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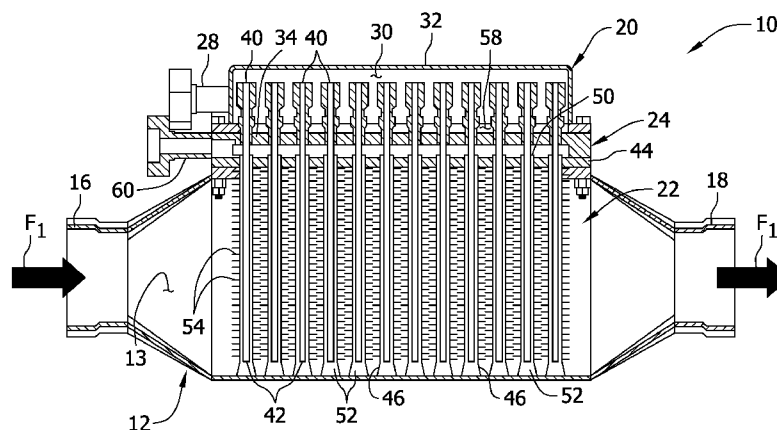
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- (54) **Title:** APPARATUS AND METHODS FOR REFORMING ETHANOL AT LOW TEMPERATURE USING POWDER CATALYSTS

**FIG. 5**

- (57) **Abstract:** Disclosed are reformer designs for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine. Also disclosed is a catalyst assembly for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine. The catalyst assembly includes a thermally-conductive, porous catalyst substrate, and an unpassivated, copper-nickel powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen.



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APPARATUS AND METHODS FOR REFORMING ETHANOL AT LOW TEMPERATURE USING POWDER CATALYSTS

BACKGROUND

[0001] The present invention generally relates to apparatus and methods for reforming alcohols.

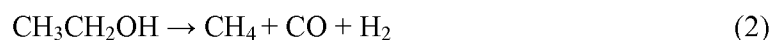
[0002] Alcohol reforming is an endothermic catalytic process that converts alcohols to a mixture of hydrogen and other gases. The product, "alcohol reformat," may be superior to the parent alcohol as a fuel for internal combustion engines. The superiority of alcohol reformat, particularly those formed from methanol and ethanol, is primarily due to the presence of hydrogen. Reformat burns faster than the starting alcohol and is more tolerant of dilution with air or exhaust. At part load, dilution benefits efficiency by reducing throttling losses and loss of heat of combustion to the coolant. In addition, the heat of combustion of reformat is greater than that of the starting alcohol. Both alcohols and reformat are high octane fuels which can tolerate high compression ratios.

[0003] In the case of excess air, the degree of dilution is typically described by the parameter lambda (λ) which represents the ratio of air introduced into the cylinders to that required stoichiometrically for combustion of the fuel. For example, methanol reformat could be utilized in an internal combustion engine with a compression ratio of 14:1 at lambda = 1.7, and achieved efficiency improvements of about 50% over gasoline at part load. See, e.g., T. Hirota, "Study of the Methanol-Reformed Gas Engine," JSAE Rev., vol. 4 (1981) 7-13; T.G. Adams, "A Comparison of Engine Performance Using Methanol or Dissociated Methanol as the Fuel," SAE Paper 845128, 1984.

[0004] Methanol reforming is typically conducted at temperatures above 250°C. The methanol reforming reaction is given in equation 1.



[0005] Some reforming catalysts contain nickel. However, an undesired side reaction, "methanation," is catalyzed by nickel at comparatively high temperatures. The methanation reaction destroys hydrogen, thus limiting the dilution which can be achieved in the engine while also reducing the enthalpy of combustion of reformat. Morgenstern and Fornango reported that copper-plated nickel sponge was active and stable for reforming of ethanol above 250°C via the pathway shown in equation 2. The catalyst is also effective for methanol reforming according to equation 1.



[0006] Using copper-plated nickel catalysts, it has been found that it is preferable to maintain catalyst temperature below 370°C and more preferably below 350°C in order to suppress methanation. Ideally, the temperature distribution of the catalyst mass is maintained as close to isothermal as possible so that all of the catalyst can maintain high activity and none is in the methanation temperature range. Copper-plated nickel sponge is an unsupported metal catalyst. Catalyst supports help to maintain the dispersion of the active metal and more structured supports can prevent catalyst movement, but they represent unproductive thermal mass.

[0007] A need still exists in the art for reforming alcohols to a mixture of gases including hydrogen which can be utilized in an internal combustion engine with high efficiency while maintaining high catalytic activity.

SUMMARY

[0008] In one aspect, a reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine generally comprises a catalytic reactor assembly, and inlet manifold assembly, and an outlet manifold. The catalytic reactor assembly includes a plurality of parallel reactor tubes having open first longitudinal ends and closed second longitudinal ends, and a plurality of catalyst assemblies disposed in the plurality of parallel reactor tubes. Each catalyst assembly includes a thermally-conductive, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen. The inlet manifold assembly includes an inlet plenum for receiving alcohol from an alcohol source, and a plurality of parallel inlet tubes extending axially through the open first longitudinal ends of the parallel reactor tubes for delivering alcohol to the catalyst assemblies. The inlet tubes have inlets disposed in the inlet plenum and outlets adjacent the closed second longitudinal ends of the reactor tubes. The outlet manifold includes an outlet plenum in fluid communication with the open first longitudinal ends of the reactor tubes for receiving the reformat mixture from the reactor tubes.

[0009] In another aspect, a reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine generally comprises a generally cylindrical, rolled reformer housing including opposing sheets of thermally conductive material defining a catalyst chamber therebetween. A catalyst assembly is disposed in the catalyst chamber. The catalyst assembly includes a thermally-conductive, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture

comprising hydrogen. The reformer further comprises an inlet header for delivering alcohol into the catalyst chamber, an outlet header for removing the reformat mixture from the catalyst chamber, and a spacer disposed between adjacent turns of the rolled reformer housing to define a plurality of exhaust plenums between the adjacent turns of the rolled reformer housing and extending longitudinally with respect to the reformer housing. The exhaust plenums define a flow path for exhaust gas from an engine to flow longitudinally through the rolled reformer in thermal contact with the opposing sheets of the rolled reformer housing.

[0010] In yet another aspect, a reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen generally comprises a shell defining a catalyst plenum having opposite first and second longitudinal ends. The shell has an inlet port adjacent the first longitudinal end of the catalyst plenum for receiving alcohol from an alcohol source, and an outlet port adjacent the second longitudinal end of the catalyst plenum for receiving the reformat mixture from the catalyst plenum. A plurality of exhaust tubes within the catalyst plenum define an exhaust flow path for an exhaust gas to flow. A catalyst assembly in catalyst plenum includes a heat-conducting, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen. The catalyst substrate includes a plurality of openings through which the exhaust tubes extend in thermal contact with the catalyst substrate.

[0011] In another aspect, a catalyst assembly for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine generally comprises a thermally-conductive, porous catalyst substrate, and an unpassivated, copper-nickel powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is an enlarged, fragmentary top plan view of a first embodiment of a catalyst assembly, including a single catalyst substrate;

[0013] Fig. 2 is an side view of the catalyst assembly in Fig. 1;

[0014] Fig. 3 is a side view of a second embodiment of a catalyst assembly, including a plurality of catalyst substrates and filters disposed between adjacent catalyst substrates;

[0015] Fig. 4 is a perspective of a reformer for reforming an alcohol to a gaseous mixture comprising hydrogen;

[0016] Fig. 5 is a longitudinal sectional view of the reformer in Fig. 4;

[0017] Fig. 6 is a perspective of a catalytic reactor assembly of the reformer in Fig. 4;

[0018] Fig. 7 is an enlarged view of one of a plurality of reactor tubes that are part of the catalytic reactor assembly of the reformer in Fig. 4;

[0019] Fig. 8 is a flow diagram for an alcohol reformat power system, such as for a vehicle, incorporating the alcohol reformer in Fig. 4;

[0020] Fig. 9 is a schematic section of modified embodiment of the reformer, similar to Fig. 7, and including an electrical heating system;

[0021] Fig. 10 is a perspective of a third embodiment of an alcohol reformer including a generally cylindrical, rolled reformer housing;

[0022] Fig. 11 is a cross section of the alcohol reformer in Fig. 10;

[0023] Fig. 12 is a sectional view of a fourth embodiment of an alcohol reformer configured in a shell and tube arrangement;

[0024] Fig. 13 is a top plan view of a catalyst substrate of the alcohol reformer in Fig. 12;

[0025] Figs. 14A and 14B are graphs of results obtained from an experiment performed in Example 4 of the present disclosure;

[0026] Figs. 15A and 15B are graphs of results obtained from an experiment performed in Example 5 of the present disclosure;

[0027] Fig. 16 is an experimental setup for Example 6 of the present disclosure; and

[0028] Fig. 17 are graph results from the experiment in Example 9.

[0029] Corresponding reference numerals indicate corresponding parts throughout the several views of the drawings.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0030] The present disclosure relates to embodiments of reformers, and associated methods, for improving efficiency and emissions of an alcohol-fueled vehicle by utilizing exhaust heat to drive an endothermic catalytic reaction of alcohols known as reforming. Disclosed embodiments of a reformer for facilitating effective heat transfer from exhaust to the catalyst. Such effective heat transfer enables rapid reformer startup, and also enables the engine to tolerate high in-cylinder dilution, which leads to higher efficiency. In one embodiment, embodiments of the catalyst assembly inside the reformer housing comprise copper-nickel

powder embedded in a heat-conducting, porous substrate that provides effective heat transfer to the catalyst. The porous substrate serves as a heat-transfer medium for transferring heat to the copper-nickel powder. In addition, internal filters may be disposed in the reformer housing to inhibit catalyst movement inside the reformer housing.

[0031] Referring to FIGS. 1 and 2, one embodiment of a catalyst assembly, for use with an alcohol reformer, is generally indicated at reference numeral 2. The catalyst assembly 2 includes a heat-conducting, porous catalyst substrate 4, and a powder catalyst 6 loaded on the substrate. The catalyst 6 may be embedded in the porous catalyst substrate 4, as shown in FIG. 1, or otherwise applied to a surface of the substrate. In one embodiment, the catalyst substrate 4 includes one or more sheets of metal mesh or felt including heat conducting fibers. The powder catalyst 6 can be easily applied to the substrate sheets and the catalyst-loaded substrate sheets then serve as convenient catalyst carriers during assembly of the reformer, providing a catalyst bed with high catalyst density and excellent thermal conductivity. The catalyst substrate 4 may include mesh, such as mesh including iron-chromium fibers (e.g., Fecralloy fibers). Examples of suitable materials for the catalyst substrate 4 include G-Mat, a Fecralloy mesh product from Micron Fiber-Tech of Debary, FL and Sinterflo F and M media from Porvair of Ashland, VA. The substrate 4 may comprise other materials, such as copper gauze (described in Example 4), steel wool, or loose metal fibers, or other fibrous metal.

[0032] In one example, the powdered catalyst 6 is loaded onto the porous catalyst substrate 4 without passivation and without the use of aggressive and time-consuming techniques such as roller mills. Copper-nickel powdered catalysts, particularly copper-plated nickel sponge, are weakly ferromagnetic if they have not been dried and passivated. The interparticle attraction causes slurries of unpassivated catalyst to have a thick consistency similar to peanut butter, allowing a thick layer of catalyst 6 to be applied to the porous substrate 4 (e.g., metal mesh, foil, or screen) by spreading a slurry (e.g. heavy slurry including at least 50% catalyst by weight) onto one or both external surfaces of the substrate 4. A magnetic force can be used to move the weakly ferromagnetic catalyst 4 into the porous substrate 4 to embed the catalyst in the porous substrate.

[0033] Referring to FIG. 3, in one embodiment, the catalyst assembly 2 may also include filters 8 disposed between adjacent sections or stages 9 of catalyst substrates. The filters 8 inhibit movement of the powdered catalyst 6 within the reformer, particularly if the catalyst is arranged in the stages 9. The filters 8 may comprise fibrous metal depth filter media such as Bekipor media from NV Bekaert SA, Zwevegem,-Belgium, fibrous metal depth filters from

Mott Corporation, Farmington, CT, sintered metal material, or other material. In at least some embodiments, the filters comprise disks (or substrates) of heat transfer media between catalyst stages. The heat transfer filters 8 may be metal meshes, wools, or foams that are low in nickel although carbon foams can also be used due to their high thermal conductivity. Examples of suitable heat transfer media include steel and copper wool, the aforementioned metal meshes such as G-Mat and sintered metals. The filters 8 promote heating and alcohol evaporation and act as a trap for trace non-volatile compounds in the fuel stream, such as tarry components of gasoline used in E85 or similar fuels.

[0034] Referring to FIGS. 4-7, a first embodiment of a reformer, suitable for use with the catalyst assembly 2 for reforming an alcohol to a gaseous mixture comprising hydrogen, is generally indicated at 10. The reformer 10 includes an exhaust duct, generally indicated at 12, to drive the endothermic catalytic reaction of alcohols. The exhaust duct 12 defines an exhaust plenum 13, and includes inlet and outlet ports 16, 18 for use in coupling the exhaust duct within (in line with) an exhaust system of the alcohol-fueled vehicle so that the exhaust gas flows through the exhaust plenum, as indicated by reference character F_1 in FIG. 5. Referring to FIGS. 4 and 5, the reformer 10 includes an alcohol (inlet) manifold assembly, generally indicated at 20, a catalytic reactor assembly, generally indicated at 22 (see also FIG. 6), and a reformat (outlet) manifold, generally indicated at 24. The alcohol (inlet) manifold assembly 20 includes an inlet coupling 28, for coupling with a source of alcohol, in fluid communication with an alcohol (inlet) plenum 30. Referring to FIG. 5, the plenum 30 is defined by a cover 32 mounted on a perforated plate 34. A plurality of parallel inlet tubes 36 extend through openings 38 in the perforated plate 34 such that inlets 40 of the inlet tubes are within and in fluid communication with the inlet plenum 30, and outlets 42 of the inlet tubes are outside the plenum.

[0035] Referring to FIGS. 5 and 7, the catalytic reactor assembly 22 includes a perforated plate 44, and a plurality of parallel reactor tubes 46 extending outward from the plate. The perforated plate 44 is mounted on the exhaust duct 12 such that the reactor tubes 46 extend into the exhaust plenum 13 in thermal communication with the exhaust flow F_1 . The reactor tubes 46 have open ends 50 (which function as outlets for reformat, as explained below), and opposite closed ends 52 in the exhaust plenum 13. The reactor tubes 46 are made from heat-conducting material, and each reactor tube 46 includes a plurality of axially spaced-apart heat-conducting fins 54 extending radially outward from the exterior surface of the tube, within the exhaust plenum 13.

[0036] The perforated plate 34 of the alcohol (inlet) manifold assembly 20 is mounted on the perforated plate 44 of the catalytic reactor assembly 22 such that the inlet tubes 36 extend axially into the reactor tubes 46 and the outlet 42 of the inlet tubes are generally adjacent to the closed ends 52 of the reactor tubes. The perforated plates 34, 44 are spaced apart to define a reformat (outlet) plenum 58 of the reformat (outlet) manifold 24 therebetween, which is in fluid communication with an outlet coupling 60. Referring to FIG. 7, the catalyst assembly 2 (or a different catalyst assembly) is disposed within the annular space 48 defined between the interior of each reactor tube 46 and the exterior of the corresponding inlet tube 36. For example, the catalyst assembly may include the catalyst stages 9 that are separated by the filters 8. Moreover, inlet and outlet filters 8 may be positioned at ends of the catalyst assembly 2.

[0037] In use, alcohol (which may already be vaporized) flows into the alcohol (inlet) plenum 30 and into the inlet tubes 36. The alcohol then enters the reactor tubes 46, via the outlets 42 of the inlet tubes 36, adjacent the closed ends of the reactor tubes, and flows axially through the catalysts assemblies 2 disposed in the annular spaces 48 defined between the reactor tubes 46 and the corresponding inlet tubes 36. After flowing through the catalyst assemblies 2, the reformed alcohol flows through the open ends 50 of the reactor tubes 46 and into the reformat (outlet) plenum 58 of the reformat (outlet) manifold 24. The reformed alcohol exits the reformer 10 through the outlet coupling 60. The individual reactor tubes 46 may be 0.5 in to 2 inches in diameter. The inlet tubes 36 may be 1/8-1/4-inch in diameter. The catalyst substrate 4 and the internal filters 8 the annulus between the tubes 36, 46 may be copper mesh, gauze, or wool because of its good thermal conductivity. Also, copper is more flexible, making it easier to insert into the annulus.

[0038] Referring to FIG. 8, an alcohol reformat power system, such as for a vehicle, incorporating the alcohol reformer 10, is generally indicated by reference numeral 70. The alcohol reformat power system includes an engine 72, and an alcohol reforming system 74. Exhaust from the engine 72 flows to the reformer 10 through a first exhaust line 76, and flows from the reformer to a vaporizer 78 through a second exhaust line 80. The first exhaust line 76 couples to the inlet port 16 of the exhaust duct 12 in FIGS. 4 and 5. The alcohol is pumped, via pump 82, from a tank 84 (e.g., a source) through a reformat cooler 86 and a vaporizer 88 before flowing through the reformer 10 via an alcohol inlet line 90 which is coupled to the inlet coupling 28. After flowing through the reformer 10, the reformed alcohol flows through an

alcohol outlet line 92, which is coupled to the outlet coupling 60, to the reformat cooler 86, and then to the engine for combustion.

[0039] Referring to FIG. 9, a modified version of the first embodiment of the reformer is generally indicated at 110. This reformer 110 is similar to the first reformer 10, with like components indicated by corresponding reference numeral plus 100. The main difference between the first reformer 10 and the modified reformer 110 is that the modified reformer includes an electrical heating system 193 for delivering electrical current to the reformer to heat the reformer. The electrical heating system 193 includes an electrical power source 194 (e.g., a battery) and electrical lead 195 electrically connected to the inlet tubes 136. The reformer 110 is grounded for safety. The inlet tubes 136 have lateral inlet openings 140 through which the alcohol enters the tubes. The inlet tubes 136 are electrically isolated through the use of swaged connections with insulating ferrules 197 or by similar components. Vespel™ may be used for the insulating ferrules 197 as it can withstand temperatures up to 350°C. The internal filters 108 of the catalyst assemblies 102 may be electrically non-conductive. For example, the internal filters may be glass wool or other electrically non-conductive material. Moreover, a glass cylinder 198 retains an upper internal filter in the reactor tube 146. Electrical startup is achieved by passing either direct or alternating current through the inlet tubes 136. The power source 194 may be the battery or the alternator of the vehicle. Preferably, current is not passed through the reformer 110 until exhaust temperature entering the reformer is at least 200°C. Otherwise, the exhaust will cool the catalyst assembly 102.

[0040] Referring to FIGS. 10 and 11, a third embodiment of a reformer for reforming an alcohol to a gaseous mixture comprising hydrogen is generally indicated at 210. This reformer 210 includes a generally cylindrical, rolled reformer housing, generally indicated at 12, and a catalyst assembly 14. The reformer housing 12 includes opposing metal layers or sheets 16 defining a catalyst chamber 18 therebetween, in which the catalyst assembly 14 is disposed. The metal sheets 16 are rolled and a spacer 20 is provided between adjacent turns of the rolled reformer housing 12. The metal sheets 16 serve to transfer heat from exhaust to catalyst assembly 14, and are preferably no thicker than required in order to withstand maximum reformer pressure and are formed from alloys which are stable to hot exhaust and ethanol. The metal sheets may be formed from stainless steels and/or copper-rich alloys such as Monel. The spacer 20 may be in the form of a sheet including a plurality of channels extending longitudinally with respect to the housing 12. Thus, the spacer 20 at least partially defines a plurality of exhaust plenums 22 extending along the reformer housing, and through which

exhaust flows in thermal contact with the metal sheets. The catalyst chamber 18 is generally at higher pressure than exhaust plenums 22, so the spacer 20 provides mechanical support for the exhaust plenums, without creating significant exhaust backpressure, to inhibit collapse of the exhaust plenums 22. In another example, the spacer may comprise a plurality of structures spaced apart along the turns of the rolled reformer housing 12 to define the plurality of exhaust plenums 22 extending along the reformer housing.

[0041] Inlet and outlet headers 24, 26, respectively, for introducing ethanol into and withdrawing reformat from the catalyst chamber 18, extend longitudinally at the outer circumference of the housing 12 and the inner circumference of the housing, respectively, in fluid communication with the catalyst chamber 18. It is understood that the locations of the inlet and outlet headers 24, 26, respectively, can be reversed. Opposite longitudinal edges 28 of the metal sheets 16 are sealed, such as by laser welding, furnace brazing or other ways, so as to seal the catalyst assembly 14 in the catalyst chamber 18 and prevent exhaust from entering the catalyst chamber.

[0042] Referring to FIG. 12, another embodiment of a reformer for reforming an alcohol to a gaseous mixture comprising hydrogen is generally indicated at 310. The reformer is generally of a shell and tube design, wherein the reformer includes tubes 312 for receiving exhaust that are disposed within a shell or housing 314 for receiving alcohol. The exhaust tubes 312 may be constructed from stainless steels and copper-rich alloys such as Monel. Inlet and outlet couplings 316, 318, respectively, for coupling with the exhaust line are in fluid communication with the exhaust tubes 312. Alcohol inlet and outlet ports 320, 322, respectively, are in fluid communication with the interior of the shell 314. The catalyst assembly 302 is received in the shell 314. The catalyst assembly 302 may be similar to the catalyst assemblies 2, 102, 202, and may include catalyst stages 308 separated by internal filters 309, as illustrated. The catalyst substrates 304 and internal filters 309 have openings 324, 326, respectively, through which the exhaust tubes 312 extend in thermal contact with the substrates and filters. The reformer 310 also includes baffles 328 for directing the flow of alcohol through the catalyst assembly 302. The baffles 328 also include openings 330 through which the exhaust tubes 312 extend, and cutouts 332 through which the alcohol flows. Heat from the exhaust flowing through the exhaust tubes 312 is transferred to the thermally conductive substrates 304 and filters 309 to heat the powdered catalysts 306 on the substrates and the alcohol flowing through the catalyst substrates.

[0043] In one example, of the reformer 310, a copper-nickel catalyst is impregnated onto Fecralloy mesh disks 304 which are perforated with the holes 324 to accommodate the exhaust tubes 312. Multiple catalyst stages 308 composed of stacks of such disks 304 followed by a similarly perforated layer of fibrous metal depth filter material 309. Accordingly, catalyst zones 308 and catalyst free zones 309 alternate to facilitate reheating of the alcohol-reformate stream in the shell 314.

[0044] In yet another embodiment, the reformer be a lightweight plate-and-frame design into which rectangular pieces of catalyst substrate 4 coated with copper-plated nickel sponge 6 are inserted. A suitable reformer housing is a heat exchanger, marketed as the "Catacel[®]" by fuel cell materials.com and described in patent publication US 2008/0072425, the entirety of which is hereby incorporated by reference.

EXAMPLES

[0045] The following examples are merely illustrative, and not limiting to this disclosure in any way.

Example 1

[0046] This Example describes the preparation of copper-plated nickel sponge. The product is a wet catalyst slurry which can be applied directly to fibrous metal supports such as G-Mat.

[0047] 796 g of Raney Nickel 2800 (WR Grace, purchased through Spectrum) was weighed out under water by Archimedes' method in a 4-liter beaker assuming a density factor of 1.16. The supernatant was decanted. 619 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (JT Baker and EMD, 20% copper with respect to substrate) was dissolved in 2508 g of Versene 100 (Dow via Spectrum), 1.05 equiv of Na_4EDTA with respect to copper) and added to the catalyst. The slurry was stirred with an overhead stirrer and 1.0 equivalents of 50% NaOH (198 g) was added dropwise over 31 minutes. The pH rose from 8.5 to 12.0. The final temperature was 50°C.

[0048] The dark blue supernatant was decanted and the beaker wrapped with heating tape. 973 g of hot 50% gluconic acid (Alfa Aesar) was added along with 0.5 liters of water. Heating and stirring were initiated. A solution of 309 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (EMD, 10% copper with respect to substrate) in 1.2 liters of water was added dropwise over 201 minutes with five minutes of additional stirring. The pH fell from 4.2 to 2.1 and the temperature rose from 56°C to 69°C.

[0049] The brown catalyst was rinsed twice with three liters of deionized water. The dull brown catalyst was stored under water.

Example 2

[0050] This Example describes preparation of copper-plated nickel sponge by the method of Example 1 followed by drying and passivation with air.

[0051] 788 g of Raney Nickel 2800 (WR Grace, purchased through Spectrum) was weighed out under water by Archimedes' method in a 4-liter beaker assuming a density factor of 1.16. The supernatant was decanted. 626 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (JT Baker and EMD, 20% copper with respect to substrate) was dissolved in 2480 g of Versene 100 (Dow via Spectrum), 1.05 equiv of Na_4EDTA with respect to copper) and added to the catalyst. The slurry was stirred with an overhead stirrer and 1.0 equivalents of 50% NaOH (201 g) was added dropwise over 32 minutes. The pH rose from 8.4 to 12.5. The final temperature was 57°C.

[0052] The dark blue supernatant was decanted and the beaker wrapped with heating tape. 983 g of hot 50% gluconic acid (Alfa Aesar) was added along with 0.5 liters of water. Heating and stirring were initiated. A solution of 313 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (EMD, 10% copper with respect to substrate) in 1.2 liters of water was added dropwise over 160 minutes with five minutes of additional stirring. The pH fell from 3.9 to 2.0 and the temperature rose from 53°C to 77°C.

[0053] The brown catalyst was rinsed twice with three liters of deionized water. The catalyst was dried overnight under vacuum at 120°C with nitrogen purge. The dry catalyst (851 g) was allowed to cool in the oven under nitrogen, and then poured out in portions into a lasagna pan in the sink, with running water keeping the outside of the pan cool and continuous stirring of the powder with a spatula. A little water (a few ml each time) was added every few minutes to control the temperature and mixed thoroughly with the catalyst by stirring. Some sparking was seen initially. The process took ten minutes. The pan then sat out for another hour to complete oxidation before re-drying the catalyst under the same conditions. 912 g of passivated dry catalyst was recovered.

Example 3

[0054] This Example describes a simple reformer built to determine the heat transfer properties of powder beds of copper-plated nickel sponge.

[0055] A large reformer was fabricated out of Monel with a cylindrical catalyst chamber, two inches in diameter. Surrounding the catalyst chamber through which hot nitrogen passed as a simulant of automotive exhaust. The bottom of the reactor was packed with glass wool supported on a metal screen with holes in it. Nine 1/16" thermocouples were fed through the bottom to different depths and in several radial positions. The depth of the chamber from the flange to the glass wool was five inches with no catalyst in the reformer.

[0056] 267.0 g of dry passivated copper-plated nickel sponge prepared according to the procedure of Example 2 was poured into the reformer forming an even cylindrical bed. No packing (such as G-Mat) was used. The bed depth was 2.25 inches. More glass wool was added above the bed in order to prevent a focused stream of ethanol from excavating a divot in the top of the catalyst bed.

[0057] Absolute ethanol was fed from the top after preheating in an evaporator and using a heat exchanger which exchanges heat between nitrogen exiting the reformer and incoming steam or ethanol. Reformate composition was monitored using a Micro-GC from Agilent.

[0058] Very little variation in catalyst temperature with depth was seen. Catalyst temperature is reported as a function of radius, representing an average of a group of thermocouples near the catalyst chamber wall, on the midline and a group at intermediate positions.

Example 4

[0059] This Example demonstrates the substantial temperature gradients that develop in beds of copper-plated Raney nickel and the use of a fibrous metal medium to largely eliminate the gradient.

[0060] The reactor system and catalyst bed of Example 3 was operated using a 5 ml/min feed rate of ethanol. The ethanol and nitrogen flowrates and nitrogen temperatures are given in Table 1 below.

[0061] After performing the experiment, the catalyst was removed from the reformer and then re-loaded mixed with 28 2-inch disks formed from copper gauze. (Copper Knitted Wire Industrial Cleaning Mesh). 28 of the disks weighing a total of 17.92 g were placed in the reformer along with the catalyst. The stack of disks extended to near the top of the catalyst bed, but did not quite reach the upper surface of it. When the catalyst was removed from the reactor it was gray in color and not pyrophoric or self-heating.

[0062] As originally prepared, the catalyst bed had cracks which disappeared over several hours of operation with occasional tapping on the reformer wall. The experiment in Table 1 was then repeated. Temperature profiles without and with copper gauze are shown in Figs. 14A and 14B, respectively. As seen in Figs. 14A and 14B, the copper gauze greatly reduced the temperature gradient across the radius of the reactor particularly between the wall and intermediate thermocouples.

Table 1: Protocol used in Example 4.

Experiment time (min)	Ethanol flowrate (ml/min)	N ₂ temperature	N ₂ flowrate (slpm)
0-70	0	520°C	200
70-160	5	520°C	200
160-250	5	540°C	200
250-340	5	560°C	200
340-430	5	580°C	200
430-460	0	No heat	200

Example 5

[0063] This Example demonstrates that methanation emerges when the catalyst temperature exceeds 350°C.

[0064] The reactor and catalyst of Examples 3 and 4 were used with the ethanol and nitrogen flowrates and nitrogen temperatures given in Table 2. This data was obtained with copper mesh incorporated into the catalyst bed. With constant nitrogen temperature and flow, the steady decrease of ethanol flowrate led to steadily increasing catalyst temperatures and eventually to methanation. The data is shown in Figs 15A and 15B.

[0065] Results showed a dramatic increase in methane formation relative to other permanent gases (H₂ and CO) after the decrease in ethanol flow from 4 to 2 ml/min at 310 minute experiment time. Catalyst temperatures were about 390°C at this point. A smaller increase in methanation is apparent at the previous flow change at 250 minutes with catalyst temperatures about 380°C.

Table 2: Reactor conditions used in Example 5.

Experiment time (min)	Ethanol flowrate (ml/min)	N ₂ temperature	N ₂ flowrate (slpm)
0-70	0	550°C	200
70-130	10	550°C	200
130-190	8	550°C	200
190-250	6	550°C	200
250-310	4	550°C	200
310-370	2	550°C	200
370-430	1	550°C	200
430-460	0	No heat	200

Example 6

[0066] This example describes the use of dry, passivated copper-plated nickel sponge prepared by the method of Example 2 impregnated into Fecralloy mesh in an HEP or “Catacel” plate-and-frame reformer described above.

[0067] The reformer had multiple (9) rectangular flow channels for the engine exhaust sandwiched between similar number of flow channels for the ethanol-reformate. A commercial Flat Plate heat exchanger was used for reformate cooling; a finned pipe heat exchanger was used as a vaporizer; and a catalytic hydrogen burner was used to generate hot stream of exhaust simulant. The configuration is shown in Fig. 16.

[0068] The HEP reformer had about 0.165 sq meter heat transfer area and weighed less than 500 g without flanges. Nine strips (23 cm L x 4 cm W x 0.16 mm thick) of a porous metal felt (G-Mat from Micron Fiber-Tech) were oxidized in air at 800°C for 16 hr and then cooled down naturally. The oxidized strips were compressed and inserted into the nine HEP channels. An aqueous slurry of copper-plated nickel sponge that had been dried and air-passivated by the procedure of Example 2 were loaded onto HEP channels and the porous felt strips were soaked for several minutes. The slurry solution was then drained out. The HEP loaded with wet catalyst was put into the furnace filled with N₂ and dried at 120°C. The soaking and drying procedures were repeated for three times. The HEP was weighed before and after catalyst loading to obtain the amount of catalyst loading. The typical catalyst weight value by this method is 95 g.

[0069] The vaporizer, a finned tube, was placed coaxially inside the hot exhaust pipeline after the HEP. The total heat transfer area of the vaporizer was 0.137 m².

[0070] Heat was introduced into the reaction chambers by the catalytic combustion of hydrogen in the burner. The heat of combustion (LHV) was about 1.4 kW while the H₂ feed rate to the burner was ~8.4 slpm during the test. The flow rate of the air to the burner was set to 141 slpm.

[0071] An ethanol-rich fuel known as Synasol 190 was used as the feed. Its composition was 83% ethanol, 6.8% water, 3.5% methanol; 5.0% ethyl acetate and ~1% other impurities). This fuel was fed parallel (co-current) to the simulated exhaust with the HEP reformer in a horizontal orientation. No internal filters were used. Some catalyst blew out of the reformer over the course of the experiment as a result. Synasol 190 flowrates of 12 and 24 ml/min were tested. The results are shown in Table 3. Conversions were about 50%, likely due to channeling in the catalyst bed which in turn is due to the lack of internal filters.

Table 3: Temperature and conversion data for the plate-and-frame reformer in Example 6.

Synasol flow	Exhaust Temp		Synasol/reformate Temp		Conversion
	Inlet	Outlet	Inlet	Outlet	
12 ml/min	375°C	310°C	240°C	310°C	50%
24 ml/min	400°C	330°C	240°C	320°C	47%

Example 7

[0072] This Example describes the construction of a shell-and-tube reformer with multiple catalyst stages.

[0073] The catalyst was copper-plated Raney nickel 4200 prepared without catalyst drying by the procedure of Example 1. The shell was a 24-inch length of Schedule 10, type 304 stainless steel pipe with an internal diameter of 6.32 inches. 24-inch lengths of ¼-inch i.d. stainless steel tubes were used for the exhaust.

[0074] Several types of internals were used in the reformer all of which were perforated with holes for the exhaust tubes using the patterns in Figure 9. Baffles were cut from 1/16" stainless steel. Fecralloy mesh (G-Mat) disks were cut using a waterjet cutter which was also used to cut the baffles. The same pattern was used for Beckaert metal fiber depth filter material, for a metal foam heat transfer material, semi-sintered S-Mat, available in sheets from Micron Fiber-Tech of Debary, F, and for two ½-inch thick tubesheets.

[0075] Approximately 2.5 kg of catalyst was spread onto 36 G-Mat disks using a metal spatula. After spreading catalyst onto one side of the disk, the disk was turned over and a heavy duty magnet (Edmunds, item no. 3071135) rubbed over it in order to pull catalyst into the mesh and perhaps slightly magnetize the disk in order to improve its catalyst holding power. More

catalyst was then applied to the disk using the spatula. Some catalyst was gently knocked out of most of the holes in the disk. The stack of 36 loaded disks stood 3.4 inches high wet and without compression or 11 disks/inch.

[0076] The first step in reformer assembly was forming a stack of the internals. A tube sheet was placed on the work table and six tubes inserted symmetrically around the periphery to hold and align the stack. The reformer internals were threaded onto the six tubes, taking care to maintain correct alignment. The sequence of internals is shown in Table 4.

Table 4: Stack of reformer internals for the shell-and-tube reformer of Example 7.

Reformer Stage	Layer No.	Component	Baffles
Evaporator/preheat		Inlet tube sheet	
	1	G-Mat (2 disks) w/o catalyst	
	2	S-Mat (2 disks)	
	3		Old baffle
	4	G-Mat (12 disks) w/o catalyst	
	5	S-Mat (3 disks)	
	6		Old baffle
	7	S-Mat (5 disks)	
	8		Old baffle
	9	G-Mat (18 disks) w/o catalyst	
	10		Old baffle
	11	S-Mat (3 disks)	
Catalyst Stage 1	12		Bottom-cut baffle
	13	G-Mat (6 disks) w/ catalyst	
	14		Top-cut baffle
	15	Bekaert disk	
	16		Bottom-cut baffle
	17	S-Mat disk	
	18		Top-cut baffle
	19	S-Mat disk	
Catalyst Stage 2	20		Bottom-cut baffle
	21	G-Mat (5 disks) w/ catalyst	
	22		Top-cut baffle
	23	Bekaert disk	
	24		Bottom-cut baffle
	25	S-Mat disk	
	26		Top-cut baffle
	27	S-Mat disk	
Catalyst Stage 3	28		Bottom-cut baffle
	29	G-Mat (6 disks) w/ catalyst	
	30		Top-cut baffle
	31	Bekaert disk	
	32		Bottom-cut baffle
	33	S-Mat disk	
	34		Top-cut baffle

	35	S-Mat disk	
	36		Bottom-cut baffle
Catalyst Stage 4	37	G-Mat (6 disks) w/ catalyst	
	38		Top-cut baffle
	39	Bekaert (2 disks)	
	40		Bottom-cut baffle
	41	S-Mat disk	
	42		Top-cut baffle
	43	S-Mat disk	
	44		Bottom-cut baffle
Catalyst Stage 5	45	G-Mat (6 disks) w/ catalyst	
	46		Top-cut baffle
	47	Bekaert disk	
	48		Bottom-cut baffle
	49	S-Mat disk	
	50		Top-cut baffle
	51	S-Mat disk	
	52		Bottom-cut baffle
Catalyst Stage 6	53	G-Mat (9 disks) w/ catalyst	
	54		Top-cut baffle
	55	Bekaert disk	
	56		Bottom-cut baffle
Exit Filter	57	Bekaert (2 disks)	
		Exit tube plate	

[0077] After the stack was fully assembled, it was inserted into the shell followed by the second tube sheet. A few more tubes were fed through to maintain alignment of the internals. The two tubesheets were then tack-welded flush into the shell. The exhaust tubes were then hammered into the reformer. After all of the exhaust tubes were inserted, the tube sheets were completely welded into the shell. The exhaust tubes were then welded into the tube sheet and, if necessary, cut flush with the tube sheet surfaces.

[0078] The reformer was fitted with a shroud which was coupled to the exhaust cones. A fraction of the exhaust passes around the reformer between the shell and the shroud, accelerating heatup and thermal expansion of the shell. This was intended to prevent the exhaust tubes from heating up faster than the shell, creating thermal stress.

[0079] 5/32" welding rod was welded to the shell in the longitudinal direction serving as a spacer. Sheet metal (18-gauge stainless steel) was cut in a rectangular shape and holes punched in order to accommodate the thermocouple ports. The sheet metal was creased between each port to allow for thermal expansion of the shroud. The shroud was then wrapped around the welding rods and welded to each of the thermocouple ports, creating a 5/32-inch channel for bypassed exhaust.

[0080] In this form, too much exhaust would be diverted around the reformer, since the cross section of the aperture created by the shroud is about 30% of the total cross sectional area of the reformer exhaust tubes. Therefore, flow through this channel was restricted by welding three six-inch lengths of 5/32" welding rod, bent to match the radius of curvature of the reformer shell, into the aperture between the shroud and the shell on the exit side. This blocked 18 inches of the aperture leaving only about three inches of open area for exhaust flow. The reformer including shroud and thermocouple ports weighed 75 pounds.

Example 8

[0081] This Example describes the modification of a Ford 5.4-liter 8-cylinder engine for operation with the alcohol reformer of Example 7 and E85 fuel.

[0082] The engine had three valves per cylinder with dual equal cam retard capability. The compression ratio was increased to 12:1 by increasing the piston height while maintaining a completely flat piston crown. E85 or gasoline was injected through port fuel injectors. Hydrogen gaseous fuel injectors manufactured by Quantum (P/N 110764-001) were used to introduce reformat fuel just upstream of the liquid fuel in the intake ports.

[0083] External EGR capability was added using a stainless steel pipe to direct exhaust flow from the engine's right bank exhaust manifold flange to the EGR valve. Engine specifications are given in Table 5.

Table 5: Engine specifications for an eight-cylinder engine operated using ethanol reformat and E85 fuel.

Properties	Value	Unit
Engine Type	4-Stroke	-
Combustion System	Spark-Ignited	-
Charging System	Naturally Aspirated	-
Fuel Injection System	Dual Port Fuel Injection	-
Valve Configuration	SOHC: 2 Intake – 1 Exhaust	-
Engine Configuration	V8	-
Displacement	5.4	L
Bore	90.2	Mm
Stroke	105.8	Mm
Compression Ratio	9.8:1	-
Conn Rod Length	169.1	Mm
Piston Pin Offset	1.0	Mm

Valvetrain	Dual Equal Variable Cam Timing	-
Rated Power	233	kW
Rated Speed	5000	Rpm
Peak Torque	515	Nm
Peak Torque Speed	3750	Rpm
Fuel	Gasoline / E85 & Reformate	

[0084] The reformer was inserted in the exhaust train downstream of the catalytic converters. A diverter valve placed in the exhaust stream controlled the amount of exhaust flow directed into the reformer.

Example 9

[0085] This Example describes the performance of the engine and reformer of Examples 7 and 8 when operating at 5.41 bar BMEP, 1500 rpm on certified E85 fuel.

[0086] The data is at steady state. Liquid components of the reformate stream (primarily gasoline and unreacted ethanol) were condensed out of the stream because droplets of liquid fuel caused combustion noise when they passed through the gaseous fuel injectors. Onboard a vehicle, the condensate would be routed to liquid port fuel injectors or back to the fuel tank. The reformer was heated only by exhaust. Exhaust backpressure across the reformer was too low to measure.

[0087] 30% of the fuel was supplied to the engine through the reformer with the balance through the port fuel injectors. The engine was run lean with the maximum cam retard compatible with stable engine operation, conventionally defined as the coefficient of variation (COV) of IMEP less than 2%. As seen in Figure 10, stable operation was achieved with reformate at a lambda value of 1.5, compared to 1.35 for E85 liquid fuel only and 1.2 for gasoline. NOx levels were low enough (about 4 g/kWh) to enable the economical use of a lean NOx trap, which is not the case for E85 or gasoline. It is therefore necessary to operate these fuels at lambda =1.

[0088] The resulting efficiency gains for the engine operating lean on 30% reformate are 13.4% relative to optimized E85 operation on the same engine at $\lambda=1$, compression ratio 12:1 and 19.6% relative to optimized gasoline operation on the same engine at $\lambda=1$, compression ratio 10:1. The gains would be approximately 1% less if the fuel required to regenerate the lean NOx trap were accounted for. Exhaust gas temperatures are adequate to maintain reformer

operation as seen in Fig. 17, particularly given the excellent heat transfer efficiency achieved in the shell-and-tube reformer.

What is claimed is:

1. A reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine, the reformer comprising:
 - a catalytic reactor assembly including
 - a plurality of parallel reactor tubes having open first longitudinal ends and
 - 5 closed second longitudinal ends, and
 - a plurality of catalyst assemblies disposed in the plurality of parallel reactor tubes, wherein each catalyst assembly includes a thermally-conductive, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen;
 - 10 an inlet manifold assembly including
 - an inlet plenum for receiving alcohol from an alcohol source, and
 - a plurality of parallel inlet tubes extending axially through the open first longitudinal ends of the parallel reactors tubes for delivering alcohol to the catalyst assemblies, wherein the inlet tubes have inlets disposed in the inlet plenum and outlets adjacent the closed
 - 15 second longitudinal ends of the reactor tubes; and
 - an outlet manifold including an outlet plenum in fluid communication with the open first longitudinal ends of the reactor tubes for receiving the reformat mixture from the reactor tubes.
 - 2. The reformer set forth in claim 1, wherein each catalyst assembly surrounds a corresponding one of the inlet tubes in the corresponding reactor tube and is in thermal contact with an interior wall of the corresponding reactor tube.
 - 3. The reformer set forth in claim 2, wherein the powder catalyst includes a copper-nickel catalyst configured to reform alcohol at a temperature below about 400 °C.
 - 4. The reformer set forth in claim 3, wherein the catalyst assembly includes at least two of the catalyst substrates loaded with the powder catalyst, the catalyst assembly further comprising at least one thermally-conductive, porous filter that is free from a alcohol-reforming catalyst loaded thereon, wherein the porous filter is disposed axially between and separates the
 - 5 at least two catalyst substrates loaded with the powder catalyst.

5. The reformer set forth in claim 3, wherein each reactor tube includes a plurality of thermally-conductive fins extending laterally outward from an exterior surface of the reactor tube.

6. The reformer set forth in claim 1, further comprising an exhaust duct defining an exhaust plenum for receiving exhaust gas from an engine, wherein the catalytic reactor assembly is mounted on the exhaust duct such that the parallel reactor tubes extend into the exhaust plenum.

7. The reformer set forth in claim 6, wherein each reactor tube includes a plurality of thermally-conductive fins extending laterally outward from an exterior surfaces of the reactor tube.

8. The reformer set forth in claim 6, in combination with an alcohol reformat power system, wherein the alcohol reformat power system includes an internal combustion engine, an alcohol reformat line for delivering alcohol reformat from the reformer to the engine, and an exhaust line for receiving combusted alcohol reformat from the engine, wherein
5 the exhaust duct is in fluid communication with the exhaust line.

9. A reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine, the reformer comprising:

a generally cylindrical, rolled reformer housing including opposing sheets of thermally conductive material defining a catalyst chamber therebetween;

5 a catalyst assembly disposed in the catalyst chamber, wherein the catalyst assembly includes a thermally-conductive, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen;

an inlet header for delivering alcohol into the catalyst chamber;

10 an outlet header for removing the reformat mixture from the catalyst chamber;
and

a spacer disposed between adjacent turns of the rolled reformer housing to define a plurality of exhaust plenums between the adjacent turns of the rolled reformer housing and extending longitudinally with respect to the reformer housing, wherein the exhaust plenums
15 define a flow path for exhaust gas from an engine to flow longitudinally through the rolled reformer in thermal contact with the opposing sheets of the rolled reformer housing.

10. The reformer set forth in claim 9, wherein the powder catalyst includes a copper-nickel catalyst configured to reform alcohol at a temperature below about 400 °C.

11. The reformer set forth in claim 10, wherein the catalyst assembly includes at least two of the catalyst substrates loaded with the powder catalyst, the catalyst assembly further comprising at least one thermally-conductive, porous filter that is free from an alcohol-reforming catalyst loaded thereon, wherein the porous filter is disposed between and separates
5 the at least two catalyst substrates loaded with the powder catalyst.

12. The reformer set forth in claim 9, wherein the opposing sheets of the reformer housing includes material having a thermal conductivity constant of at least about 10 W/(m•K).

13. A reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen, the reformer comprising:

a shell defining a catalyst plenum having opposite first and second longitudinal ends, the shell having an inlet port adjacent the first longitudinal end of the catalyst plenum for
5 receiving alcohol from an alcohol source, and an outlet port adjacent the second longitudinal end of the catalyst plenum for receiving the reformat mixture from the catalyst plenum;

a plurality of exhaust tubes within the catalyst plenum defining an exhaust flow path for an exhaust gas to flow;

a catalyst assembly in catalyst plenum, the catalyst assembly including a heat-
10 conducting, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen, wherein the catalyst substrate includes a plurality of openings through which the exhaust tubes extend in thermal contact with the catalyst substrate.

14. The reformer set forth in claim 13, further comprising a plurality of baffles in the catalyst plenum disposed between the inlet port and the outlet port for directing the flow of alcohol through the catalyst plenum.

15. The reformer set forth in claim 13, wherein the powder catalyst includes a copper-nickel catalyst configured to reform alcohol at a temperature below about 400 °C.

16. The reformer set forth in claim 15, wherein the catalyst assembly includes at least two of the catalyst substrates loaded with the powder catalyst, the catalyst assembly further

comprising at least one thermally-conductive, porous filter that is free from an alcohol-reforming catalyst loaded thereon, wherein the porous filter is disposed between and separates
5 the at least two catalyst substrates loaded with the powder catalyst.

17. A catalyst assembly for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine, the catalyst assembly comprising:
a thermally-conductive, porous catalyst substrate; and
an unpassivated, copper-nickel powder catalyst loaded on the substrate for
5 reforming alcohol to the gaseous reformat mixture comprising hydrogen.

18. The catalyst assembly set forth in claim 17, wherein the catalyst substrate comprises a mesh catalyst substrate.

19. The catalyst assembly set forth in claim 18, wherein the mesh catalyst substrate comprises iron-chromium fibers.

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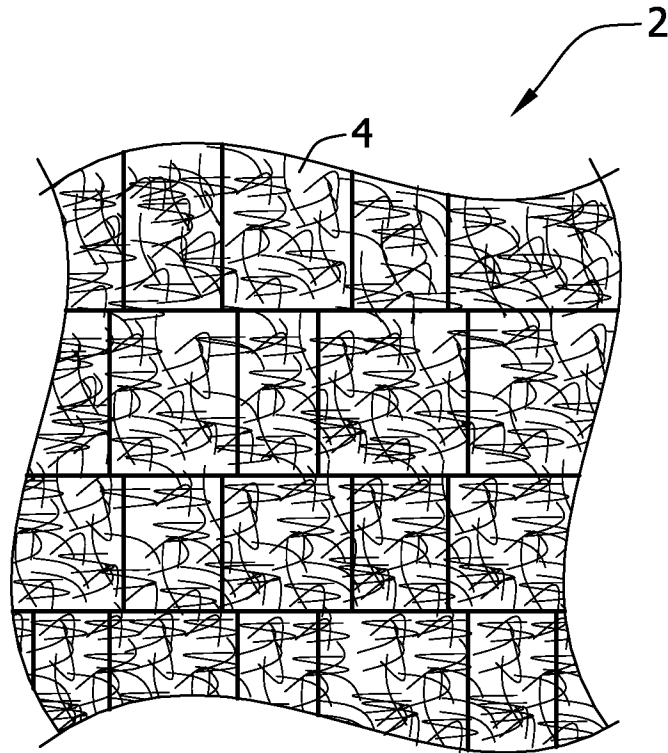


FIG. 1

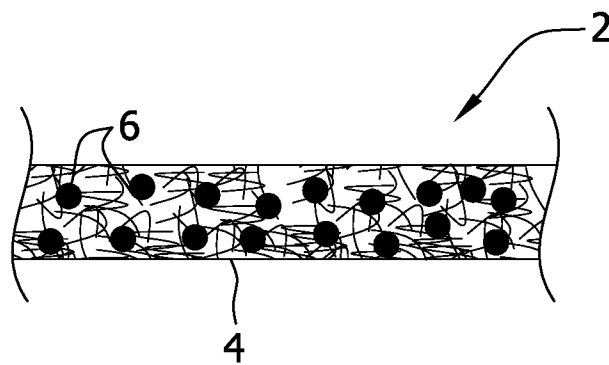
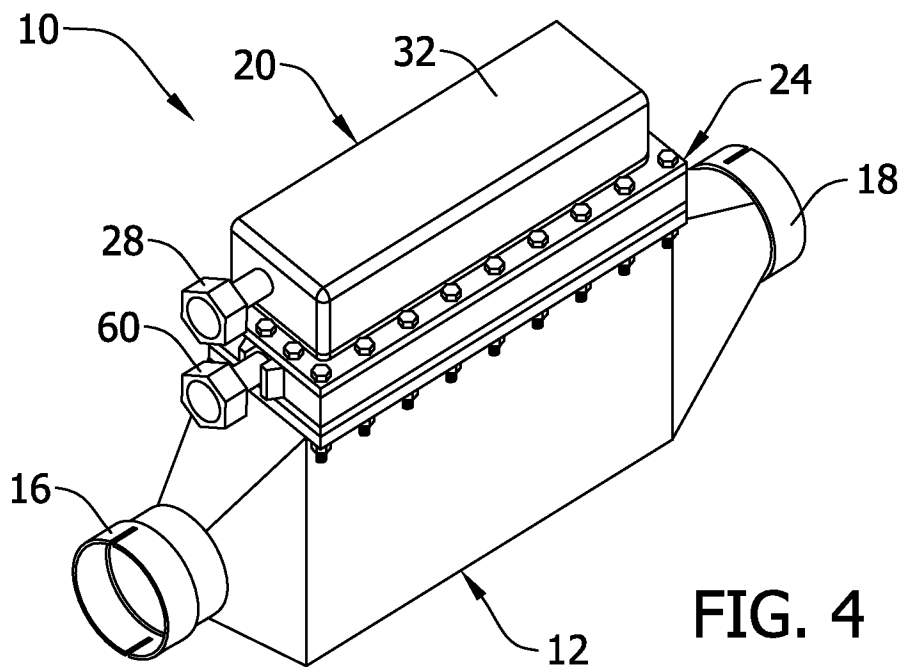
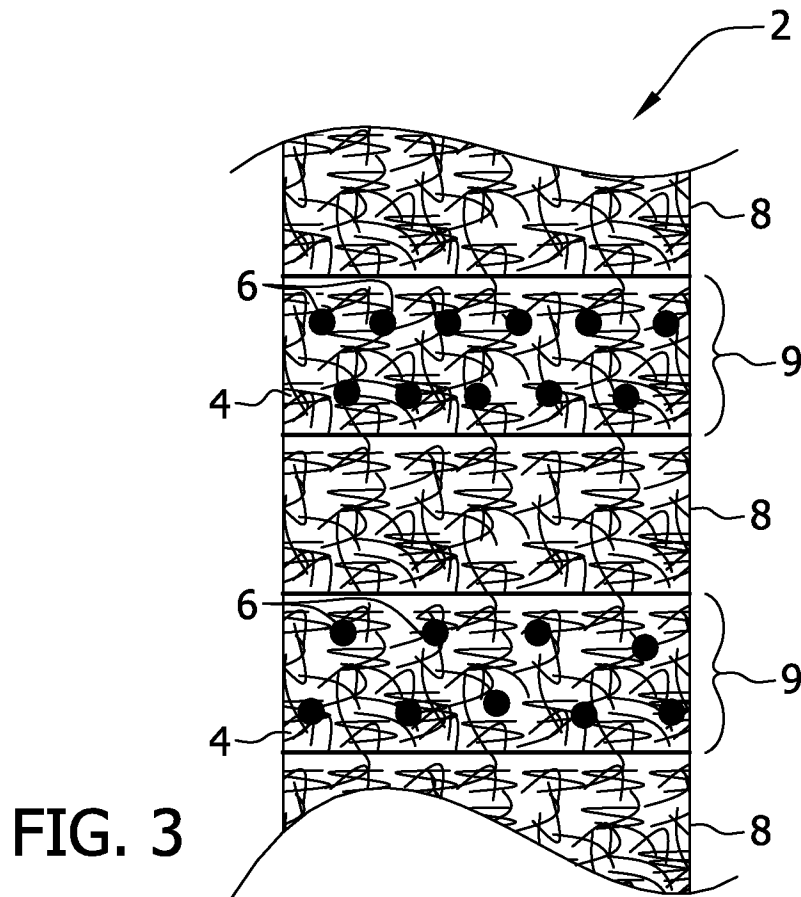


FIG. 2

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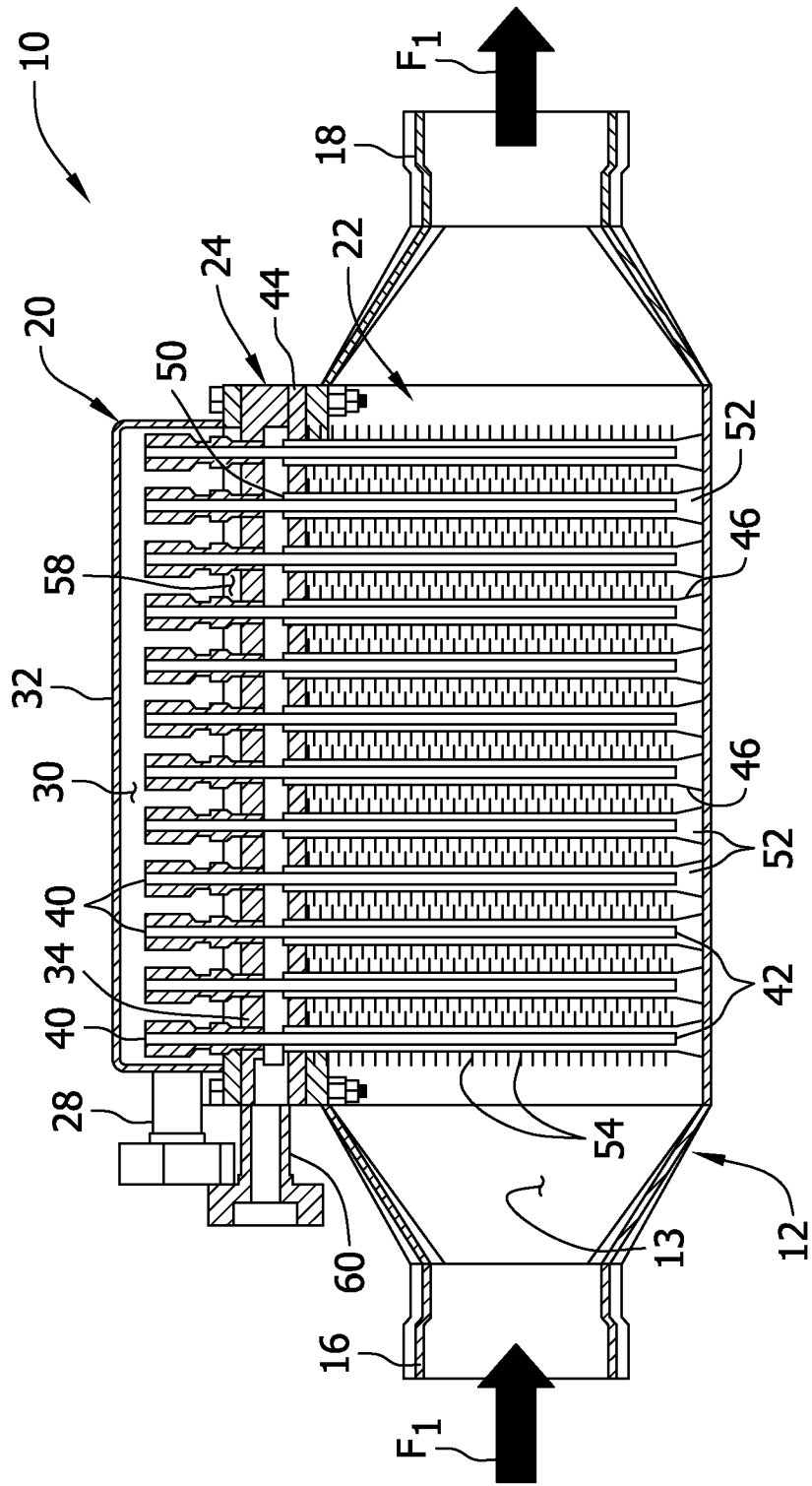


FIG. 5

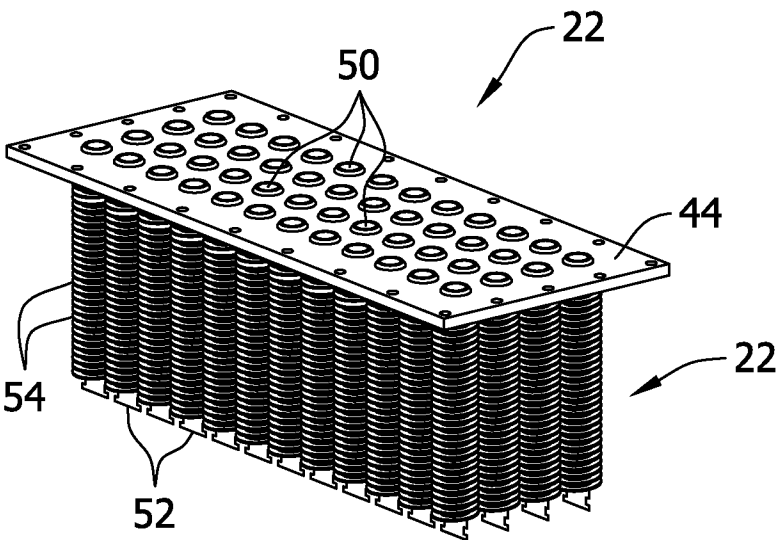


FIG. 6

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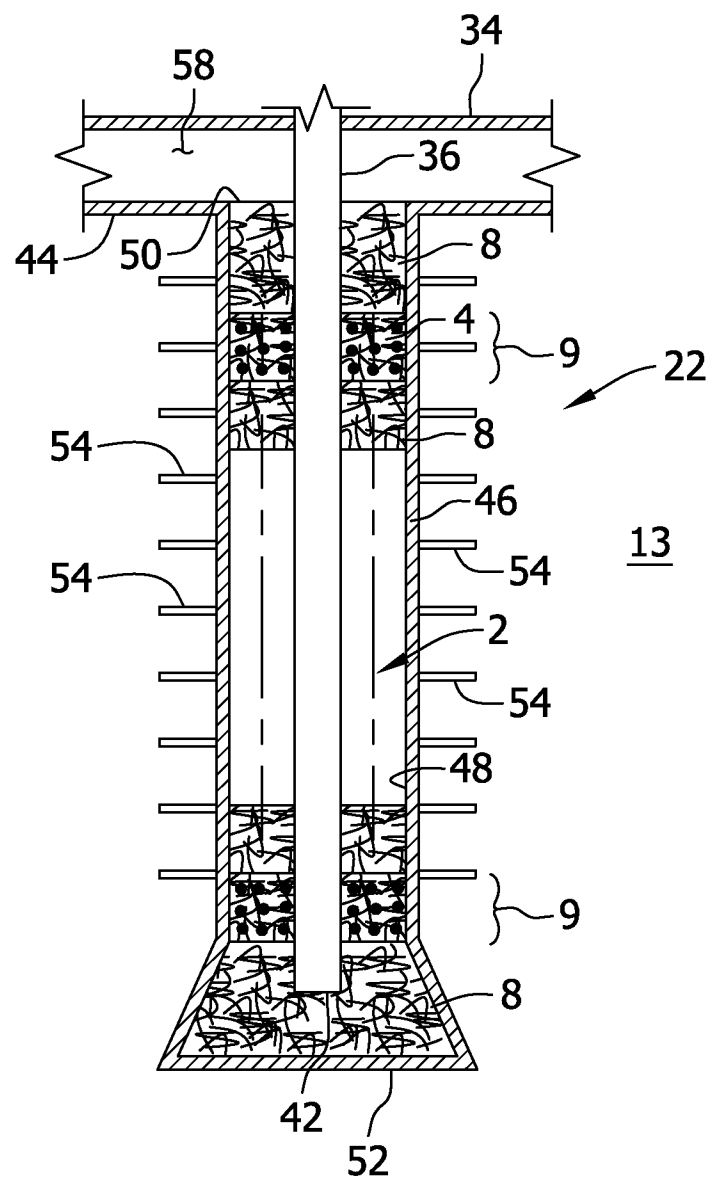


FIG. 7

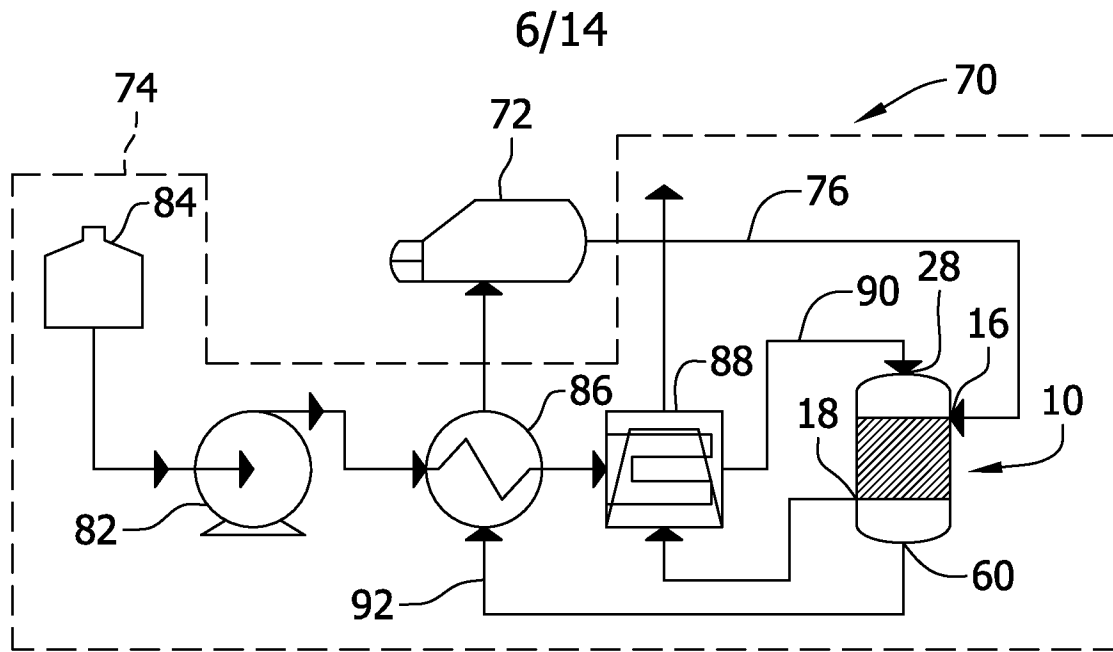


FIG. 8

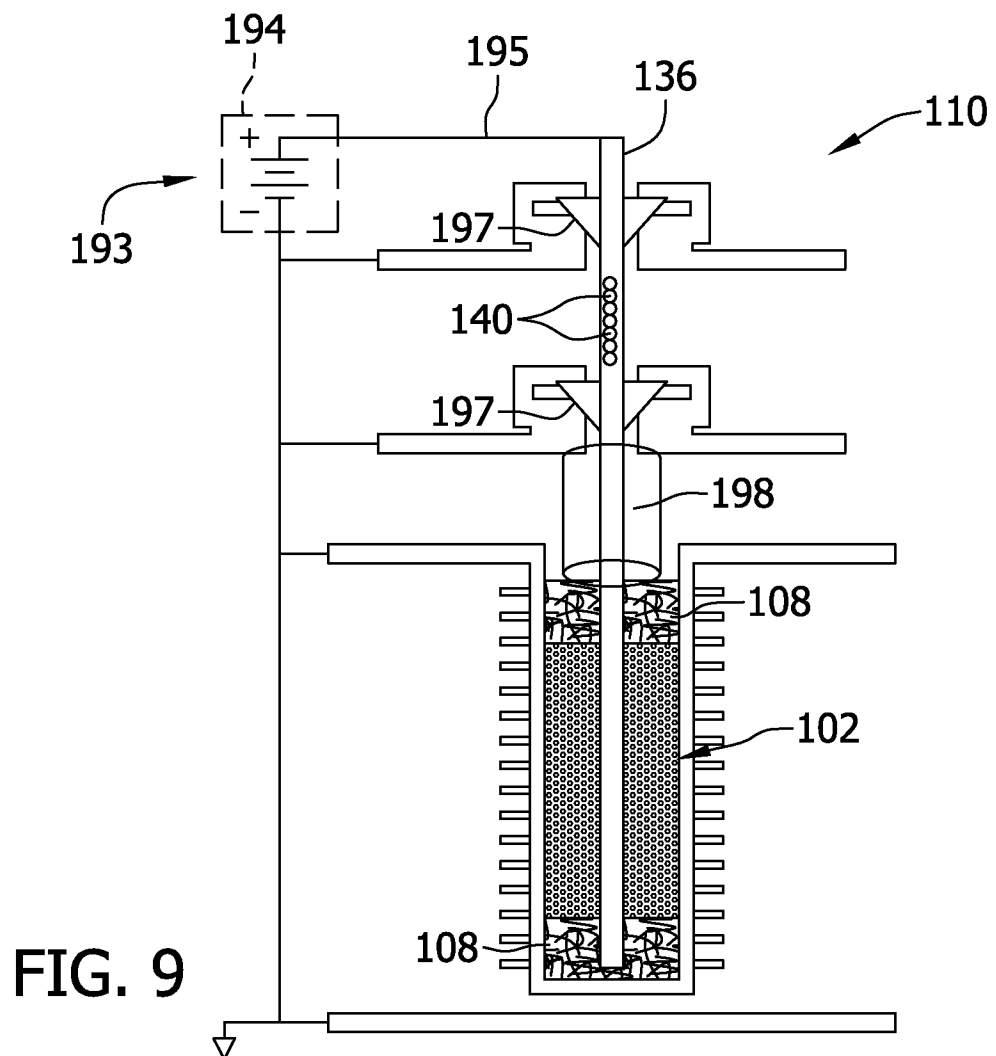


FIG. 9

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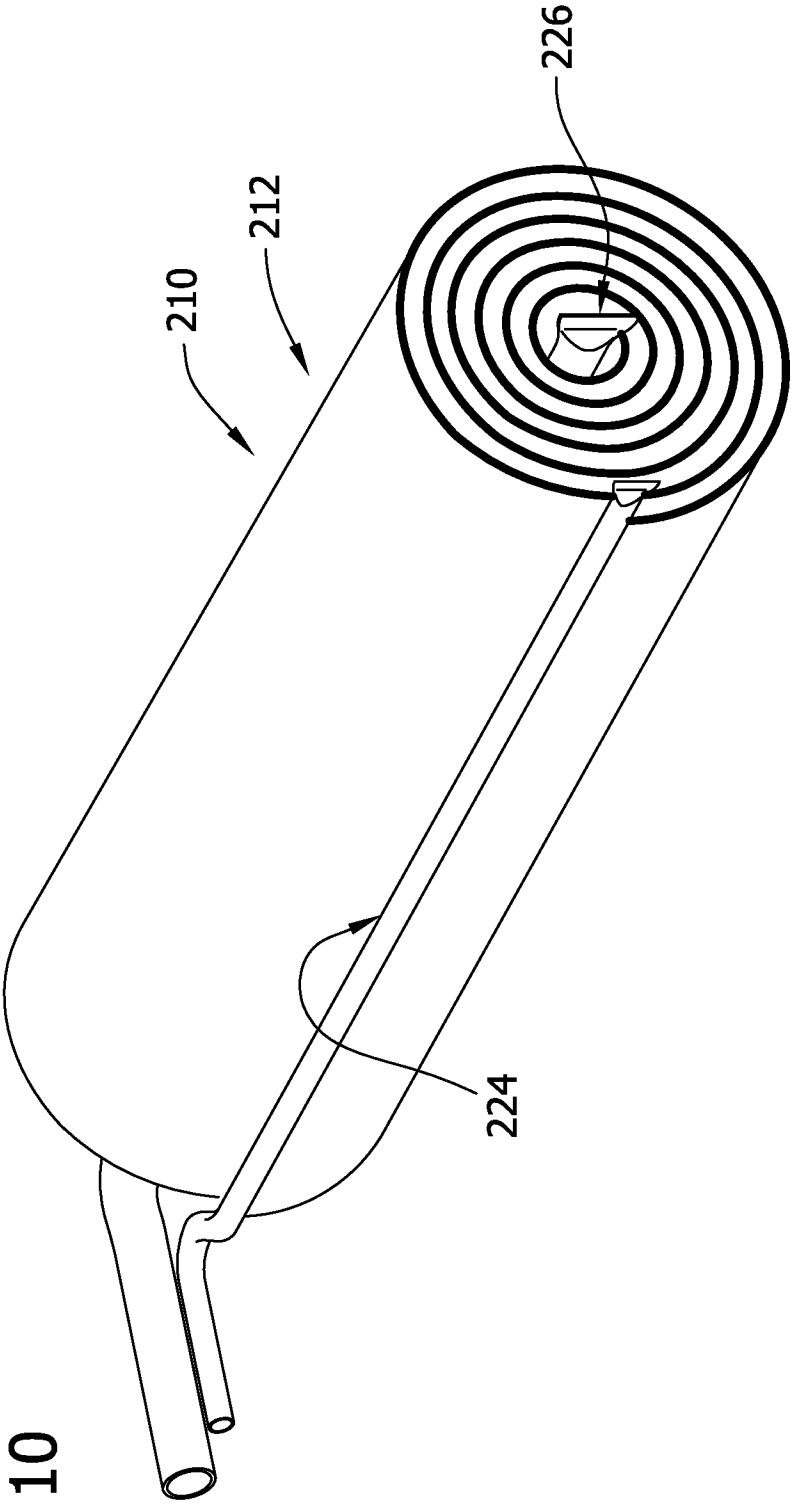
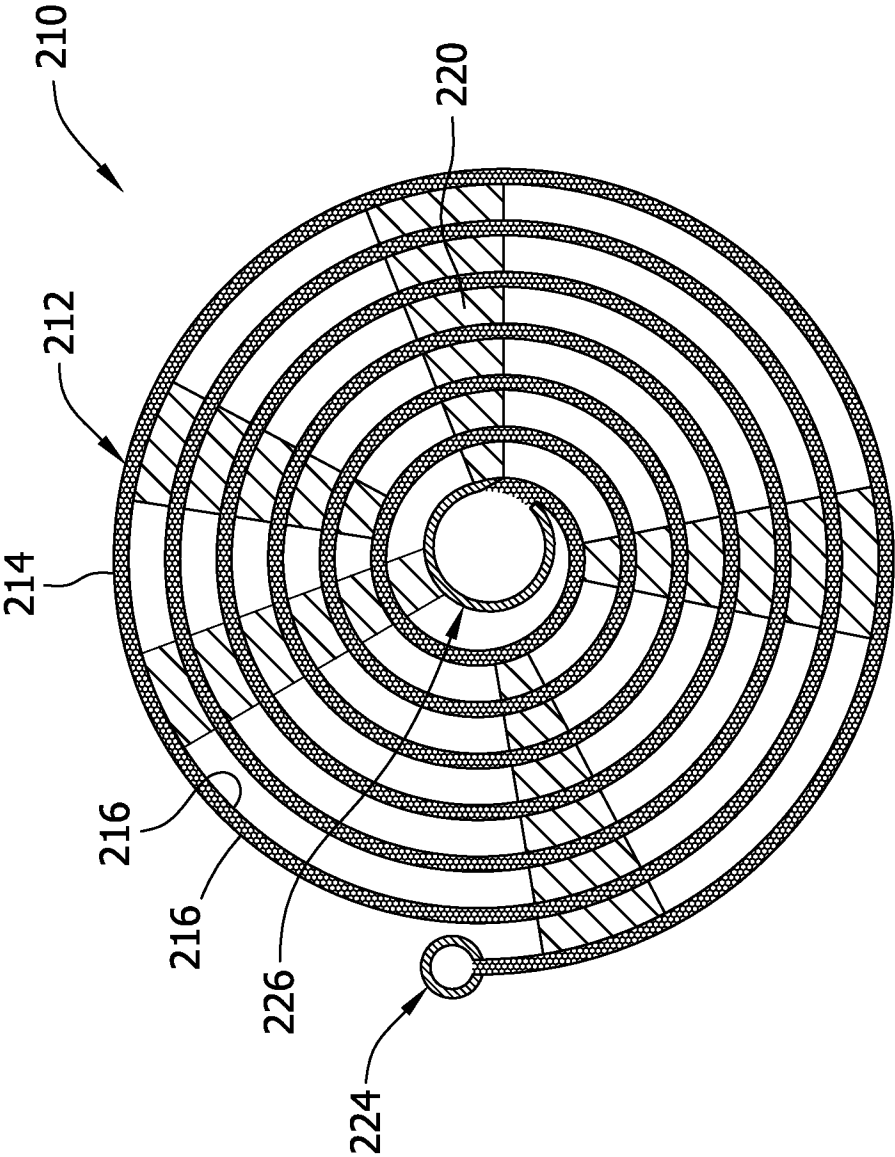


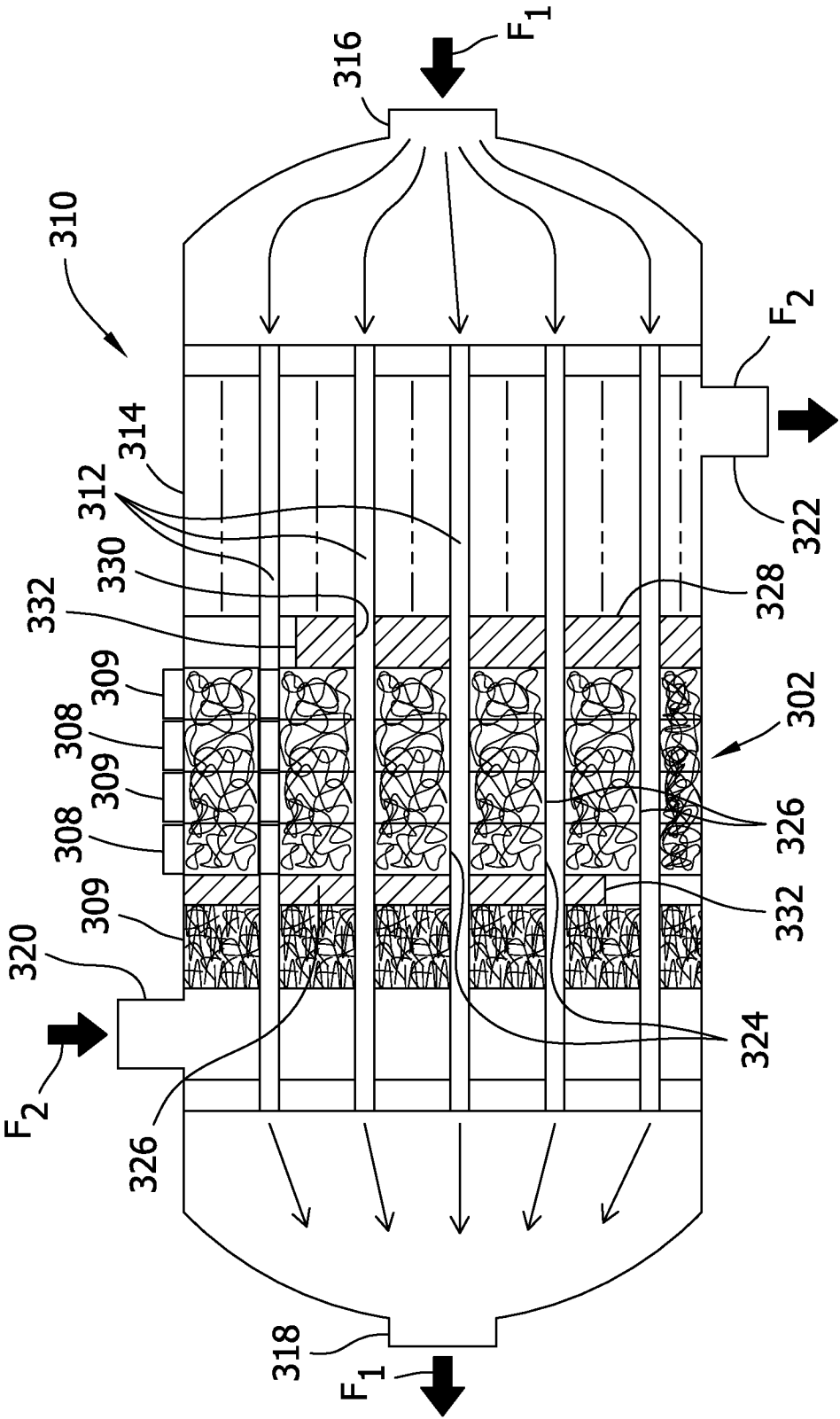
FIG. 10

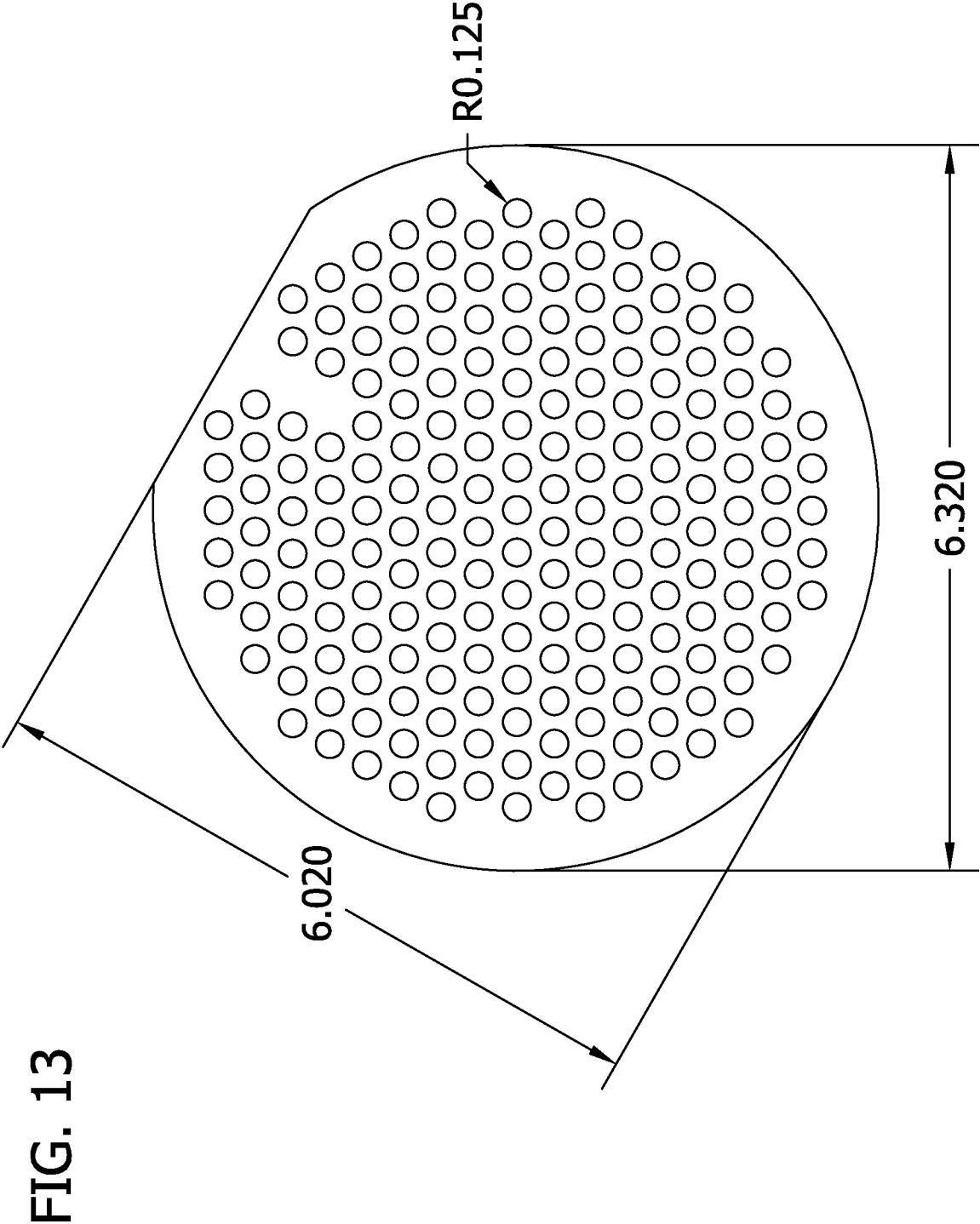
FIG. 11



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FIG. 12





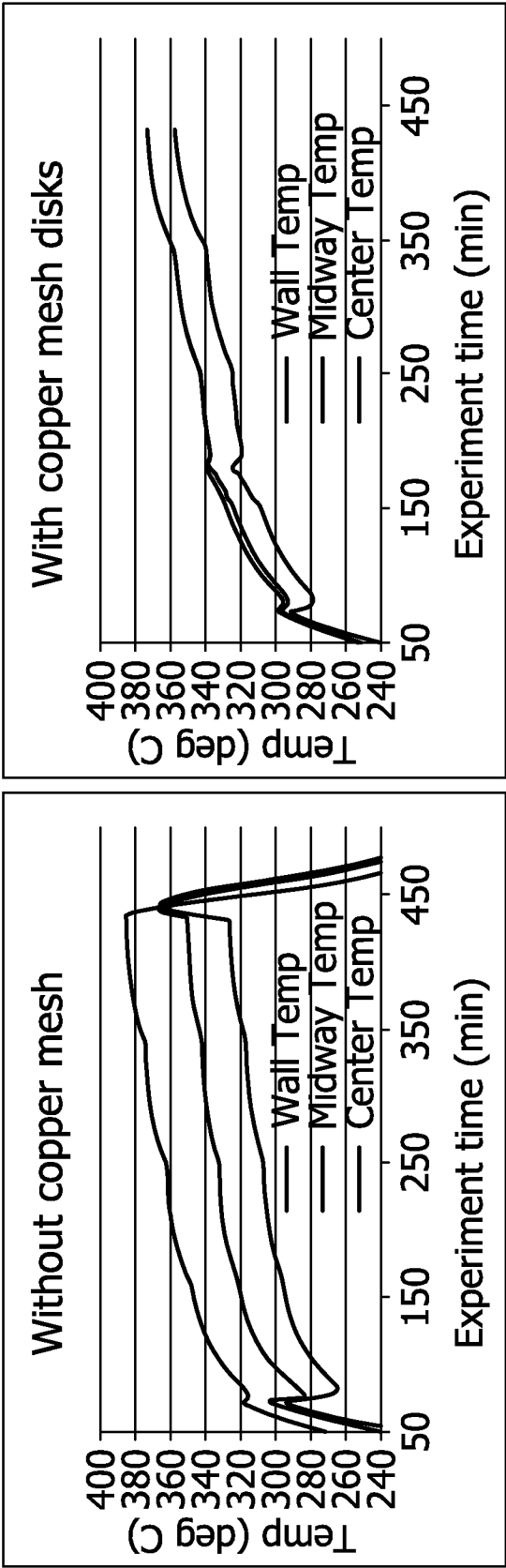


FIG. 14A

FIG. 14B

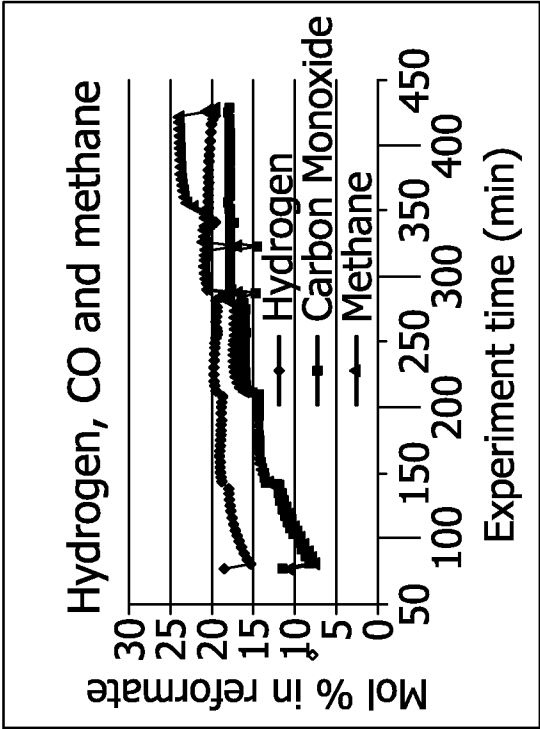


FIG. 15B

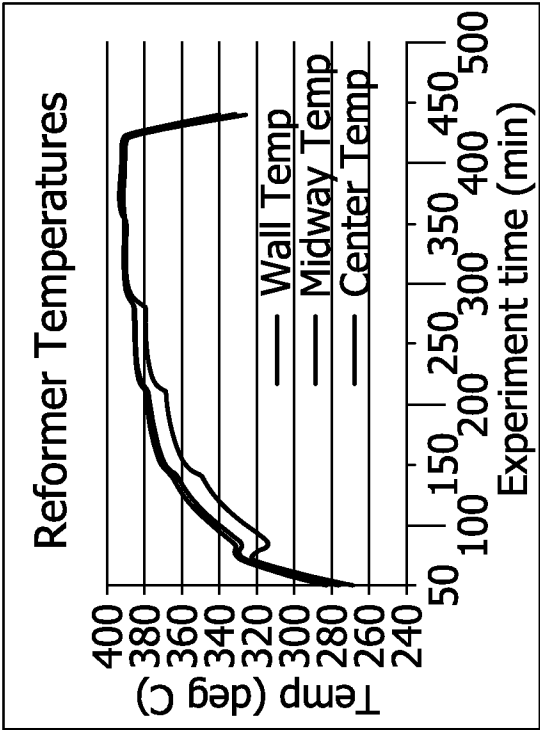
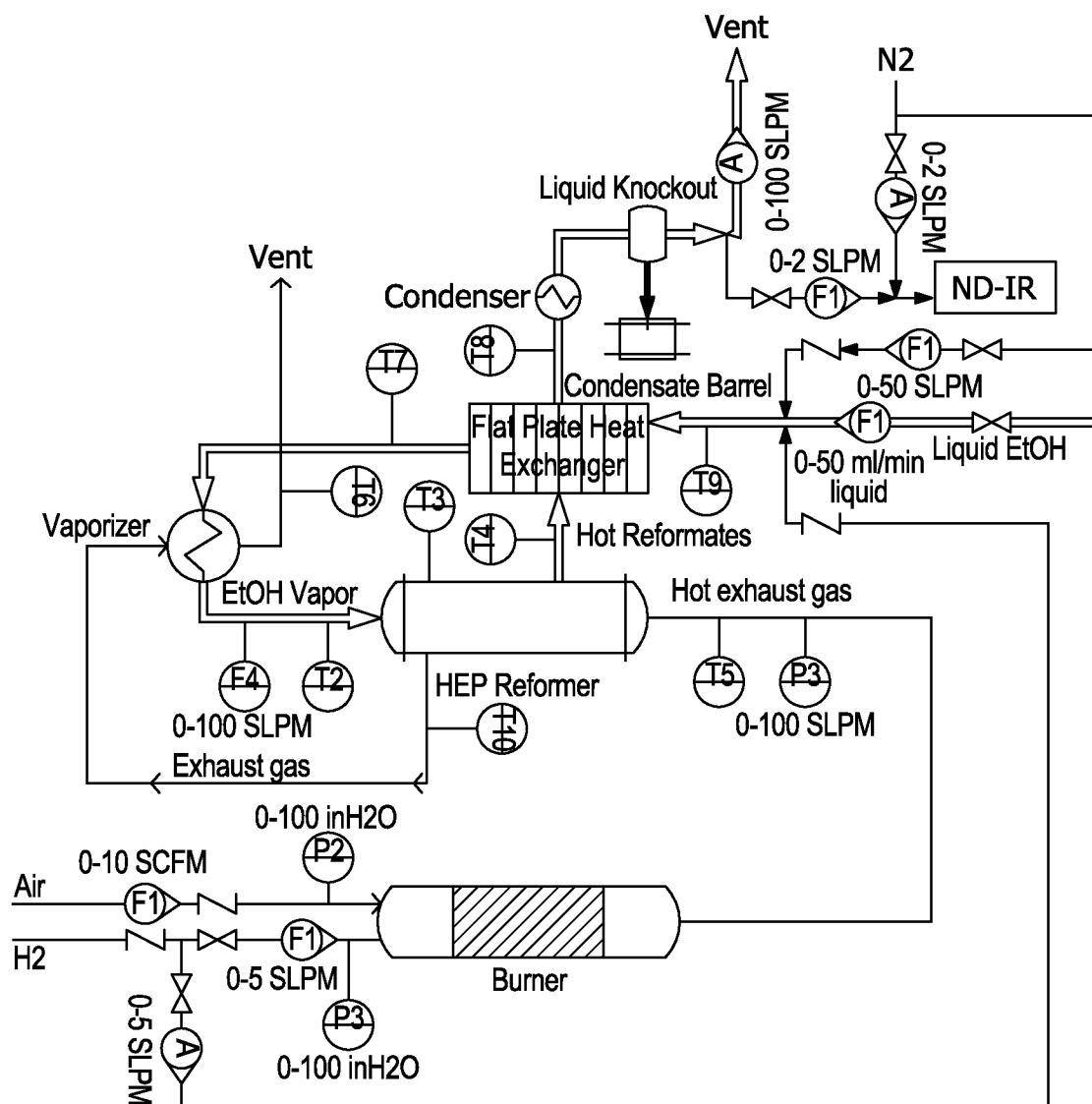


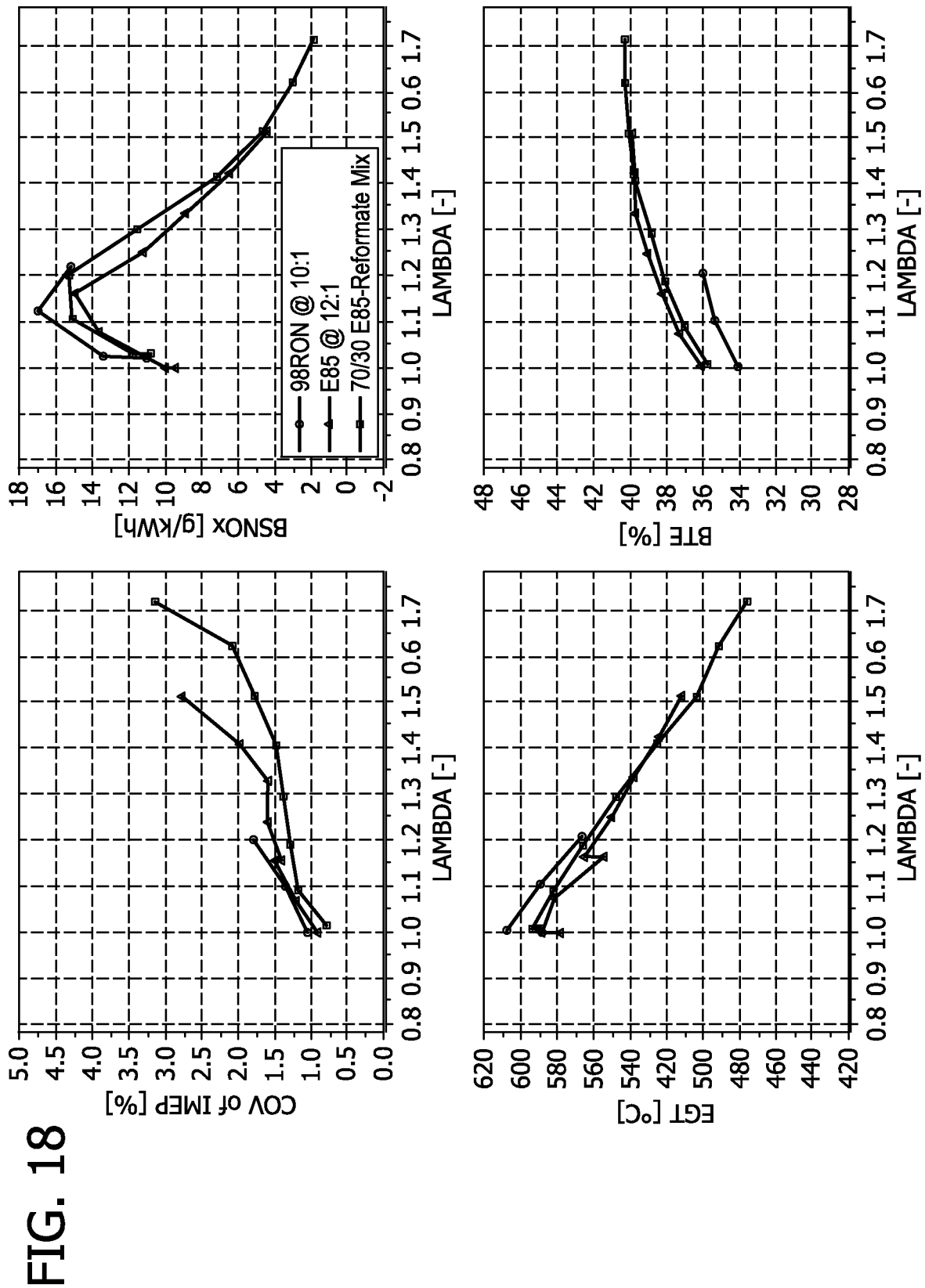
FIG. 15A

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FIG. 17



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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/031382

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/06 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)
B01J 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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/118950 A1 (INST FRANCAIS DU PETROLE [FR]; BERTHOLIN STEPHANE [FR]; GIROUDIERE FAB) 25 October 2007 (2007-10-25) abstract page 19, line 1 - line 12; claim 1; figure 3	1-8
X	US 2010/254891 A1 (GIROUDIERE FABRICE [FR] ET AL) 7 October 2010 (2010-10-07) abstract page 2, paragraph 32 - paragraph 35; figure 2 ----- -/--	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

15 June 2012

Date of mailing of the international search report

27/08/2012

Name and mailing address of the ISA/

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Authorized officer

Thomasson, Philippe

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/031382

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 103 46 267 A1 (DAIMLER CHRYSLER AG [DE]) 28 April 2005 (2005-04-28) abstract page 2, paragraph 1 page 5, paragraph 35 - paragraph 36; figure 1 page 7, paragraph 53; figure 4 -----	1-8
Y	WO 2006/045744 A1 (SHELL INT RESEARCH [NL]; VAN DEN BRINK PETER JOHN [NL]; KRAMER GERT JA) 4 May 2006 (2006-05-04) abstract page 7, line 30 - page 9, line 15; figures 3, 4 -----	1-8
Y	US 2007/028860 A1 (HEMSATH KLAUS H [US] HEMSATH KLAUS HEINRICH [US]) 8 February 2007 (2007-02-08) abstract; figures 1, 4 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/031382

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007118950	A1	25-10-2007	NONE
US 2010254891	A1	07-10-2010	CA 2692701 A1 26-02-2009 CN 101754803 A 23-06-2010 EP 2170497 A1 07-04-2010 FR 2918904 A1 23-01-2009 JP 2010534128 A 04-11-2010 RU 2010106107 A 27-08-2011 US 2010254891 A1 07-10-2010 WO 2009024664 A1 26-02-2009
DE 10346267	A1	28-04-2005	NONE
WO 2006045744	A1	04-05-2006	NONE
US 2007028860	A1	08-02-2007	US 2007028860 A1 08-02-2007 WO 2007018992 A2 15-02-2007

INTERNATIONAL SEARCH REPORT

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

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Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8

A reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine, the reformer comprising: a catalytic reactor assembly including a plurality of parallel reactor tubes having open first longitudinal ends and closed second longitudinal ends, and a plurality of catalyst assemblies disposed in the plurality of parallel reactor tubes, wherein each catalyst assembly includes a thermally-conductive, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen; an inlet manifold assembly including an inlet plenum for receiving alcohol from an alcohol source, and a plurality of parallel inlet tubes extending axially through the open first longitudinal ends of the parallel reactor tubes for delivering alcohol to the catalyst assemblies, wherein the inlet tubes have inlets disposed in the inlet plenum and outlets adjacent the closed second longitudinal ends of the reactor tubes; and an outlet manifold including an outlet plenum in fluid communication with the open first longitudinal ends of the reactor tubes for receiving the reformat mixture from the reactor tubes.

2. claims: 9-12

A reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine, the reformer comprising: a generally cylindrical, rolled reformer housing including opposing sheets of thermally conductive material defining a catalyst chamber there between; a catalyst assembly disposed in the catalyst chamber, wherein the catalyst assembly includes a thermally-conductive, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen; an inlet header for delivering alcohol into the catalyst chamber; an outlet header for removing the reformat mixture from the catalyst chamber; and a spacer disposed between adjacent turns of the rolled reformer housing to define a plurality of exhaust plenums between the adjacent turns of the rolled reformer housing and extending longitudinally with respect to the reformer housing, wherein the exhaust plenums define a flow path for exhaust gas from an engine to flow longitudinally through the rolled reformer in thermal contact with the opposing sheets of the rolled reformer housing.

3. claims: 13-16

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

A reformer for reforming an alcohol to a gaseous reformat mixture comprising hydrogen, the reformer comprising: a shell defining a catalyst plenum having opposite first and second longitudinal ends, the shell having an inlet port adjacent the first longitudinal end of the catalyst plenum for receiving alcohol from an alcohol source, and an outlet port adjacent the second longitudinal end of the catalyst plenum for receiving the reformat mixture from the catalyst plenum; a plurality of exhaust tubes within the catalyst plenum defining an exhaust flow path for an exhaust gas to flow; a catalyst assembly in catalyst plenum, the catalyst assembly including a heat- conducting, porous catalyst substrate, and a powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen, wherein the catalyst substrate includes a plurality of openings through which the exhaust tubes extend in thermal contact with the catalyst substrate.

4. claim: 17

A catalyst assembly for reforming an alcohol to a gaseous reformat mixture comprising hydrogen for combustion in an engine, the catalyst assembly comprising: a thermally-conductive, porous catalyst substrate; and an unpassivated, copper-nickel powder catalyst loaded on the substrate for reforming alcohol to the gaseous reformat mixture comprising hydrogen.
