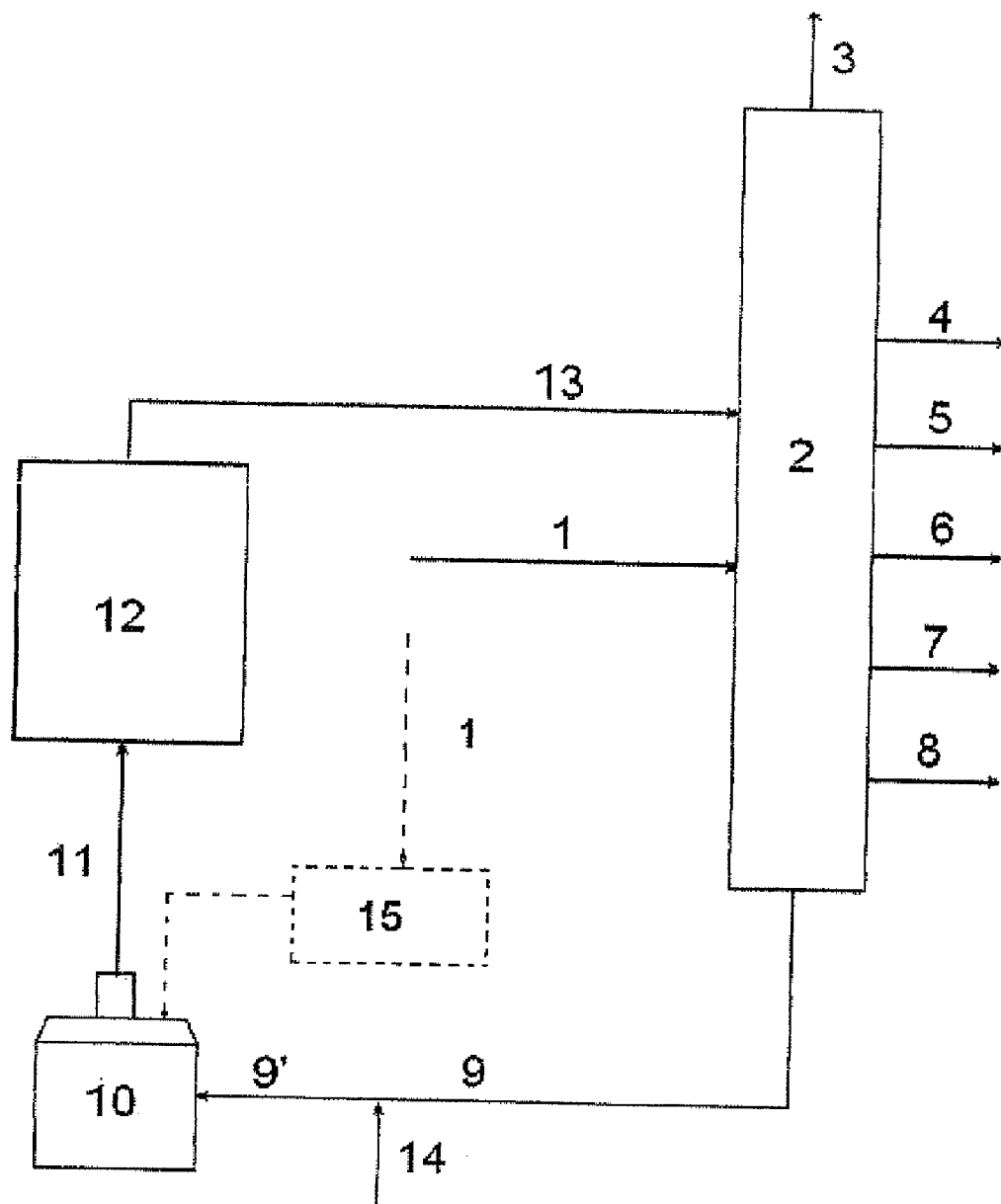


FIG. 4

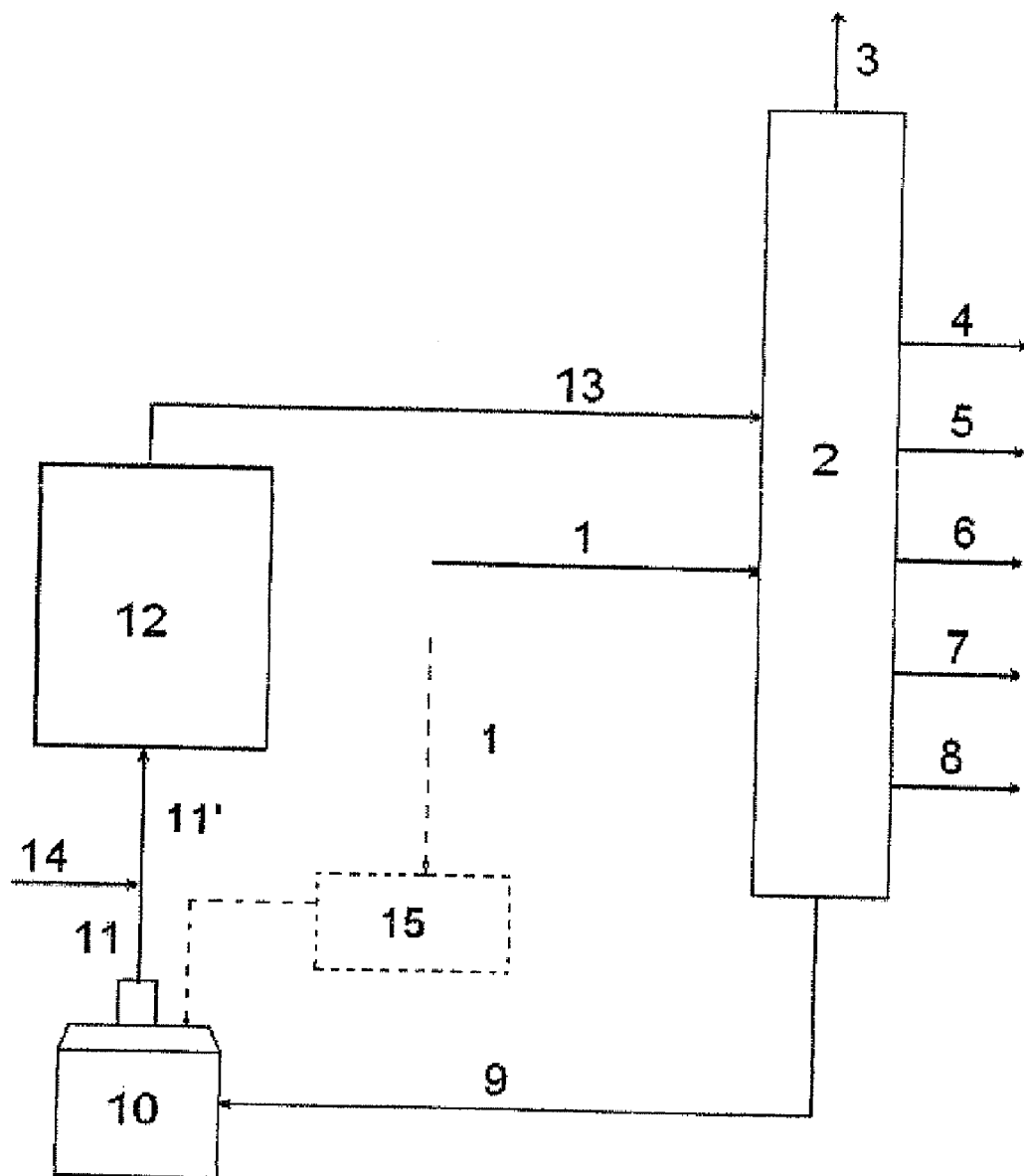


FIG. 5

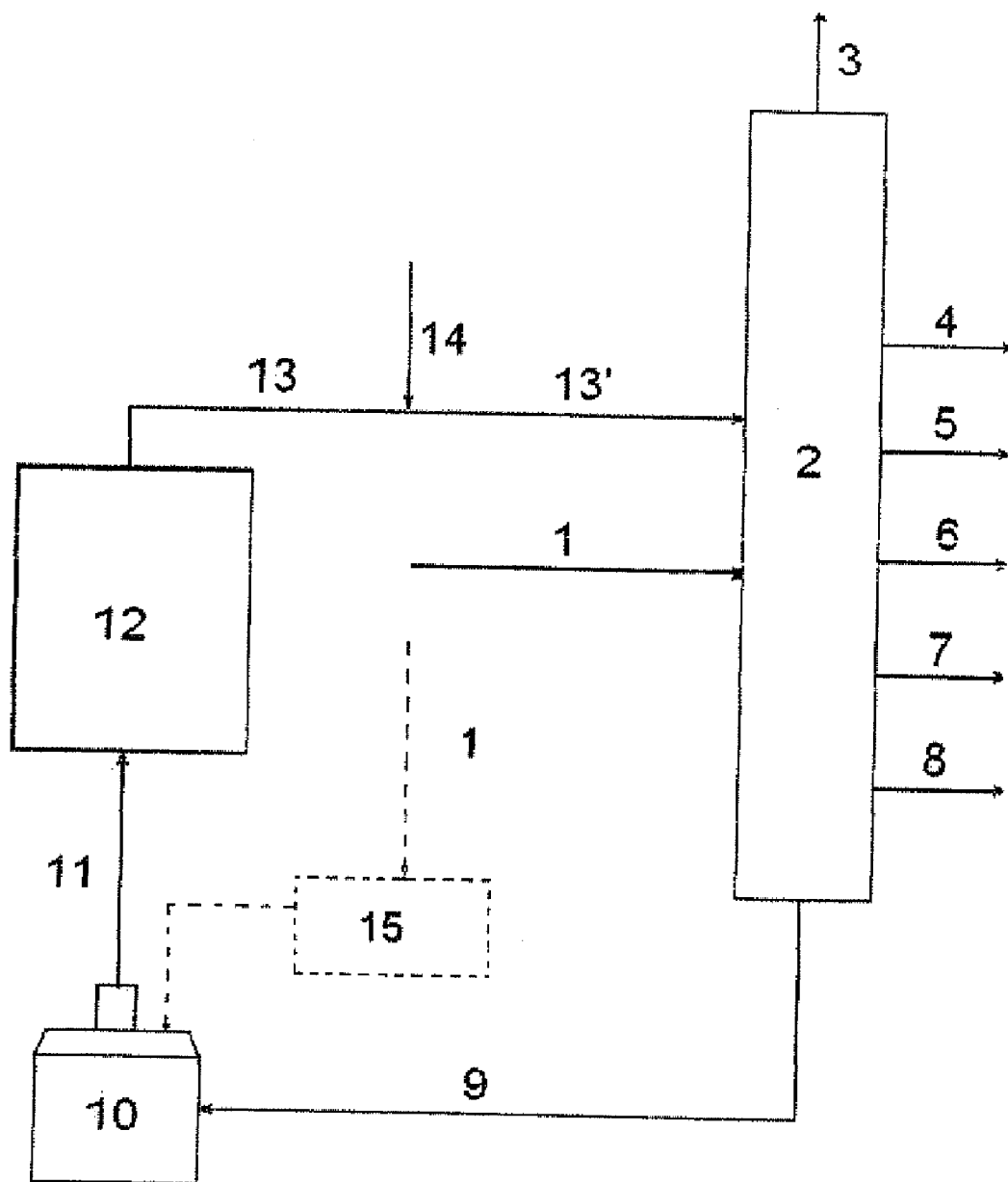


FIG. 6

PROCESS FOR PRODUCTION OF BIO-OIL BY COPROCESSING OF BIOMASS IN A DELAYED COKING UNIT

FIELD OF THE INVENTION

[0001] The present invention relates to processes of thermal cracking. More specifically the present invention relates to a process for production of Bio-Oil in a delayed coking unit by coprocessing of biomass together with the conventional fresh feed of hydrocarbons.

BACKGROUND OF THE INVENTION

[0002] The delayed coking process of residual fractions of petroleum has long been used in the oil refining industry. This process makes possible the conversion of heavy petroleum fractions to lighter products of higher added value, for example, liquefied petroleum gas (LPG), naphtha and gas oils from coke.

[0003] However, owing to the world oil prices, research is being conducted into renewable energy sources, and the production of fuels from alternative sources, for example, from the transformation of vegetable oils and agricultural waste, is appearing to be more and more promising, owing to the world oil crises.

[0004] The present invention presents a process for the production of Bio-Oil in delayed coking units, by the coprocessing of biomass together with a conventional fresh feed of hydrocarbons.

RELATED TECHNOLOGY

[0005] The delayed coking process, as well as the processing of various types of petroleum-derived feedstocks, are already sufficiently well known.

[0006] One of the oldest processes is disclosed in U.S. Pat. No. 3,563,884, which describes a process in which coal tar pitch is used as feedstock.

[0007] Some variant routes were introduced, based on this invention. U.S. Pat. No. 4,213,846 discloses a delayed coking process for the formation of premium coke in which hydrofined gas oil is added to the fresh feed of the unit and fed to the coke drum.

[0008] U.S. Pat. No. 5,711,870 discloses a delayed coking process in which the fresh feed is mixed with water and, optionally, with a hydrogen donor, such as methane or gas oil derived from the recycle, to optimize the yield of liquid products and lower the yields of coke and gas.

[0009] U.S. Pat. No. 4,177,133 describes a delayed coking process for the formation of premium coke in which the fresh feed passes through a stage of preheating and then undergoes flash distillation for removal of non-crystalline substances.

[0010] U.S. Pat. No. 4,455,219 and U.S. Pat. No. 4,518,487 present delayed coking processes in which part or all of the heavy hydrocarbon, usually employed as recycle, is replaced with a lighter hydrocarbon, which is combined with the fresh feed of the unit.

[0011] U.S. Pat. No. 4,624,775 describes a coking process, preferably a delayed coking, for the production of premium coke in which a mixture of 60 to 90 wt. % of tar obtained from a pyrolysis process and 10 to 40 wt. % of coal tar obtained from a distillation process is employed as feedstock.

[0012] U.S. Pat. No. 4,740,293 describes the production of a premium coke, suitable for use in the production of graphite

electrodes, from a mixture of tar obtained from a pyrolysis process and hydrofined decanted oil.

[0013] U.S. Pat. No. 4,259,78 describes the delayed coking of mixtures of 10% to 30 wt. % of coal and heavy petroleum residues mixed at temperatures below 50° C.

[0014] U.S. Pat. No. 4,720,338 describes the production of a more uniform premium coke in a delayed coking process by adding an aliphatic fraction of petroleum to the feedstock during the final stages of the cycle, preferably added gradually, in ever increasing amounts.

[0015] The process described in U.S. Pat. No. 5,389,234 relates to the deployment of wet heavy fuel oils in the delayed coking process, which undergo a pretreatment separately, to vaporize and remove water and light hydrocarbons, and are then diluted and heated to a suitable temperature, and are then fed to the top of the coke drums.

[0016] Patent EP 0 393 278 describes a process in which the residual oil from the refinery is mixed with an oil for fluidization obtained from delayed coking and this mixture goes to a system for evaporation of the water, comprising several stages of evaporators, and then, after evaporation of the water, the mixture is fed to the top of the coke drum, where it will be subjected to the delayed coking process together with the feedstock of the unit.

[0017] At present, with the discovery of heavier and heavier oils, the delayed coking process in the refineries has experienced an increase in its degree of importance, principally due to an increase in the yield of residues from these oils.

[0018] Furthermore, modern industrial activities developed by the 14 most industrialized countries generate solid wastes estimated to be of the order of 3.5 billion tones per year. The management of these waste products, at all stages: production, transport, storage, processing and distribution, is becoming a matter of considerable global concern. The currently available technologies for the management of solid wastes, including agricultural technologies, aim at minimizing them, the recycling of waste materials, treatment of the latter and disposal in landfill. The efficient application of these technologies could lead to the conversion of the solid wastes into useful products, their reduction, or their elimination, and thermal treatments can significantly reduce the volume and mass of solid wastes and permit recovery of energy, while being able to destroy dangerous and pathogenic components.

[0019] Technologies for coprocessing of waste materials are being investigated and applied in the management of solid wastes throughout the world, in place of incineration. In the case of pyrolysis, the products obtained are: a gas rich in light hydrocarbons and inorganic compounds, two liquid phases (an aqueous phase and an organic phase) and a solid phase (charcoal). The amount generated of each product depends on the biomass used and on the reaction temperature.

[0020] In accordance with the global trend, there is a need to develop processes for the use of renewable raw materials, as well as the recycling of materials that are currently discarded.

[0021] The present invention fits into this context and offers the possibility of the direct use of biomasses, comprising organic solid wastes and/or vegetable oils, employed separately or mixed in any proportions, in the delayed coking process.

[0022] It is becoming clear that the biomasses in question display a considerable potential for being coprocessed with the fresh feeds of hydrocarbons in delayed coking units, using

the infrastructure that already exists in oil refineries, or if necessary with some modifications or adjustments to the unit.

[0023] The aim of the present invention is to present an innovative solution for the utilization of biomass in the installations already existing in the petroleum industry, through the transformation of vegetable oils or solid wastes of organic origin in conventional delayed coking units into products with higher added value.

[0024] The application of this invention makes possible the utilization of various sources of raw material for the production of Bio-Oil, by means of the delayed coking process.

SUMMARY OF THE INVENTION

[0025] The process for production of Bio-Oil by delayed coking of a modified feedstock, according to the present invention, envisages an innovation that permits the addition of biomasses directly in certain stages of the process, and their coprocessing with the fresh feed of hydrocarbon in a conventional delayed coking unit.

[0026] According to the present invention, the feedstock of the conventional delayed coking unit envisages, apart from the fresh feed of hydrocarbon (vacuum residue, atmospheric residue etc.), the feeding of biomass, which can be selected from, but is not limited to, the group comprising raw materials of vegetable origin such as straw from sugar cane, sugar cane bagasse, castor seed cake, coconut shells, rice husks, raw soya, castor seed, canola, oil palm, and cottonseed oils, and raw materials of animal origin such as oils and fats. Biomass of various types and natures can be used in the present invention, fed separately in the industrial units, or mixed in any proportions.

[0027] This feed can be effected in the fresh feed of the unit, in the coke drum during the reaction stage or quenching stage (stream of hydrocarbons that lowers the temperature of the effluent), in the inlet line to the furnace, in the outlet line from the furnace or, moreover, in the outlet line from the coke drum. The percentage by volume of said amount of biomass relative to the fresh feed is in a range from 0.01% to 80%, preferably in a range from 0.5% to 30%.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] The process for production of Bio-Oil through delayed coking with feedstock modified with biomass, according to the present invention, will be better understood from the detailed description given below, together with the drawings referred to below, which form an integral part of the present specification.

[0029] FIG. 1 shows schematically a delayed coking process according to the prior art.

[0030] FIG. 2 shows schematically a delayed coking process with modified feed, according to a first embodiment of the present invention.

[0031] FIG. 3 shows schematically a delayed coking process with modified feed, according to a second embodiment of the present invention.

[0032] FIG. 4 shows schematically a delayed coking process with modified feed, according to a third embodiment of the present invention.

[0033] FIG. 5 shows schematically a delayed coking process with modified feed, according to a fourth embodiment of the present invention.

[0034] FIG. 6 shows schematically a delayed coking process with modified feed, according to a fifth embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0035] The delayed coking process with modified feed, according to the present invention, will be described on the basis of the diagrams and in its preferred embodiments.

[0036] FIG. 1 shows schematically a delayed coking process according to the prior art.

[0037] A fresh feed (1) is fed into a fractionating tower (2), from where various products are withdrawn, for example fuel gas and LPG (3), light naphtha (4), heavy naphtha (5), light gas oil (6), medium gas oil (7) and heavy gas oil from coke (8).

[0038] The bottom product (9) from the fractionating tower (2) is fed into a furnace (10) so that the reactions of thermal cracking can begin. The effluent from the furnace (11) is then sent to a coke drum (12), where the reactions of thermal cracking and coking or carbonization go to completion, producing coke and an effluent from the coke drum (13), composed of light hydrocarbons, which is sent to the fractionating tower (2).

[0039] In a first embodiment of the invention, a process of modification of a feed in a delayed coking unit is represented schematically in FIG. 2, according to which the biomass is added directly in the fresh feed. As can be seen, a fresh feed (1) receives the addition of a certain amount of biomass (14), producing a new stream (1') which is fed into a fractionating tower (2), from where various products are withdrawn, for example fuel gas and LPG (3), light naphtha (4), heavy naphtha (5), light gas oil (6), medium gas oil (7) and heavy gas oil from coke (8). A percentage by volume of the aforesaid amount of biomass (14) relative to the fresh feed (1) is used in a range from 0.01% to 80%, preferably in a range from 0.5% to 30%.

[0040] The bottom product (9) from the fractionating tower (2) is fed into a furnace (10), so that the reactions of thermal cracking can begin. Optionally the fresh feed (1) can be fed to a charging tank (15) or similar apparatus, located before the furnace inlet (10).

[0041] The effluent from the furnace (11) is then sent to a coke drum (12), where the reactions of thermal cracking and of coking or carbonization go to completion, producing coke and an effluent from the coke drum (13), composed of light hydrocarbons, which is sent to the fractionating tower (2).

[0042] Another possibility for application of the invention is presented in FIG. 3, in which a second embodiment of the invention is represented schematically, in which the biomass is added directly in the coke drum during the reaction or quenching stage. The details are described below.

[0043] A fresh feed (1) is fed into a fractionating tower (2), from where various products are withdrawn, for example fuel gas and LPG (3), light naphtha (4), heavy naphtha (5), light gas oil (6), medium gas oil (7) and heavy gas oil from coke (8).

[0044] The bottom product (9) from the fractionating tower (2) is fed into a furnace (10), so that the reactions of thermal cracking can begin. Optionally the fresh feed (1) can be fed to a charging tank (15) or similar apparatus, located before the furnace inlet (10). The effluent from the furnace (11) is then sent to a coke drum (12) and a certain amount of biomass (14) is added directly in the coke drum (12), during the reaction or quenching stage, where the reactions of thermal cracking and

of coking or carbonization go to completion, producing coke and an effluent from the coke drum (13), composed of light hydrocarbons, which is sent to the fractionating tower (2). The percentage by volume of the aforesaid amount of biomass (14) relative to the fresh feed (1) is in a range from 0.01% to 80%, preferably in a range from 0.5% to 30%.

[0045] In a third embodiment of the invention, presented in FIG. 4, a process of modification of a feed in a delayed coking unit is represented schematically. In this case the biomass (14) is added directly in the furnace feed line, as described below.

[0046] A fresh feed (1) is fed into a fractionating tower (2), from where various products are withdrawn, for example fuel gas and LPG (3), light naphtha (4), heavy naphtha (5), light gas oil (6), medium gas oil (7) and heavy gas oil from coke (8).

[0047] A certain amount of biomass (14) is added to the bottom product (9) from the fractionating tower (2), producing a new stream (9') that is fed into a furnace (10), so that the reactions of thermal cracking can begin. In this case too, the percentage by volume of the aforesaid amount of biomass (14) relative to the fresh feed (1) is in a range from 0.01% to 80%, preferably in a range from 0.5% to 30%. Optionally the fresh feed (1) can be fed to a charging tank (15) or similar apparatus, located before the furnace inlet (10), shown with dashed lines.

[0048] The effluent from the furnace (11) is then sent to a coke drum (12), where the reactions of thermal cracking and of coking or carbonization go to completion, producing coke and an effluent from the coke drum (13), composed of light hydrocarbons, which is sent to the fractionating tower (2).

[0049] Alternatively, in a fourth embodiment of the invention presented in FIG. 5, a process of modification of a feed in a delayed coking unit is represented schematically. In this embodiment the biomass (14) is added directly in the outlet line from the furnace. The procedure employed is described in detail below.

[0050] A fresh feed (1) is fed into a fractionating tower (2), from where various products are withdrawn, for example fuel gas and LPG (3), light naphtha (4), heavy naphtha (5), light gas oil (6), medium gas oil (7) and heavy gas oil from coke (8).

[0051] The bottom product (9) from the fractionating tower (2) is fed into a furnace (10), so that the reactions of thermal cracking can begin.

[0052] Optionally the fresh feed (1) can be fed to a charging tank (15) or similar apparatus, located before the furnace inlet (10), shown with dashed lines.

[0053] A certain amount of biomass (14) is added to the effluent from the furnace (11), producing a new stream (11'), which is then sent to a coke drum (12), where the reactions of thermal cracking and of coking or carbonization go to completion, producing coke and an effluent from the coke drum (13), composed of light hydrocarbons, which is sent to the fractionating tower (2). The percentage by volume of the aforesaid amount of biomass (14) relative to the fresh feed (1) is in a range from 0.01% to 80%, preferably in a range from 0.5% to 30%.

[0054] Moreover, another possibility for application of the invention is presented in FIG. 6, in a fifth embodiment of the invention. In this possibility the biomass (14) is added directly in the outlet line from the coke drum. The process is carried out as follows. A fresh feed (1) is fed into a fractionating tower (2), from where various products are withdrawn,

for example fuel gas and LPG (3), light naphtha (4), heavy naphtha (5), light gas oil (6), medium gas oil (7) and heavy gas oil from coke (8).

[0055] The bottom product (9) from the fractionating tower (2) is fed into a furnace (10), so that the reactions of thermal cracking can begin. The effluent from the furnace (11) is then sent to a coke drum (12), where the reactions of thermal cracking and of coking or carbonization go to completion, producing coke and an effluent from the coke drum (13), composed of light hydrocarbons. A certain amount of biomass (14) is added to the effluent from the coke drum (13), producing a new stream (13'), which is sent to the fractionating tower (2).

[0056] The percentage by volume of the aforesaid amount of biomass (14) relative to the fresh feed (1) is in a range from 0.01% to 80%, preferably in a range from 0.5% to 30%.

Examples

[0057] The present invention will be understood and assessed more easily from the examples presented below. However, these examples are only to be regarded as being representative of the scope of the present invention and do not in any way limit the invention.

Example 1

[0058] Raw cottonseed oil was processed in a delayed coking unit at the pilot-plant scale. The furnace temperature was maintained at 500° C. and the pressure at the top of the coke drum was 2 kgf/cm²g.

[0059] We obtained mass yields of 58% in the range of diesel oil from coke and 14% in the range of heavy gas oil from coke. The mass yield of coke was 3.5% and that of gas was 18%.

Example 2

[0060] Refined soya oil was processed in a delayed coking unit at the pilot-plant scale, maintaining the furnace temperature at 500° C. and the pressure at the top of the coke drum at 2 kgf/cm²g.

[0061] We obtained mass yields of 65% in the range of diesel oil from coke and 6% in the range of heavy gas oil from coke. The mass yield of coke was 2.6% and that of gas was 17%.

Example 3

[0062] A mixture of 90% of vacuum residue derived from the processing of petroleum obtained from the Marlim field (PETROBRAS—Bacia de Campos) and 10% of raw cottonseed oil was processed in a delayed coking unit at the pilot-plant scale. The furnace temperature was maintained at 500° C. and the pressure at the top of the coke drum was 2 kgf/cm²g.

[0063] We obtained mass yields of 40% in the range of diesel oil from coke and 19% in the range of heavy gas oil from coke. The mass yield of coke was 25% and that of gas was 9%.

[0064] As can be seen, although the present invention has been described in its preferred embodiments and with representative examples, the basic concept guiding the present invention of a process for production of Bio-Oil from the coprocessing of biomass together with hydrocarbon feedstock in a delayed coking unit is preserved with respect to its innovative character, in which a person skilled in the art will

be able to envisage and put into practice conceivable variations, modifications, changes, adaptations and substitutions that are compatible with the subject matter treated here, though without deviating from the spirit and scope of the present invention, as represented by the appended claims.

1. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, comprising the stages:

feeding of a fresh feed (1) in a fractionating tower (2), from where products are withdrawn from the group comprising fuel gas and LPG (3), light naphtha (4), heavy naphtha (5), light gas oil (6), medium gas oil (7) and heavy gas oil from coke (8);

feeding of the bottom product (9) from the fractionating tower (2) to the furnace (10) for starting the reactions of thermal cracking;

sending the effluent from the furnace (11) to a coke drum (12) to complete the reactions of thermal cracking and of coking or carbonization and produce coke and an effluent from the coke drum (13) comprising light hydrocarbons;

sending the effluent from the coke drum (13) to the fractionating tower (2); characterized in that a certain amount of biomass (14) is added directly in said delayed coking unit in order to be processed together with the fresh feed (1).

2. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that said biomass is coprocessed with the fresh feeds of hydrocarbons in conventional delayed coking units using the same infrastructure and conditions already existing in oil refineries, with adjustments as necessary.

3. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that said biomass is selected from the group comprising sugar cane straw, sugar cane bagasse, castor seed cake, coconut shells, rice husks, raw soya, castor seed, canola,

oil palm, and cottonseed oils, oils and fats of animal origin, which can be used separately, or as mixtures thereof in any proportions.

4. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that said certain amount of biomass (14) is added directly to said fresh feed (1) of said delayed coking unit.

5. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that said certain amount of biomass (14) is added directly to said coke drum (12), during the reaction or quenching stage.

6. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that said certain amount of biomass (14) is added to said bottom product (9) from said fractionating tower (2).

7. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that said certain amount of said biomass (14) is added directly to said effluent from the furnace (11).

8. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that said certain amount of said biomass (14) is added directly to said effluent from the coke drum (13).

9. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that optionally said fresh feed (1) is fed to a charging tank (15) or similar apparatus located before the furnace inlet (10).

10. Process for production of Bio-Oil by coprocessing of biomass in a delayed coking unit, according to claim 1, characterized in that the percentage by volume of the certain amount of said biomass (14) relative to said fresh feed (1) is in a range from 0.01% to 80%, preferably in a range from 0.5% to 30%.

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