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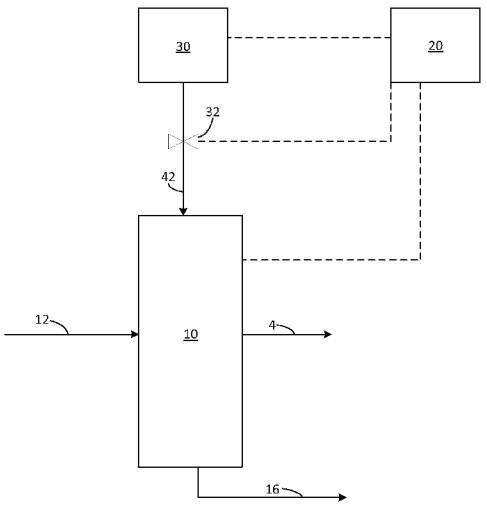
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[Continued on next page]

(54) Title: METHOD FOR DECREASING SMR TUBE TEMPERATURE

FIG. 1



(57) Abstract: A method for decreasing steam methane reformer (SMR) tube temperature is provided. The method can include the steps of introducing a hydrocarbon containing feed to be reformed to a plurality of SMR tubes in the presence of steam under conditions effective to produce hydrogen and carbon monoxide, monitoring the temperature of at least a plurality of the tubes within the SMR during operation, comparing the monitored temperature against a first predetermined value, and introducing an effective amount of water to a reformer tube when the monitored temperature of the reformer tube is at or above the predetermined value, such that the temperature of the reformer tube is reduced.

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METHOD FOR DECREASING SMR TUBE TEMPERATURE

Technical Field of Invention

The present invention relates to a method for reducing the tube temperature of a steam methane reformer (SMR).

Background

During normal operation of a steam methane reformer (SMR), some portion of the catalyst tubes may experience unexpectedly higher temperatures. Therefore, on account of the small number of tubes, the overall burner power has to be reduced and/or the steam to carbon ratio has to be increased to bring the temperature down; however, both of these methods globally affect plant efficiency. Additionally, predicting which tubes will be affected by this problem cannot be easily done since the tubes affected by this problem can vary. Therefore, a solution with which the temperature of each tube can be controlled independently has been sought to date, but no practical approach has been found.

Summary

The present invention is directed to a method that satisfies at least one of these needs. The present invention is directed to a method that satisfies the need to reduce temperature of particular SMR tubes. Certain embodiments of the present invention relate to introducing water into an individual tube that is affected by abnormally high temperatures in order to reduce the temperature of the tube, such that the temperature is below a given threshold temperature. Embodiments of the invention allow the plant to run more efficiently because the burner and steam to carbon changes are not necessary.

In one embodiment, a method for decreasing the temperature of an SMR tube includes the following steps: introducing a hydrocarbon containing feed to be reformed to SMR tubes in the presence of steam under conditions effective to produce hydrogen and carbon monoxide, monitoring the temperature of at least a plurality of the tubes within the SMR during operation, comparing the monitored temperature against a first predetermined value, and introducing an effective amount of water to a reformer tube when the monitored temperature of the reformer tube is at or above the predetermined value, such that the temperature of the reformer tube is reduced.

Optional embodiments can also include:

- reducing, maintaining or stopping the introduction of water in step d) once the monitored temperature falls below a second predetermined value,
- wherein the amount of steam introduced to the SMR remains unaffected by the introduction of water,
- reducing the amount of steam introduced to the SMR when water is introduced. Preferably, the reduced amount of steam is approximately equal to the effective amount of water,
- wherein the water is introduced in sufficiently small droplet sizes to vaporize prior to contacting catalysts such that the pressure drop across the catalysts within the SMR tube is substantially unaffected,
- spraying the water using a hydraulic sprayer,
- atomizing the water in an atomizer such that the water is made up of water droplets of sufficiently small diameters to vaporize prior to contacting catalysts such that the water droplets do not adversely affect catalyst performance within the SMR tube,

- atomizing the water using a gas,
- atomizing the water using natural gas,
- atomizing the water in an atomizer such that the water is made up of water droplets, and then directing the water droplets through a foam, preferably a high surface area metallic or ceramic foam, to promote further vaporization of the water droplets, thereby reducing the risk of adversely affecting catalyst performance within the SMR tube,
- using a water tube in fluid communication with a demineralized water source and an atomizing nozzle to introduce the water, wherein the water tube has a delivery end disposed within the tube of the SMR at a point above catalysts, such that the water atomizes upon exiting the atomizing nozzle and entering the tube of the SMR,
- wherein the water, when introduced, consists essentially of water droplets having droplet sizes less than 500 microns and preferably 100 microns,
- wherein the first predetermined value is the maximum operating temperature rating of the tube, preferably 10°C less than the maximum operating temperature rating of the tube,
- wherein the second predetermined value is the same as the first predetermined value, preferably 10°C less than the first predetermined value, and
- wherein the water is demineralized water, preferably, originating from the same water source as steam used in the SMR, although any suitable source will work.

Brief Description of the Figures

These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, claims, and accompanying drawings. It is to be noted, however, that the drawings illustrate only several embodiments of the invention and are therefore not to be considered limiting of the invention's scope as it can admit to other equally effective embodiments.

FIG. 1 illustrates an embodiment of the present invention.

FIG. 2 illustrates a top view of an embodiment of the present invention.

FIG. 3 illustrates an embodiment of the present invention.

FIG. 4 illustrates comparative data for certain embodiments of the present invention.

FIG. 5 illustrates increased pressure drop as a function of inlet velocity.

Description of Preferred Embodiments

While the invention will be described in connection with several embodiments, it will be understood that it is not intended to limit the invention to those embodiments. On the contrary, it is intended to cover all the alternatives, modifications and equivalence as may be included within the spirit and scope of the invention defined by the appended claims.

Certain embodiments of the present invention provide a straightforward approach in that water, preferably demineralized, is introduced directly, preferably by injection, into a particular SMR tube in order to reduce the SMR tube temperature.

In one embodiment, water, preferably demineralized water can be introduced into a particular tube in order to reduce that tube's temperature. Demineralized water is

typically available in the SMR plant to supply clean feedwater to the boilers for the steam production for the steam reforming process. In one embodiment, the water used for temperature regulation can be supplied directly from the plant's demineralized water source or from any returned condensate if the plant produces any excess steam that is not otherwise valorized. In a preferred embodiment, the water entering the SMR tube vaporizes prior to coming into contact with SMR tube catalysts.

FIG. 1 illustrates a general process overview of an embodiment of the invention. SMR furnace 10 receives hydrocarbon steam mixture 12 and produces syngas 4 and hot stream 16. As noted previously, some SMR tubes (not shown) within SMR furnace will exceed the desired operating temperature. In order to combat this issue, monitoring system 20 monitors the temperature of each SMR tube in order to identify any tubes that are running too hot. In the event an SMR tube is running hot, monitoring system can then initiate a sequence that will allow for water from water source 30 to be introduced to SMR tubes within SMR furnace 10. In the embodiment shown, monitoring system 20 communicates (e.g., wired or wireless communication) with water source 30 and/or valve 32 to allow for the flow of water 42. Monitoring system 20 continues to monitor the temperatures, and once the temperature of the affected SMR tube is below a desired value, monitoring system initiates a sequence to either stop the introduction of water to SMR furnace 10 or send a reduced amount of water that is effective for maintaining the tube's temperature below the desired value.

It should be noted that use of a valve is not intended to limit the invention, as a person of ordinary skill in the art will recognize other methods of controlling flow of water can be utilized.

In another embodiment, rather than taking the temperature of all of the tubes, a smaller subset of temperatures can be taken, preferably, those areas of tubes that exhibit higher temperatures than normal.

In one embodiment, the flow rate of the incoming water 42 is determined by the upstream pressure. However, those of ordinary skill in the art will recognize that other methods for determining the flow rate can also be used, for example, flow meters.

FIG. 2 depicts a top view of a water distribution system 1. In the embodiment shown, header 66 carries water 42 to SMR tubes 50, which can be aligned in rows. In one embodiment, the flow rate at which the water is introduced to header 66 depends on the pressure of the system. Water 42 introduced to water distribution system 1 is usually readily available elsewhere in the plant operation. In one embodiment, each SMR tube 50 has its own valve 33 to control the flow of water to SMR tube 50. In one embodiment, check valves 35 can be installed to help improve the overall safety of the device. While FIG. 2 only shows two rows of SMR tubes 50, those of ordinary skill in the art will recognize that there can be more than two rows.

FIG. 3 provides a cross sectional view of SMR tube 50 in accordance with an embodiment of the invention. Hydrocarbon steam mixture 12 enters SMR tube 50 via feed inlet 60 before entering mixing zone 62. Hydrocarbon steam mixture 12 then travels down the length of SMR tube 50 coming into contact with catalyst 76, wherein the reforming reaction takes place. In the event SMR tube 50 exceeds a desired temperature, water 42, originating from water source 30, is introduced to mixing area 62 via water tube 44. In one embodiment, water tube 44 can vary in length. In an optional embodiment, SMR tube 50 can include a nozzle 56 that is configured to

create small water droplets within mixing zone 62 to help improve overall water contact and speed up the cooling process. In one embodiment, insulation 52 can be utilized in top of SMR tube 50 to help reduce heat transfer through the top of SMR tube 50. Insulation holder 54 can also be included to provide support for insulation 52, and in certain embodiment, it can provide a seal from outside SMR tube 50.

In an optional embodiment, SMR tube 50 can also include foam 70, which helps to vaporize the water such that water droplets are prevented from making contact with catalyst 76. Advantageously, foam 70, in conjunction with operating conditions (e.g., temperature and pressure), provide sufficient surface area for evaporation of water droplets. In the embodiment shown, foam holder 74 provides support for foam 70, while ceramic fiber seal 72 provides a seal, such that substantially all of the water droplets are forced through foam 70. Orifice plate 75 can also be provided in order to control the pressure drop across foam 70. In one embodiment, foam 70 can be high surface area metallic foam or high surface area ceramic foam.

In one embodiment, nozzle 56 introduces water 42 before water 42 enters mixing area 62. Nozzle 56 may atomize water 42, which helps to further preserve the stability of SMR tube 50 by preventing liquid water droplets from harming catalyst performance in the lower part of SMR tube 50. The atomization process can make use of any acceptable gas, for example air or natural gas; however, use of natural gas is preferred since its use in the atomization process enables the steam and carbon ration to remain constant. In one embodiment, harm to the catalyst can be identified by a substantial pressure drop across SMR tube 50.

FIG. 4 represents the impact of introducing a small amount of water to the high temperature SMR tube. As shown in FIG. 1, a relatively small amount of water (10-

30ml/s) can effectively reduce the tube temperature. In one embodiment, the water can be introduced by injection. Depending on the water injection methodology (i.e., additive or replacement), water can be added to the total flowrate (NG/steam + water) of a particular tube or water can displace a specific amount of steam at the inlet. As depicted in FIG. 4, the former method produces a greater temperature drop, which makes the addition of fluid to the total flow rate more effective in temperature reduction.

Examples

FIG. 5 is a graphical representation depicting pressure drop across various foams as a function of inlet velocity. As seen in FIG. 5, as inlet velocity is increased, the pressure drop across the foam also increases (this is shown by each individual line). Additionally, FIG. 5 shows that increasing the density of the foam increases the pressure drop across the foam. Therefore, pressure drop is directly related to both foam density and inlet velocity. It is preferred to select a foam having a low pressure drop and while maintaining a high vaporization potential.

Table I includes collected data, which includes resulting droplet sizes as a function of various pressures and capacities for various spray pattern types. Based on the data in Table I, higher spraying pressures yields smaller droplet sizes, with lower flow rates (at the same pressures) having smaller droplet sizes. Additionally, hydraulic spraying yields droplet sizes that are generally higher than atomizers.

Table I: Droplet Size by Spray Pattern at Various Pressures and Capacities

	10 psi (0.7 bar)			40 psi (2.8 bar)			100 psi (7 bar)		
	Capacity		VMD	Capacity		VMD	Capacity		VMD
Spray Pattern Type	gpm	lpm	microns	gpm	lpm	microns	gpm	lpm	microns
	0.005	0.02	20	0.008	0.03	15	12	45	400
Air Atomizing	0.02	0.08	100	8	30	200	—	—	—

	0.22	0.83	375	0.03	0.1	110	0.05	0.2	110
Fine Spray	—	—	—	0.43	1.6	330	0.69	2.6	290
	0.05	0.19	360	0.1	0.38	300	0.16	0.61	200
Hollow Cone	12	45	3400	24	91	1900	38	144	1260
	0.05	0.19	260	0.1	0.38	220	0.16	0.61	190
Flat Fan	5	18.9	4300	10	38	2500	15.8	60	1400
	0.1	0.38	1140	0.19	0.72	850	0.3	1.1	500
Full Cone	12	45	4300	23	87	2800	35	132	1720

The values in Table I are not intended to limit the invention to the pressure ranges or droplet sizes listed. Rather, the contents of Table I are provided for exemplary purposes.

While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations that fall within the spirit and broad scope of the appended claims. The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. Furthermore, if there is language referring to order, such as first and second, it should be understood in an exemplary sense and not in a limiting sense. For example, it can be recognized by those skilled in the art that certain steps can be combined into a single step.

The singular forms "a", "an" and "the" include plural referents, unless the context clearly dictates otherwise.

“Comprising” in a claim is an open transitional term which means the subsequently identified claim elements are a nonexclusive listing i.e. anything else may be additionally included and remain within the scope of “comprising.” “Comprising” is

defined herein as necessarily encompassing the more limited transitional terms "consisting essentially of" and "consisting of"; "comprising" may therefore be replaced by "consisting essentially of" or "consisting of" and remain within the expressly defined scope of "comprising".

"Providing" in a claim is defined to mean furnishing, supplying, making available, or preparing something. The step may be performed by any actor in the absence of express language in the claim to the contrary.

Optional or optionally means that the subsequently described event or circumstances may or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

Ranges may be expressed herein as from about one particular value, and/or to about another particular value. When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within said range.

All references identified herein are each hereby incorporated by reference into this application in their entireties, as well as for the specific information for which each is cited.

What is claimed is:

1. A method for decreasing reformer tube temperature within a steam methane reformer (SMR), the method comprising the steps of:

a) introducing a hydrocarbon containing feed to be reformed to reformer tubes (50) in the presence of steam under conditions effective to produce hydrogen and carbon monoxide;

b) monitoring (30) the temperature of at least a plurality of the reformer tubes within the SMR during operation;

c) comparing the monitored temperature against a first predetermined value; and

d) introducing an effective amount of water (42) to a selected reformer tube when the monitored temperature of the selected reformer tube is at or above the predetermined value, such that the temperature of the selected reformer tube is reduced.

2. The method as claimed in Claim 1, further comprising the step of reducing the introduction of water in step d) once the monitored temperature falls below a second predetermined value.

3. The method as claimed in Claim 2, wherein the second predetermined value is the same as the first predetermined value.

4. The method as claimed in Claim 2, wherein the second predetermined value is about 10°C less than the first predetermined value.

5. The method as claimed in any of the preceding claims, wherein the amount of steam introduced to the SMR during step a) remains unaffected by the introduction of water during step d).

6. The method as claimed in any of the preceding claims, further comprising the step of reducing the amount of steam introduced to the SMR during step a) when water is introduced during step d).

7. The method as claimed in Claim 6, wherein the reduced amount of steam is approximately equal to the effective amount of water introduced in step d).

8. The method as claimed in any of the preceding claims, wherein the water is introduced during step d) in sufficiently small droplet sizes to vaporize prior to contacting catalysts, such that the pressure drop across catalysts within the reformer tube is substantially unaffected.

9. The method as claimed in any of the preceding claims, wherein step d) further comprises spraying the water using a hydraulic sprayer.

10. The method as claimed in any of the preceding claims, wherein step d) further comprises atomizing the water in an atomizer such that the water is comprised of water droplets of sufficiently small diameters to vaporize prior to contacting catalysts, such that the water droplets do not adversely affect catalyst performance within the reformer tube.

11. The method as claimed in Claim 10, wherein natural gas is used to atomize the water.

12. The method as claimed in any of the preceding claims, wherein step d) further comprises atomizing the water in an atomizer such that the water is comprised of water droplets, and then directing the water droplets through a foam (70) to promote further vaporization of the water droplets, thereby reducing the risk of adversely affecting catalyst performance within the reformer tube.

13. The method as claimed in Claim 12, wherein the foam is selected from the group consisting of metallic foam and ceramic foam.

14. The method as claimed in any of the preceding claims, wherein the water is introduced using a water tube (44) in fluid communication with a demineralized water source and an atomizing nozzle (56), wherein the water tube has a delivery end disposed within the reformer tube at a point above catalysts, such that the water atomizes upon exiting the atomizing nozzle and entering the reformer tube.

15. The method as claimed in any of the preceding claims, wherein the water introduced in step d) consists essentially of water droplets having droplet sizes less than 500 microns.

16. The method as claimed in any of the preceding claims, wherein the water introduced in step d) consists essentially of water droplets having droplet sizes less than 100 microns.

17. The method as claimed in any of the preceding claims, wherein the first predetermined value is the maximum operating temperature rating of the tube.

18. The method as claimed in any of the preceding claims, wherein the first predetermined value is about 10°C less than the maximum operating temperature rating of the tube.

19. The method as claimed in any of the preceding claims, wherein the water is demineralized water.

20. The method as claimed in any of the preceding claims, wherein the water originates from the same water source as steam used in the SMR.

FIG. 1

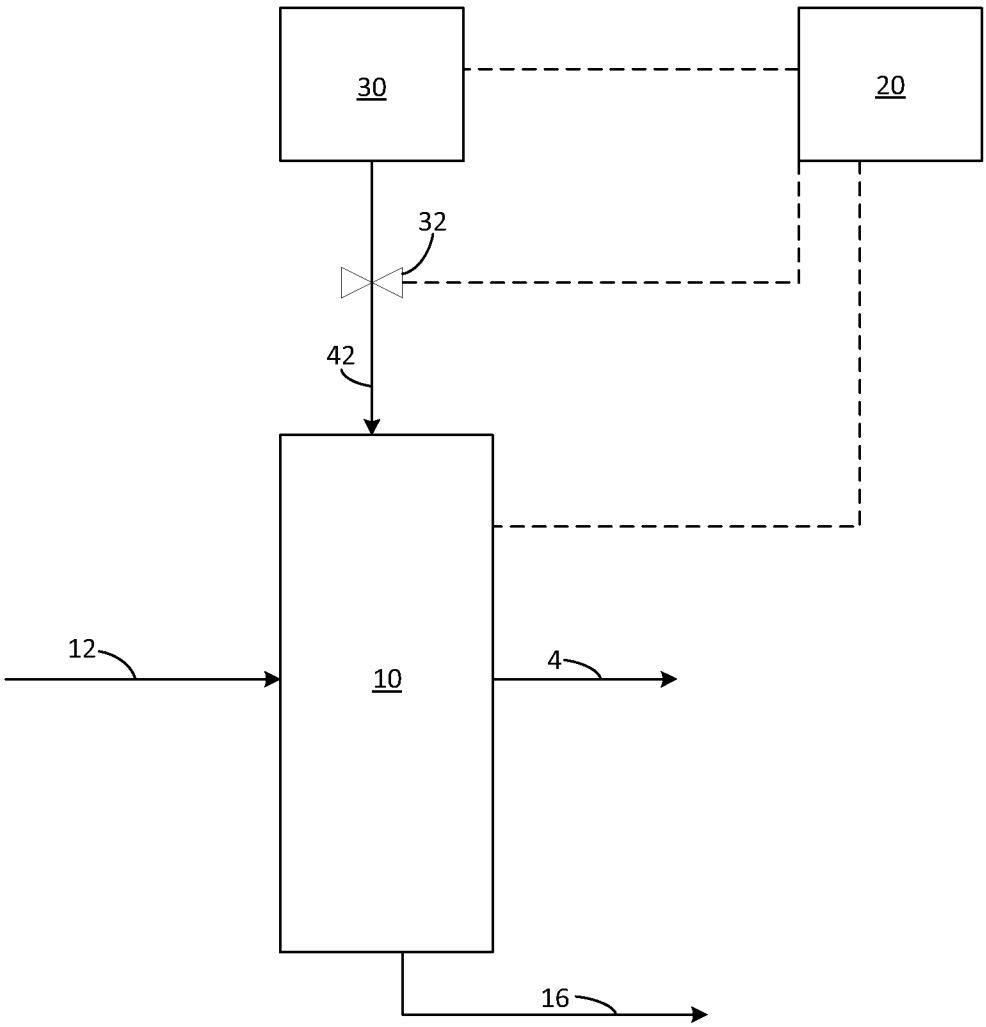
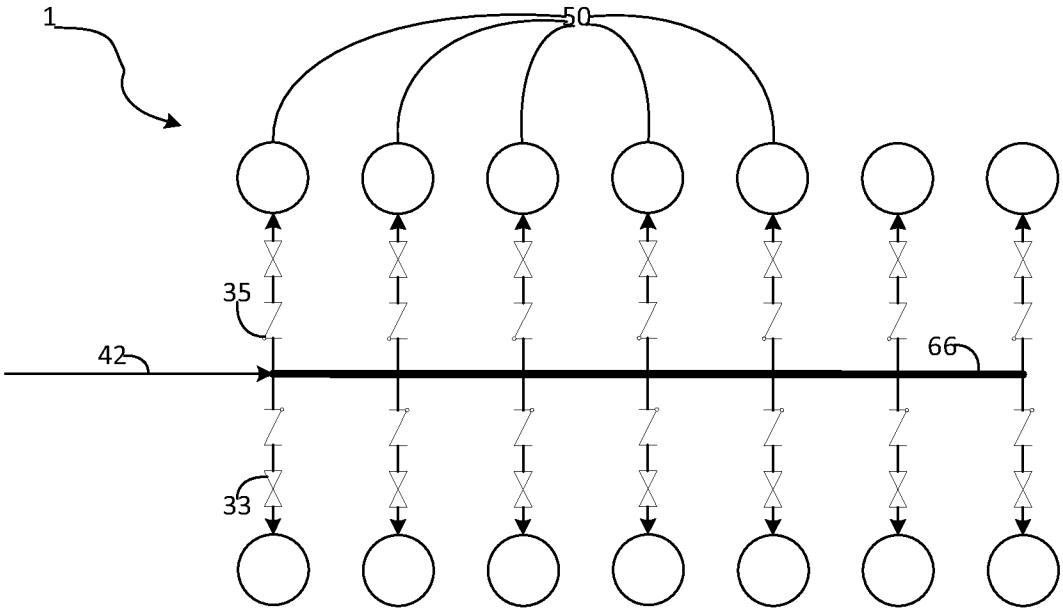


FIG. 2



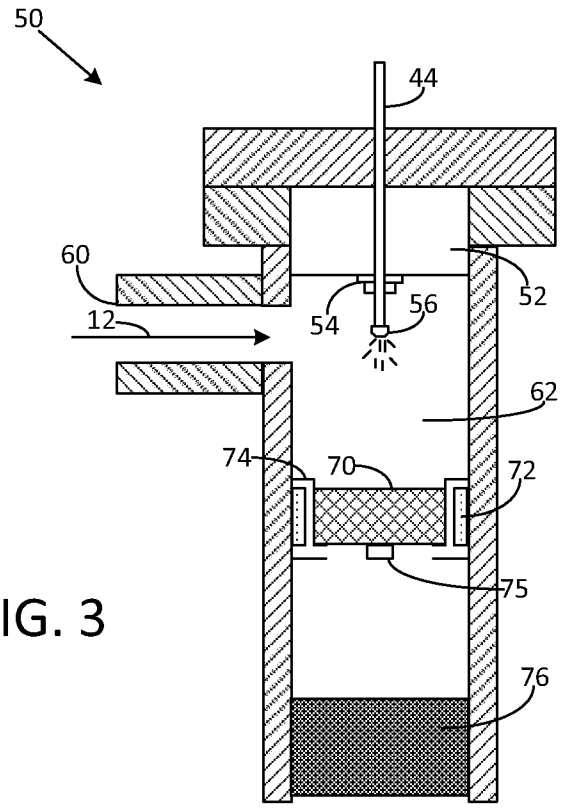


FIG. 3

FIG. 4

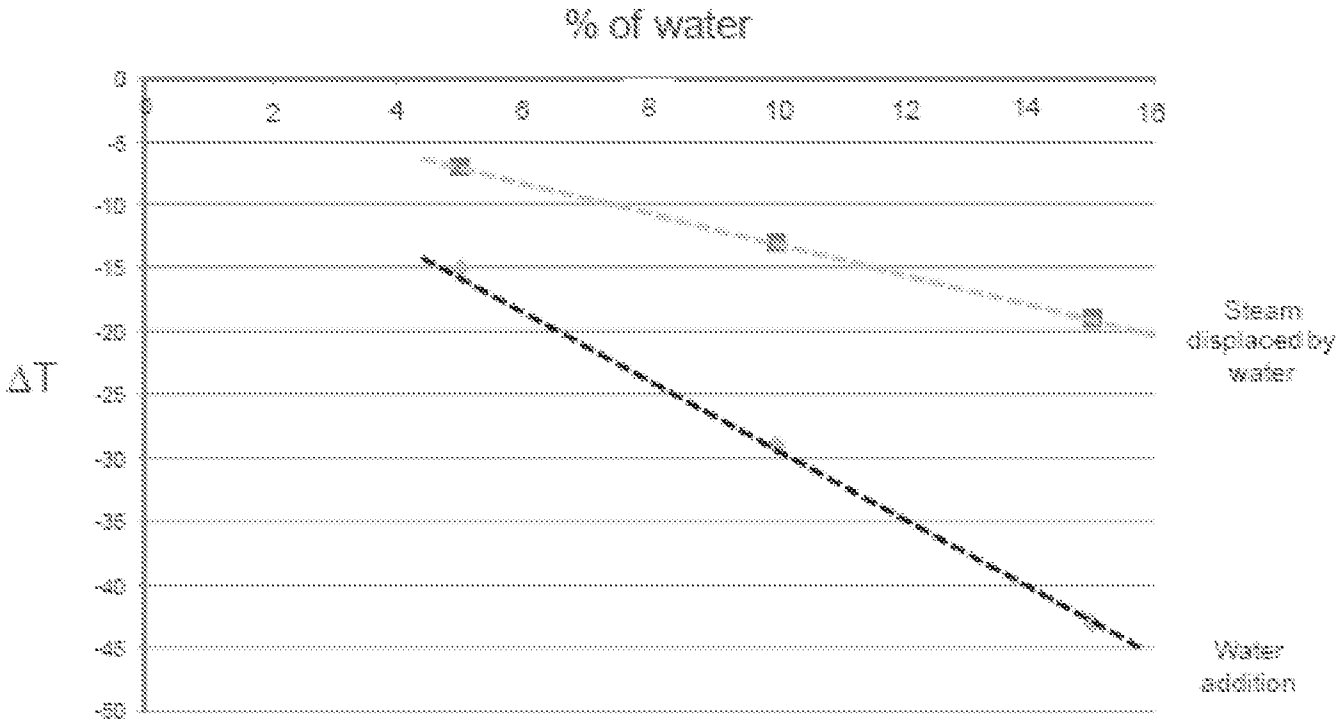
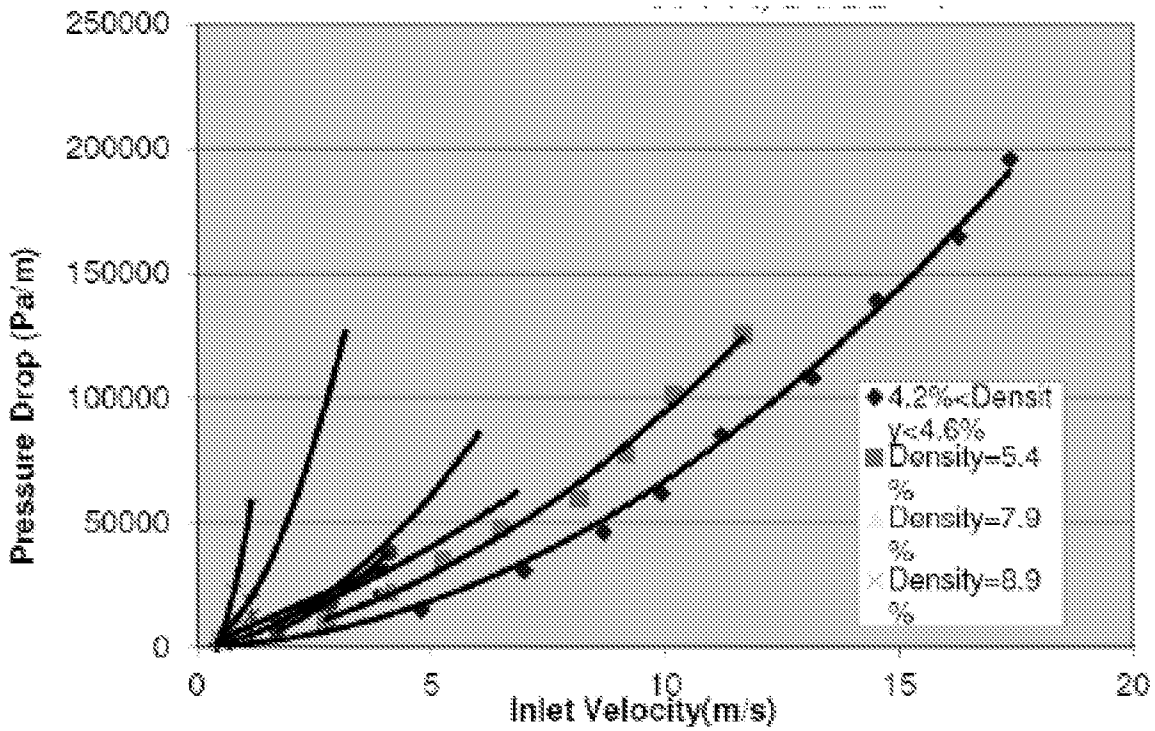

% of water
0
2
4
6
8
10
12
14
16
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
ΔT
Steam displaced by water
Water addition

FIG. 5


250000
200000
150000
100000
50000
0
Pressure Drop (Pa/m)
0
5
10
15
20
Inlet Velocity(m/s)
4.2%<Density<4.6%
Density=5.4 %
Density=7.9 %
Density=8.9 %

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068055

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/104641 A1 (AHMED M M [US] ET AL) 10 May 2007 (2007-05-10) abstract paragraphs [0001], [0009], [0010], [0013], [0039]	1-20
A	US 2010/042370 A1 (GALLARDA JEAN [FR]) 18 February 2010 (2010-02-18) abstract paragraphs [0004], [0008], [0029], [0034], [0069]	1-20
A	FR 2 888 920 A1 (AIR LIQUIDE [FR]) 26 January 2007 (2007-01-26) abstract claims 1,2,4 page 2, lines 14-20 page 3, lines 24-35	1-20

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
12 March 2015	10/04/2015

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068055

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/132179 A1 (FURTADO JADER [FR] ET AL) 3 June 2010 (2010-06-03) the whole document	1-20
A	ASHOK KUMAR RAY ET AL: "Analysis of failed reformer tubes", ENGINEERING FAILURE ANALYSIS, PERGAMON, GB, vol. 10, 1 January 2003 (2003-01-01), pages 351-362, XP002487893, ISSN: 1350-6307, DOI: 10.1016/S1350-6307(02)00029-8 the whole document	1-20

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/068055

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007104641 A1	10-05-2007	US 2007104641 A1	10-05-2007
		WO 2007056004 A1	18-05-2007
US 2010042370 A1	18-02-2010	AT 473044 T	15-07-2010
		CN 101578133 A	11-11-2009
		DK 2101906 T3	01-11-2010
		EP 2101906 A1	23-09-2009
		ES 2347833 T3	04-11-2010
		PT 2101906 E	11-10-2010
		US 2010042370 A1	18-02-2010
		WO 2008087306 A1	24-07-2008
FR 2888920 A1	26-01-2007	NONE	
US 2010132179 A1	03-06-2010	CN 101563154 A	21-10-2009
		EA 200970613 A1	30-12-2009
		EP 2114559 A2	11-11-2009
		FR 2910623 A1	27-06-2008
		US 2010132179 A1	03-06-2010
		WO 2008084172 A2	17-07-2008
		ZA 200903813 A	28-07-2010