



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
21.04.2010 Bulletin 2010/16

(51) Int Cl.:
C10J 3/62 (2006.01) C10J 3/66 (2006.01)

(21) Application number: **08166952.5**

(22) Date of filing: **17.10.2008**

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

(72) Inventor: **The designation of the inventor has not yet been filed**

(74) Representative: **Hatzmann, Martin Vereenigde Johan de Wittlaan 7 2517 JR Den Haag (NL)**

(71) Applicant: **Resetec Patent Sarl Geneve (CH)**

(54) **Method and apparatus for pyrolysis of a feed comprising hydrocarbons and gasification of a pyrolysis residue**

(57) The invention is directed to a method and apparatus for processing a feed comprising hydrocarbons. More in particular, the present invention provides a method for pyrolysis of a feed stream comprising hydrocarbons comprising:

- a first step, wherein said feed stream is fed to a pyrolysis reactor, which is operated at a temperature sufficient to obtain pyrolysis of at least part of said hydrocarbons, which temperature is at least 400 °C, thus producing a gas (pyrolysis gas) and a solid or liquid residue (pyrolysis residue).
- a second step, wherein said pyrolysis residue is fed to a gasification oven, in which said residue gas is contacted with a gaseous reaction medium, and which oven is operated at a temperature higher than the temperature in the first step and which temperature is at least 800 °C, thus producing a gas (coke gas) and a solid or liquid residue (coke residue).

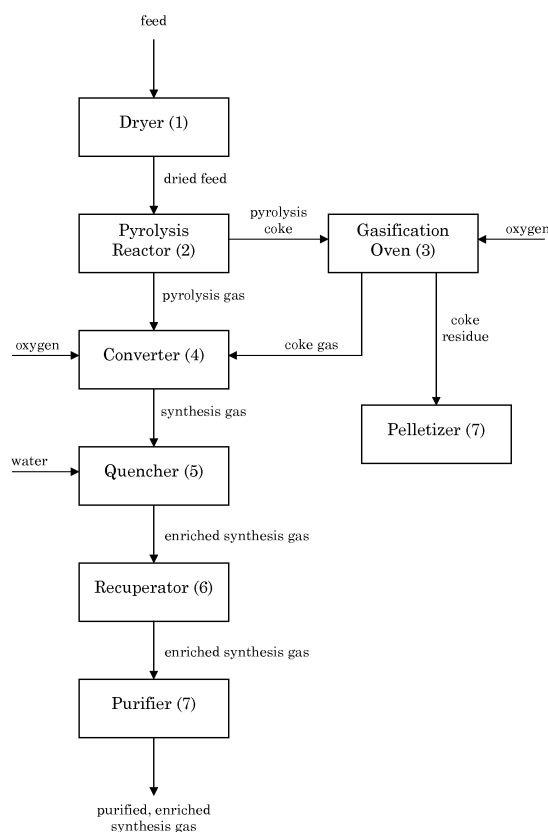


Fig. 1

Description

[0001] The invention is directed to a method and an apparatus for processing a feed comprising hydrocarbons.

[0002] It is known in the art that a feed comprising hydrocarbons, such as *e.g.* biomass, can be converted into useful energy by combustion of said feed. The disadvantage of combustion of a feed comprising hydrocarbons is the formation of large amounts of smoke, which smoke is costly to purify. Because of the need of a purification step, an energy conversion efficiency of only 20% is reached using combustion methods, *viz.* the ratio between the useful energy output of the synthesis gas and the input energy into the process is 0.20.

[0003] European patent application No. 07115971.9 describes a process in which synthesis gas is produced from a feed comprising hydrocarbons. The hydrocarbons are converted by pyrolysis into synthesis gas, which synthesis gas is quenched by contacting it with water at such a high temperature that at least part of said water is converted into hydrogen and oxygen. The resulting synthesis gas is enriched in hydrogen and oxygen, which adds considerably to its caloric value. The process may further comprise a step, wherein a solid stream of pyrolysis residue is obtained and fed to a process comprising a smelter, which is operated at a temperature that is sufficient to vaporize at least part of the heavy metals present in the feed of said smelter and sufficient to obtain a liquid slag. Disadvantage of this method is that the yield of the synthesis gas is low.

[0004] Object of the present invention is to provide a method for converting a feed comprising hydrocarbons, such as *e.g.* biomass, into a gaseous product comprising synthesis gas, which method has a high energy conversion efficiency and a high yield of synthesis gas.

[0005] In a first aspect this object is met by providing a method for pyrolysis of a feed stream comprising hydrocarbons, which method comprises:

- a first step, wherein said feed stream is fed to a pyrolysis reactor, which is operated at a temperature sufficient to obtain pyrolysis of at least part of said hydrocarbons, which temperature is at least 400 °C, thus producing a first gas (pyrolysis gas) and a first residue (pyrolysis residue), which can be solid and/or liquid;
- a second step, wherein at least part of said pyrolysis residue is fed to a gasification oven, in which said pyrolysis residue is contacted with a gaseous reaction medium, and which oven is operated at a temperature higher than the temperature in the first step and which temperature is at least 800 °C, thus producing a second gas (coke gas) and a second residue (coke residue), which can be solid and/or liquid.

[0006] It was surprisingly found that the high temperatures used in the method of the present invention, which

temperatures are generally considered to be undesirable because of high energy losses, were very suitable to increase the yield and/or quality of produced synthesis gas.

[0007] The method according to the invention has the advantage over the prior art that only little purification is needed before it can be used in combustion engines, gas engines, or gas turbines. Consequently, the method of the invention has an energy conversion efficiency of up to 40% to 50%, which means that 40% to 50% of the theoretical (chemical) energy is converted into work or electricity.

[0008] The first heating step is conducted in a pyrolysis reactor. For example, a rotating oven, such as the one described in EP-A-0 653 478 may be used as a pyrolysis reactor. Heat is provided to the pyrolysis reactor by a heat source, for example a burner that is typically operated using natural gas (in particular during start-up of the process) or synthesis gas produced by the process of the present invention (once the process is operational). The feed comprising hydrocarbons is heated in the pyrolysis reactor to a temperature of preferably 400 - 950 °C, more preferably 700 - 900 °C, even more preferably *ca.* 800 °C, which temperature is sufficient to gasify most volatile components of the feed and to obtain pyrolysis of at least part of the hydrocarbons present in the feed. Thus, a gas referred to as a pyrolysis gas and a pyrolysis residue are obtained. The pyrolysis gas comprises hydrocarbons, CO and/or H₂, and usually also CO₂ and/or H₂O, and commonly also sulfur compounds, such as sulfur oxides. The pyrolysis residue comprises non-volatile hydrocarbons, solid carbons and any minerals that were present in the feed. The pyrolysis residue can be solid, liquid or partly solid and partly liquid.

[0009] The second step may be conducted in any suitable kind of gasification oven, such as a rotating oven, a fluid bed reactor, and the like. The temperature of the oven is preferably higher than the temperature used in the pyrolysis reactor and is preferably 800 - 1200 °C, more preferably 1000 - 1100 °C. Such high temperatures may be reached by a burner that is typically operated using natural gas (in particular during start-up of the process) or synthesis gas produced by the process of the present invention (once the process is operational). The solid residue is brought in contact with a gaseous reaction medium in the gasification oven. The gaseous reaction medium may be a gas comprising oxygen and/or water, and is preferably a gas comprising molecular oxygen (O₂). Air may be used for this purpose. More preferably a gas stream enriched in molecular oxygen or consisting essentially of molecular oxygen is used in order to limit the presence of nitrogen at the high temperature gasification step. The presence of nitrogen in this gasification step generally leads to the formation of nitrogen oxides (NO_x) which is an undesirable pollutant. At such high temperatures, the pyrolysis residue reacts with the gaseous reaction medium to form a coke gas, which coke gas comprises at least part of the carbon and hydrocarbons of the pyrolysis residue in the form of carbon mon-

oxide (CO) and methane (CH₄). Furthermore, a residue remains, referred to as coke residue, which residue can be liquid, solid or partly liquid and partly solid and mainly comprises minerals that were present in the feed stream. It was found that the coke gas still contained a considerable amount of useful hydrocarbons that could be converted to synthesis gas, thereby increasing the yield of synthesis gas of the method.

[0010] The method according to the invention is suitable for pyrolysing many different types of biomass. However, the method is in particular suitable for pyrolysis of organic materials having a relative low mineral content, *e.g.* organic materials with a mineral content of 8 wt.% or less, preferably a mineral content of 3 wt.% or less. Reason for this is that the amount of coke residue is minimized.

[0011] The method of the present invention may include a drying step prior to the first step, in which the water content of the feed is reduced. The resulting dried feed preferably comprises less than 20 wt.%, more preferably less than 15 wt.%. To minimize energy losses, the drying step is preferably conducted with waste heat generated in the first and second step.

[0012] The method of the present invention may further comprise a third step, wherein the pyrolysis gas and coke gas are contacted with oxygen or an oxygen containing gas stream, such as air, and heated with a burner to a temperature of preferably 1200 - 2000 °C, more preferably 1200 - 1600 °C. The addition of oxygen in this step reduces formation of nitrogen oxide (NO_x). Preferably all, or substantially all (*e.g.* more than 99 wt.%) of the hydrocarbons present in the pyrolysis and coke gas are converted to synthesis gas in this step. This step may be carried out using a burner, *e.g.* an Oxy-Fuel Burner, wherein methane is combusted using pure oxygen.

[0013] The synthesis gas obtained in the third step may be quenched by contacting it with water at a temperature that is sufficiently high to convert at least part of said water into hydrogen and oxygen, thus producing synthesis gas enriched in hydrogen and oxygen. According to the method of the invention, the synthesis gas has a temperature of 1000 - 2000 °C when bringing it in contact with water. Because of this high temperature, at least part of the water is decomposed into H₂ and O₂ when brought in contact with the gas. This process, called thermal dissociation, enriches the synthesis gas with H₂ and O₂. Such enrichment in H₂ and O₂ adds considerably to the calorific value of the synthesis gas, *viz.* the amount of heat released during the combustion of a certain volume of the gas is increased. Thus, the quality of the synthesis gas is increased by the quenching step. Quenching may be done in a quencher. Preferably the temperature in the quencher prior to quenching is at least about 1200 °C, more preferably 1250-2000 °C, even more preferably about 1300-1600 °C, *e.g.* about 1350 °C.

[0014] The obtained synthesis gas may be cooled by bringing it in heat-exchanging contact with *e.g.* boiling water. In this way, water is evaporated to steam, which

steam can be used for example as a heat source in the pyrolysis reactor, as a heat source in a possible drying step, or for generating electric power. The synthesis gas may further be treated with conventional gas treatments, and purified with for example scrubbers, such as H₂S scrubbers and/or HCl scrubbers, dust removers, *etc.* For example, any sulfur compounds, such as H₂S and dust therefrom, are preferably removed from the synthesis gas.

[0015] The synthesis gas thus produced can be employed for various applications, including generation of heat and/or work (electricity) and/or as starting material for chemical synthesis. It was found that the coke residue obtained in the second step could be used as fertilizer.

[0016] Figure 1 is a schematic representation of an embodiment of the method according to the present invention. In the method depicted in Figure 1, solid and/or liquid feed comprising hydrocarbons is fed to dryer (1). The resulting dried feed comprises 10-20 wt.% water and is fed to pyrolysis reactor (2). In said reactor, a temperature of about 800 °C is provided by using a burner. Thus, pyrolysis gas and pyrolysis residue are obtained. The pyrolysis residue is then fed to gasification oven (3), where it is heated in the presence of an oxygen and/or water (steam) containing gas to about 1000 °C, obtaining a coke gas and a coke residue. The pyrolysis gas and the coke gas are fed to converter (4), wherein these gases were heated to about 1400 °C under the addition of an oxygen containing gas. The thus obtained synthesis gas is led to quencher (5), with the temperature of the synthesis gas still being 1400 °C. Water is added in the quencher to the hot synthesis gas and a cooled synthesis gas with a heightened concentration H₂ and O₂ is thus obtained. The gas coming from the quench cooler has a temperature of around 1200 °C. The heat from this gas may be recovered in a recuperation section, *e.g.* using boiler water, which is converted to steam for further use elsewhere. The synthesis gas coming from the recuperator is then subjected to further cleaning steps (7) to remove sulfur compounds, such as H₂S, acids such as HCl and dust therefrom. The coke residue containing minerals is pelletized in pelletizer (8) and can be used as artificial fertilizer.

[0017] The hydrocarbons used in the method of the invention can be of any suitable source. For example, the source of hydrocarbons may be organic feeds such as wood or crops, domestic waste or industrial waste. Organic feeds may for example originate from agriculture and silviculture. Preferably non-fermentable biomass, in particular olive seeds, oranges or grape skins, is used in the method of the present invention.

Claims

1. Method for pyrolysis of a feed stream comprising hydrocarbons, comprising:

- a first step, wherein said feed stream is fed to a pyrolysis reactor, which is operated at a temperature sufficient to obtain pyrolysis of at least part of said hydrocarbons, which temperature is at least 400 °C, thus producing a first gas (pyrolysis gas) and a first residue (pyrolysis residue), which may be solid and/or liquid;
 - a second step, wherein at least part of said pyrolysis residue is fed to a gasification oven, in which said pyrolysis residue is contacted with a gaseous reaction medium, wherein said oven is operated at a temperature higher than the temperature in the first step and which temperature is at least 800 °C, thus producing a second gas (coke gas) and a second residue (coke residue), which may be solid and/or liquid.
2. Method according to claim 1, wherein said gaseous reaction medium is a gas comprising oxygen and/or water.
 3. Method according to any of the previous claims, further comprising:
 - a third step, wherein the pyrolysis gas and coke gas are contacted with an oxygen containing gas stream and heated to a temperature of 1200 - 2000 °C, thus producing a synthesis gas; and
 - a fourth step, wherein the synthesis gas obtained in the third step is quenched by contacting it with water at a temperature that is sufficiently high to convert at least part of said water into hydrogen and oxygen, thus producing synthesis gas enriched in hydrogen and oxygen.
 4. Method according claim 3, wherein the synthesis gas in the fourth step has a temperature of 1200 - 2000 °C when contacted with water.
 5. Method according to any of the previous claims, wherein said pyrolysis reactor is operated at a temperature of 400 - 900 °C.
 6. Method according to any of the previous claims, wherein said pyrolysis reactor is operated at a temperature of 700 - 900 °C.
 7. Method according to any of the previous claims, wherein said gasification oven is operated at a temperature of 800 - 1200 °C.
 8. Method according to any of the previous claims, wherein said gasification oven is operated at a temperature of 1000 - 1200 °C.
 9. Method according to any of the previous claims, further comprising a drying step prior to the first step, wherein the water content of the biomass is reduced.
 10. Method according to any of the previous claims, further comprising a drying step prior to the first step, wherein biomass is dried to a water content less than 20 wt.%, more preferably less than 15 wt.%.
 11. Method according to any of the previous claims, wherein said feed stream comprises a mineral content of 5 wt.% or less, preferably a mineral content of 3 wt.% or less.
 12. Method according to any of the previous claims, wherein said stream comprising hydrocarbons originates at least in part from olive seeds, oranges and/or grape skins.
 13. Apparatus for processing feeds comprising hydrocarbons, comprising a pyrolysis reactor having a gas exit and a solid exit, wherein said gas exit is connected to one or more pieces of equipment for increasing the temperature of the gas and increasing the amount of synthesis gas, while decreasing the amount of hydrocarbon, the exit of which equipment is connected to a quencher, and wherein said solid exit is connected to a gasification reactor having a gas exit, a gas entrance and a gas exit, wherein said gas exit is connected to one or more pieces of equipment for increasing the temperature of the gas and increasing the amount of synthesis gas, while decreasing the amount of hydrocarbon, the exit of which equipment is connected to said quencher.

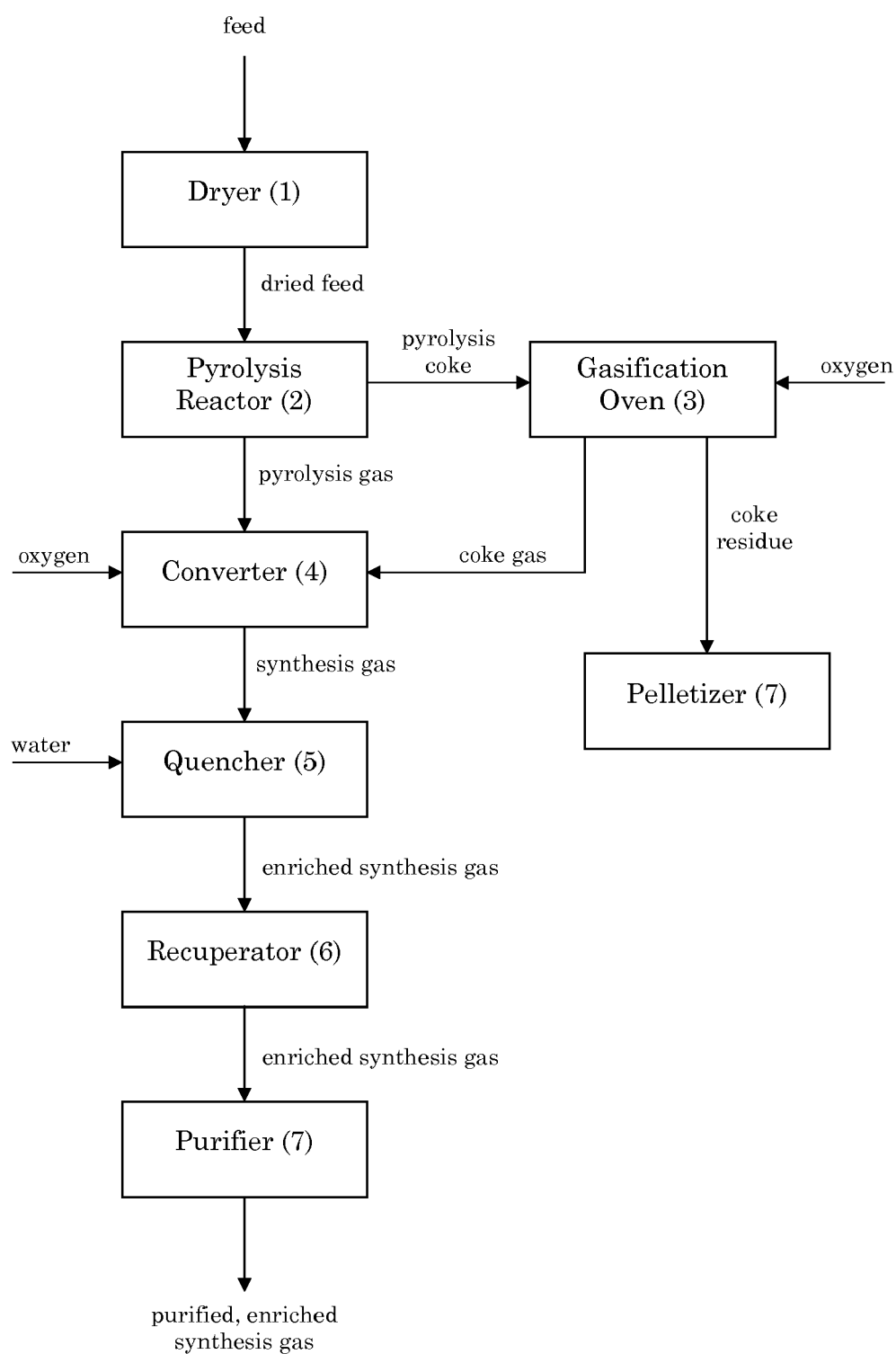


Fig. 1



EUROPEAN SEARCH REPORT

Application Number
EP 08 16 6952

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	FR 2 792 926 A (AIR LIQUIDE [FR]) 3 November 2000 (2000-11-03) * page 1, line 16 - page 2, line 8; figure 1 *	1-13	INV. C10J3/62 C10J3/66
X	WO 2008/104058 A (PLASCO ENERGY GROUP INC [CA]; TSANGARIS ANDREAS [CA]; BACON MARC [CA]) 4 September 2008 (2008-09-04) * page 19; figures 1,14,17 * * page 15 - page 16 * * page 24 - page 25 * * page 27 * * page 31 - page 32 * * page 42 - page 43 * * page 46 - page 47 * * page 85 *	1-13	
X	DE 44 46 803 A1 (NOELL EN UND ENTORGUNGSTECHNI [DE] KRC UMWELTECHNIK GMBH [DE]) 27 June 1996 (1996-06-27) * figure 1 * * column 3, line 32 - line 38 * * column 4, line 10 - line 21 * * column 5, line 50 - line 52 * * column 6, line 25 - line 29 *	1-13	TECHNICAL FIELDS SEARCHED (IPC) C10J
A	US 5 347 068 A (RABE WOLFGANG [DE] ET AL) 13 September 1994 (1994-09-13) * the whole document *	1-13	
A	EP 1 696 177 A (DRECHSLER DANIEL [DE]; HAGEDORN MARION [DE]) 30 August 2006 (2006-08-30) * the whole document *	1-13	
A	DE 40 26 272 A1 (KUGLER KURT [DE]) 27 February 1992 (1992-02-27) * the whole document *	1-13	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 20 March 2009	Examiner Gzil, Piotr
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

 4
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 16 6952

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-03-2009

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2792926	A	03-11-2000	NONE	
WO 2008104058	A	04-09-2008	NONE	
DE 4446803	A1	27-06-1996	NONE	
US 5347068	A	13-09-1994	CZ 9200837 A3	17-02-1993
			DE 4125521 C1	29-10-1992
			GB 2258240 A	03-02-1993
			JP 5202371 A	10-08-1993
			JP 8023026 B	06-03-1996
EP 1696177	A	30-08-2006	NONE	
DE 4026272	A1	27-02-1992	NONE	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 07115971 A [0003]
- EP 0653478 A [0008]