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CA 2622096 C 2011/09/20

(11)(21) **2 622 096**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 2008/02/20

(41) Mise à la disp. pub./Open to Public Insp.: 2008/08/20

(45) Date de délivrance/Issue Date: 2011/09/20

(30) Priorité/Priority: 2007/02/20 (ES200700442)

(51) Cl.Int./Int.Cl. *C10J 1/12* (2006.01),
B09B 3/00 (2006.01)

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(54) Titre : PROCÉDE DE GAZEIFICATION DE LA GLYCERINE

(54) Title: PROCEDURE FOR GASIFICATION OF GLYCERINE

(57) **Abrégé/Abstract:**

Procedure for the use of glycerine as biomass, for the production of energy by means of a spray gasification process, based on the use of a mixture of oxygen, vapour and atmospheric air as gasifying agents, which are introduced into a Gasification Chamber at temperatures above 900°C, so that the gas produced is transferred to a Reformer wherein, also at temperatures above 900°C, the different partial oxidation/thermal cracking reactions in the presence of metal oxides are completed and, subsequently, hot cycloned to retain ashes greater than 5 microns in size, whereupon the gas is sharply cooled using a basket-type Evaporator.



ABSTRACT

Procedure for the use of glycerine as biomass, for the production of energy by means of a spray gasification process, based on the use of a mixture
5 of oxygen, vapour and atmospheric air as gasifying agents, which are introduced into a Gasification Chamber at temperatures above 900°C, so that the gas produced is transferred to a Reformer wherein, also at temperatures above 900°C, the different partial oxidation/thermal cracking reactions in the presence of metal oxides are completed and, subsequently, hot cycloned to
10 retain ashes greater than 5 microns in size, whereupon the gas is sharply cooled using a basket-type Evaporator.

PROCEDURE FOR GASIFICATION OF GLYCERINE

FIELD OF THE INVENTION

The present invention is encompassed in the renewable energy technology sector and, more specifically, the industrial sector relative to gasification technology, and relates to a new gasification system that uses
5 glycerine as biomass.

STATE OF THE ART

The use of glycerine as a combustible raw material is interesting in that a surplus of said compound is expected in the production of biodiesels, as its use
10 as a product poses a serious problem, acquiring the category of waste due to the need to eliminate it. Applications in chemical-type transformations can be found in the long term, but the development of conventional combustion processes is not expected in the short and medium term, due to the very low volatility of glycerine, which impedes its ignition.

15 The present invention aims to offer a novel alternative to energy production from glycerine using gasification processes.

Gasification is a well-known thermochemical process, widely used during World War II, whereby organic matter is transformed into a combustible gas with low calorific power, by means of a series of reactions that take place at a
20 certain temperature and in the presence of a gasifying agent. The main objective of gasification is to transfer the maximum amount of chemical energy from gas feed to fractioning and receive a high-performance combustible gas comprised mainly of gaseous products with a low molecular weight. This technology enables the production of renewable and less contaminating energy.
25 In conventional gasification systems, treatment of solids is carried out on a large scale using fluidized bed gasifiers, but treatment of liquids, such as glycerine, requires spray gasification in high-temperature gas currents, an unknown technique that has been specifically designed for application to glycerine.

Decomposition of the molecular structure of glycerine requires prior
30 thermal increase, above 900°C, and maintenance thereof in the reaction system until its full conversion, as the presence of particulate matter in the gas flow compromises the feasibility of the expected applications. Additionally, the temperature must be maintained between 900°C and 1,000°C to prevent the formation of NOx and, at the same time, reach sufficient reaction speed for high
35 glycerine conversions. Patent EP1724326 relates to a solid biomass gasification

system that uses oxygen to remove the soot produced by the pyrolysis of lignocellulose, wherein temperatures of between 600°C and 900°C are applied in the gasification chamber, said temperatures not being high enough for application to glycerine.

5 Plasma gasification requires very high temperatures in almost total absence of oxygen to decompose waste materials to a basic molecular structure. Plasma gasification does not burn in the manner of boilers. It converts organic waste into a gas comprised of carbon monoxide (CO) and hydrogen (H) that still contains all of the waste's energy. It converts inorganic waste into an
10 inert glass. Plasma is considered a differentiated state of matter. Electricity is supplied to a torch with two electrodes, which ionizes a gas (normally air or water vapour). The gas generated during the gasification process passes through the torch generated in the recombination of the ionized gas and heats said gas at internal temperatures as high as 25,000°F. This gasification system
15 ensures high temperatures but does not simultaneously ensure adequate residence times, i.e. the permanence of the substance until its total disappearance by means of reaction or consumption, which makes its application to glycerine inadequate.

In order to solve the aforementioned problems, the present invention
20 relates to a novel method of using glycerine as biomass in gasification processes.

DESCRIPTION OF THE INVENTION

The invention is fundamentally based on the use of glycerine as biomass in a spray gasification process, for the production of energy, based on the use
25 of a mixture of oxygen, vapour and atmospheric air as gasifying agents and maintaining the whole cyclone gasifying system at a temperature of between 900°C and 1,000°C. The mixture of oxygen, air and water vapour may vary according to the characteristics required for the gas product. A greater proportion of air-vapour reduces production costs but causes more nitrogen to
30 be incorporated to the output gas, while a greater proportion of oxygen-vapour reduces the presence of nitrogen, but at a higher cost.

The procedure consists of several phases:

1. High-temperature gasification chamber (>900°C) into which the gasifying agents and glycerine are introduced, the latter by means of spraying.
- 35 2. Reformer wherein, also at temperatures above 900°C, the different

partial oxidation/thermal cracking reactions in the presence of metal oxides are completed.

3. Hot cycloning that retains ashes greater than 5 microns in size.

4. Basket-type evaporator wherein the gas is sharply cooled. This
5 evaporator imposes conditions on the enclosure, by means of turbulent mixture
($T = 450^{\circ}\text{C}$) and generates vapour within the pipes at 275°C (60 bar) which can
be added to the expansion cycle of a single-cycle vapour turbine combined or
used in the process. The gas at 450°C is cooled, counter-current, using
compressed air at 20 bar or by means of exchange with process currents (if
10 energetic integration is applicable), to below 100°C for compression thereof at
20 bar in isothermal operation, approximately, for subsequent humidity
treatment with acid for retention of ammonia and, afterwards, with a reactive
limestone suspension for retention of acidic components, thereby producing a
"clean" gas, compressed at 20 bar, that can be used in energy production,
15 modified in a new reformer to produce synthesis gas or, by means of CO_2
absorption, to produce quality hydrogen.

In order to complement the preceding description and with the aim of
aiding towards a better understanding the characteristics of the invention, a
detailed description of a preferred embodiment is provided below.

20 The glycerine produced as a waste in biodiesel production processes is
introduced into a gasification chamber by means of spraying at temperatures
above 900°C , together with a mixture of a oxygen, vapour and atmospheric air
as gasifying agents. In the case of gasification with pure oxygen, the amount of
oxygen required is between 0.05 and 0.1 Kg O_2/Kg of glycerine and, in case of
25 using oxygen-enriched air or atmospheric air, higher loss due to dilution and
cooling of a greater flow and higher compression and manipulation costs would
have to be considered. Consideration must be given to the fact that the
glycerine used is not a pure chemical product, but rather the waste of biodiesel
production which, accompanied by different impurities, requires adjustment of
30 the composition of the combustive or gasifying mixture to ensure composition
and thermal conditions within the gasifier.

Subsequently, the product produced is transferred to a reformer wherein
the different partial oxidation/thermal cracking reactions in the presence of
metal oxides are completed, maintaining the temperature above 900°C , and is
35 subsequently cycloned to retain the ashes produced, whereupon the gas is

finally cooled. As glycerine has a standard combustion heat of 3,855 Kcal/Kg but the accompanying organic impurities have a higher calorific power, 2,335 moles of gas per glycerine formula weight (elemental formula $\text{CH}_2\text{-670}$) is produced, the approximate composition of which ranges from 0.1 to 0.4 moles of CO_2 , 0.3 to 0.36 moles of CO and 0.52 to 0.56 moles of H_2 , with a calorific power that may vary from 10MJ/Nm^3 to 14MJ/Nm^3 .

In any case, the procedure shall be optimized in accordance with oxygen availability and price, the comparison with enriched or atmospheric air and the possible energetic integration of clean gas application upon production of vapour at ambient temperature, due to which its combustion requires high temperatures for the vapour phase to exist.

CLAIMS

1. A process for gasification of glycerine, comprising the following steps:

- i) spraying glycerine into a gasification chamber with a mixture of oxygen, steam and atmospheric air as gasifying agents to form a reaction product consisting of partial oxidation products and partial thermal cracking products;
- ii) reforming the reaction product in a reformer in the presence to metal oxides to complete oxidation and thermal cracking of the partial oxidation products and the partial thermal cracking products;
- iii) cycloning the reformed reaction products in cycloning equipment which retains ashes having particle sizes greater than 5 microns to produce a cycloning product; and
- iv) cooling the cycloning product in a basket-type evaporator to produce a cooled gas;

wherein steps i), ii) and iii are performed at a temperature between 900°C and 1,000°C.

2. The process for gasification of glycerine according to claim 1, characterized in that pure oxygen is used as a gasifying agent in a proportion of between 0.05 and 0.1 Kg O₂/Kg of glycerine.

3. The process for gasification of glycerine according to claim 1, characterized in that the cooled gas produced is subsequently subjected to a humidity treatment with acid followed by treatment with a reactive limestone suspension.