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(54) **FUEL PROCESSOR FOR PRODUCING HYDROGEN FROM HYDROCARBON FUELS**

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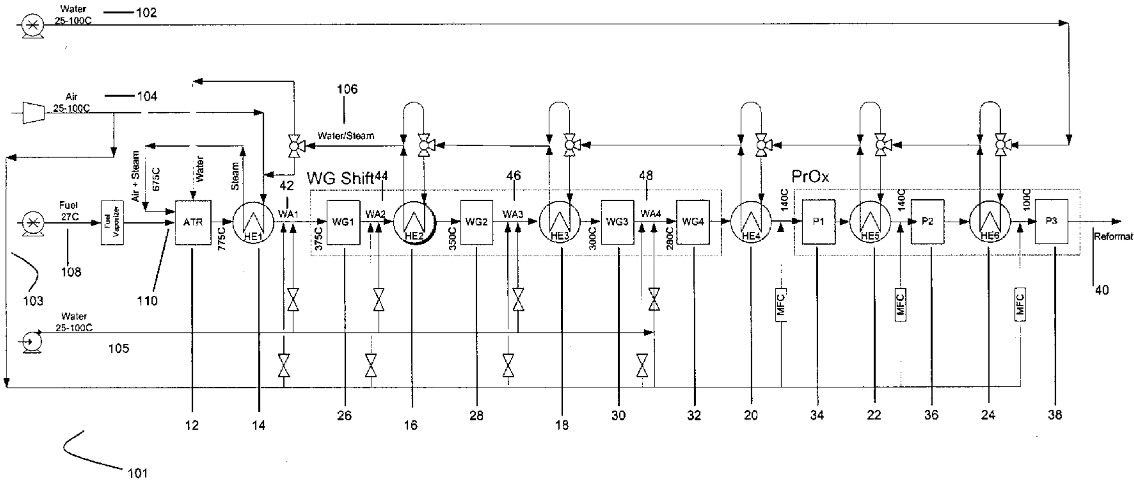
(52) **U.S. Cl.** .... **48/127.9**; 48/119; 48/61; 48/62 R

(57) **ABSTRACT**

A fuel processor having a dynamically controlled thermal integration mechanism and a method for dynamically controlling temperatures in a fuel processor. Such dynamic control accomplished by the use of an autothermal reformer, a steam/air superheater, water/air injectors, water gas shift reactors, heat exchangers, preferential oxidation reactors, wherein the feed/reactant streams are used as the coolant to remove heat from the reformate gas stream.



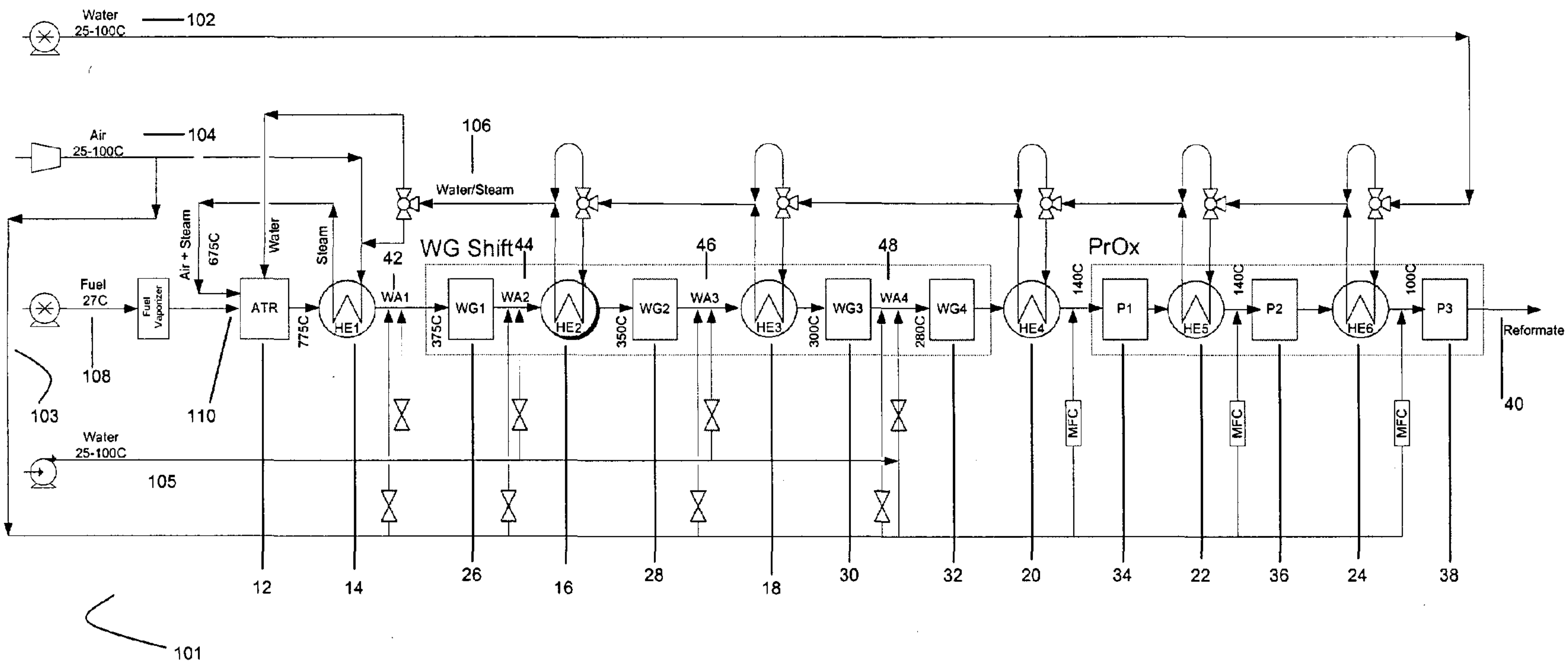

Water
25-100C
102
Air
25-100C
104
106
Water/Steam
Fuel
27C
Fuel Vaporizer
108
103
110
Air + Steam
675C
Water
Steam
ATR
775C
HE1
42
WA1
WG Shift
44
375C
WG1
WA2
HE2
350C
WG2
46
WA3
HE3
300C
WG3
48
WA4
280C
WG4
HE4
140C
PrOx
P1
HE5
140C
P2
HE6
100C
P3
Reformate
40
MFC
MFC
MFC
Water
25-100C
105
12
14
26
16
28
18
30
32
20
34
22
36
24
38
101

Fig. 1

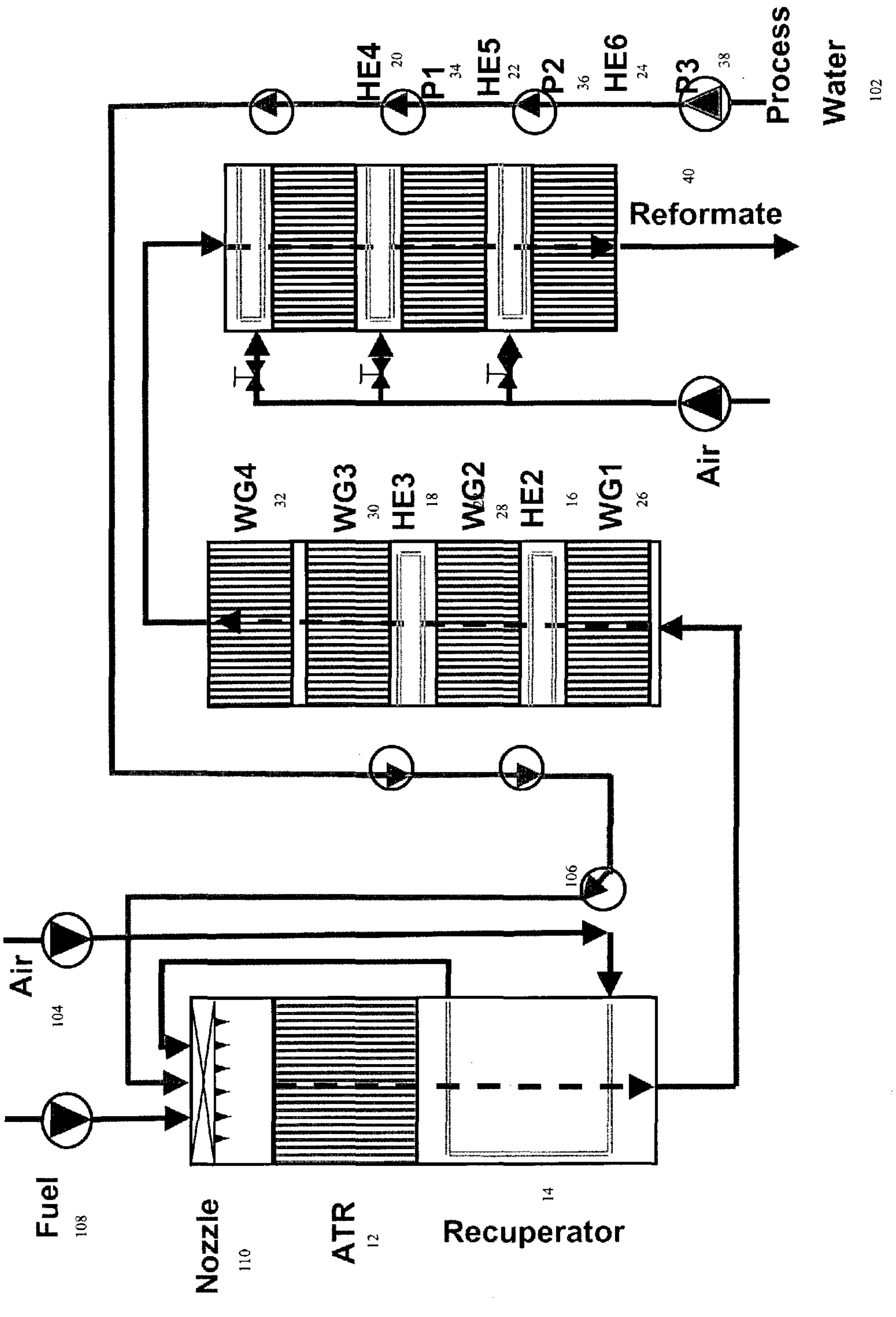

Fuel
108
Air
104
Nozzle
110
ATR
12
Recuperator
14
106
WG4
32
WG3
30
HE3
18
WG2
28
HE2
16
WG1
26
Air
Reformate
40
HE4
20
P1
34
HE5
22
P2
36
HE6
24
P3
38
Process
Water
102

Fig. 2

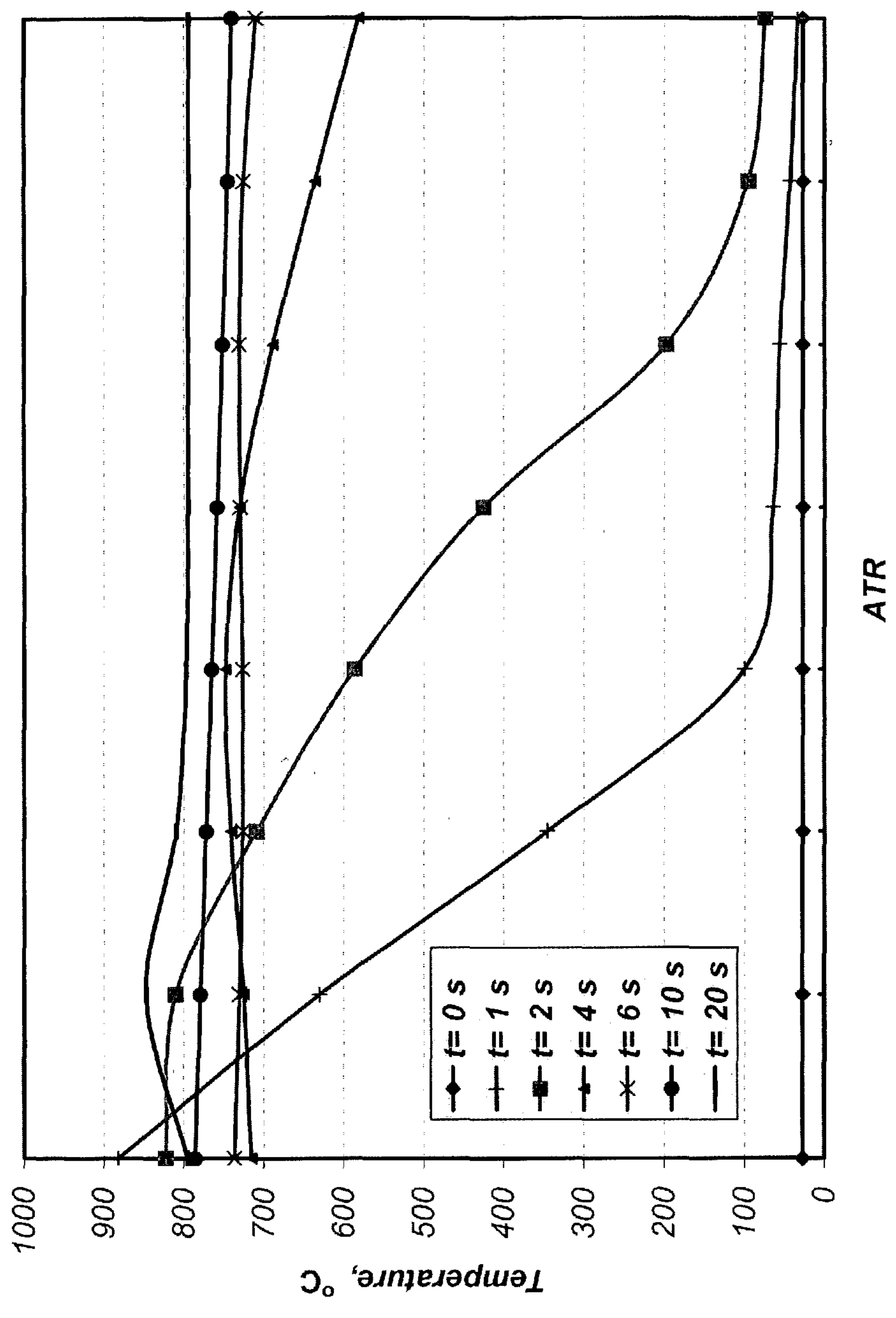

1000
900
800
700
600
500
400
300
200
100
0
Temperature, oC
t= 0 s
t= 1 s
t= 2 s
t= 4 s
t= 6 s
t= 10 s
t= 20 s
ATR

Fig. 3

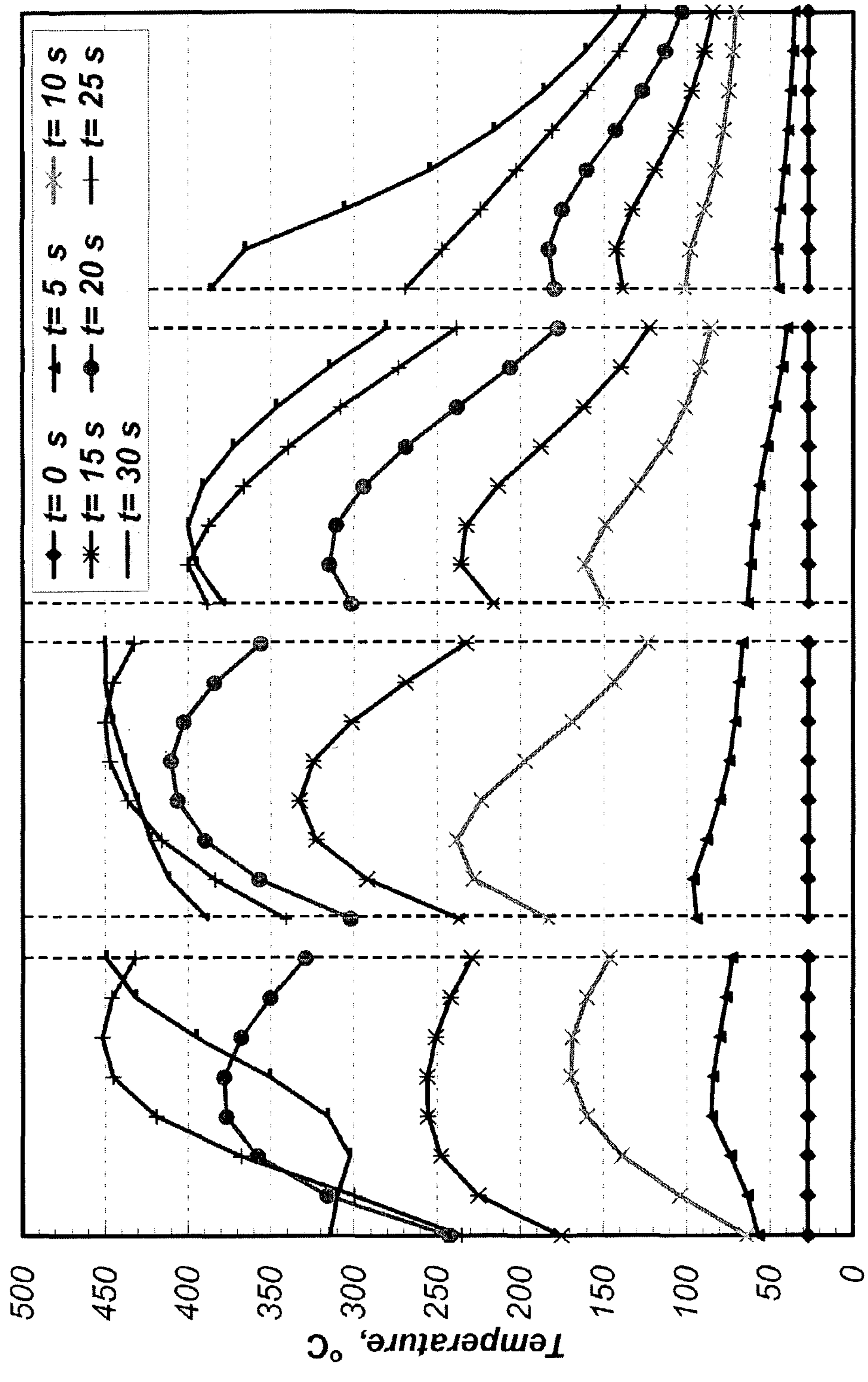

t= 0 s
t= 5 s
t= 10 s
t= 15 s
t= 20 s
t= 25 s
t= 30 s
Temperature, °C
500
450
400
350
300
250
200
150
100
50
0
WG1
WG2
WG3
WG4

Fig. 4

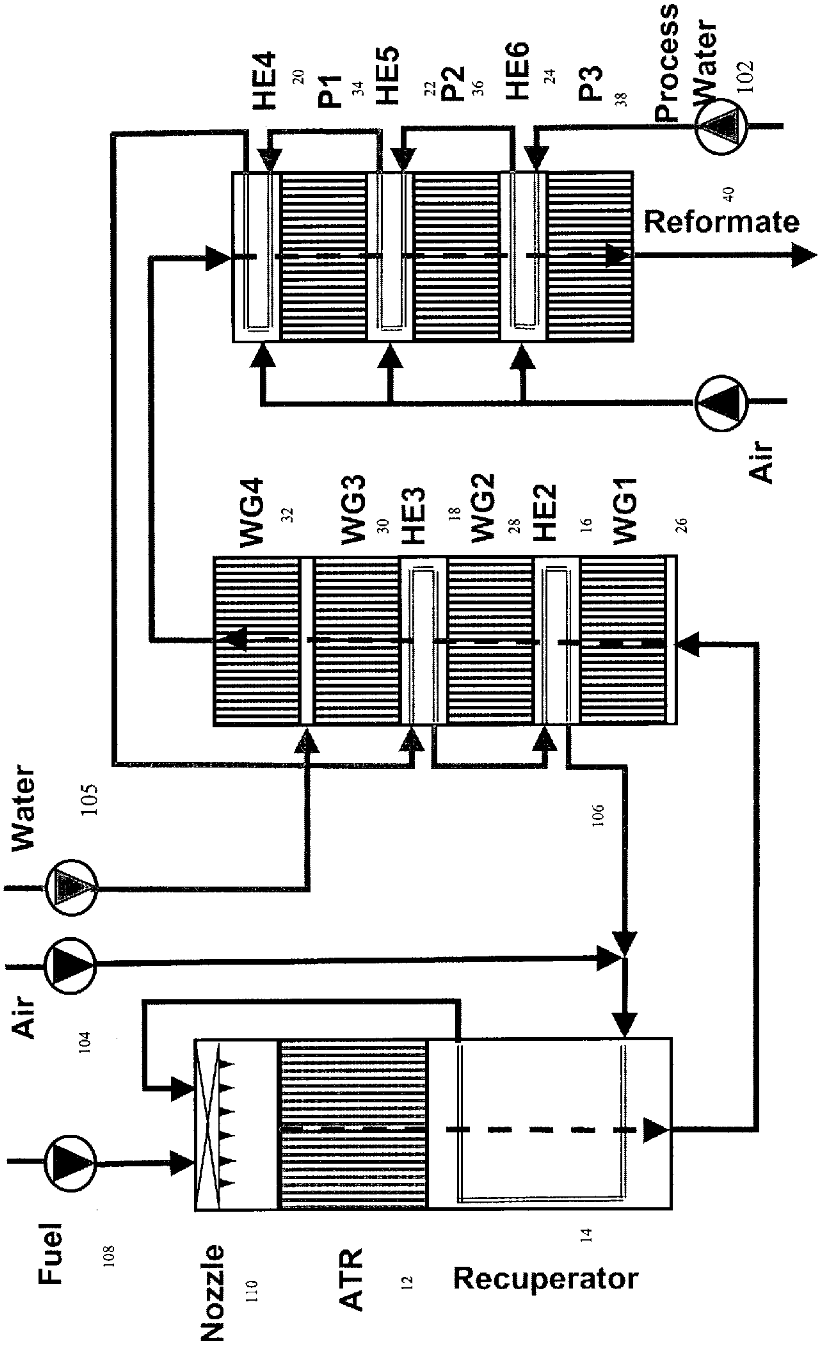

HE4
20
P1
34
HE5
22
P2
36
HE6
24
P3
38
Process Water
102
40
Reformate
Air
WG4
32
WG3
30
HE3
18
WG2
28
HE2
16
WG1
26
Water
105
106
Air
104
Fuel
108
Nozzle
110
ATR
12
Recuperator
14

Figure 5

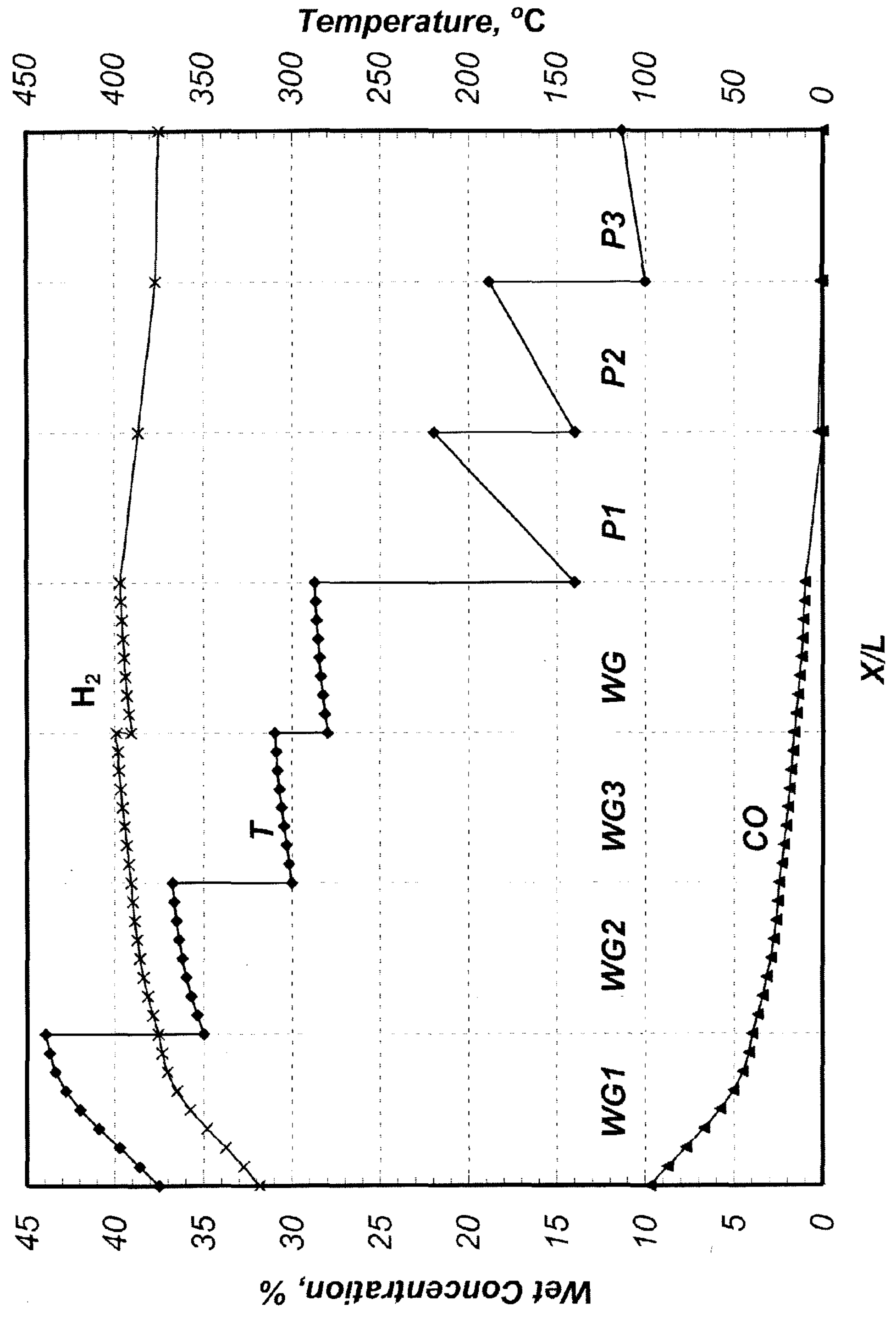

Temperature, °C
450
400
350
300
250
200
150
100
50
0
Wet Concentration, %
45
40
35
30
25
20
15
10
5
0
H$_2$
T
CO
WG1
WG2
WG3
WG
P1
P2
P3
X/L

Figure 6

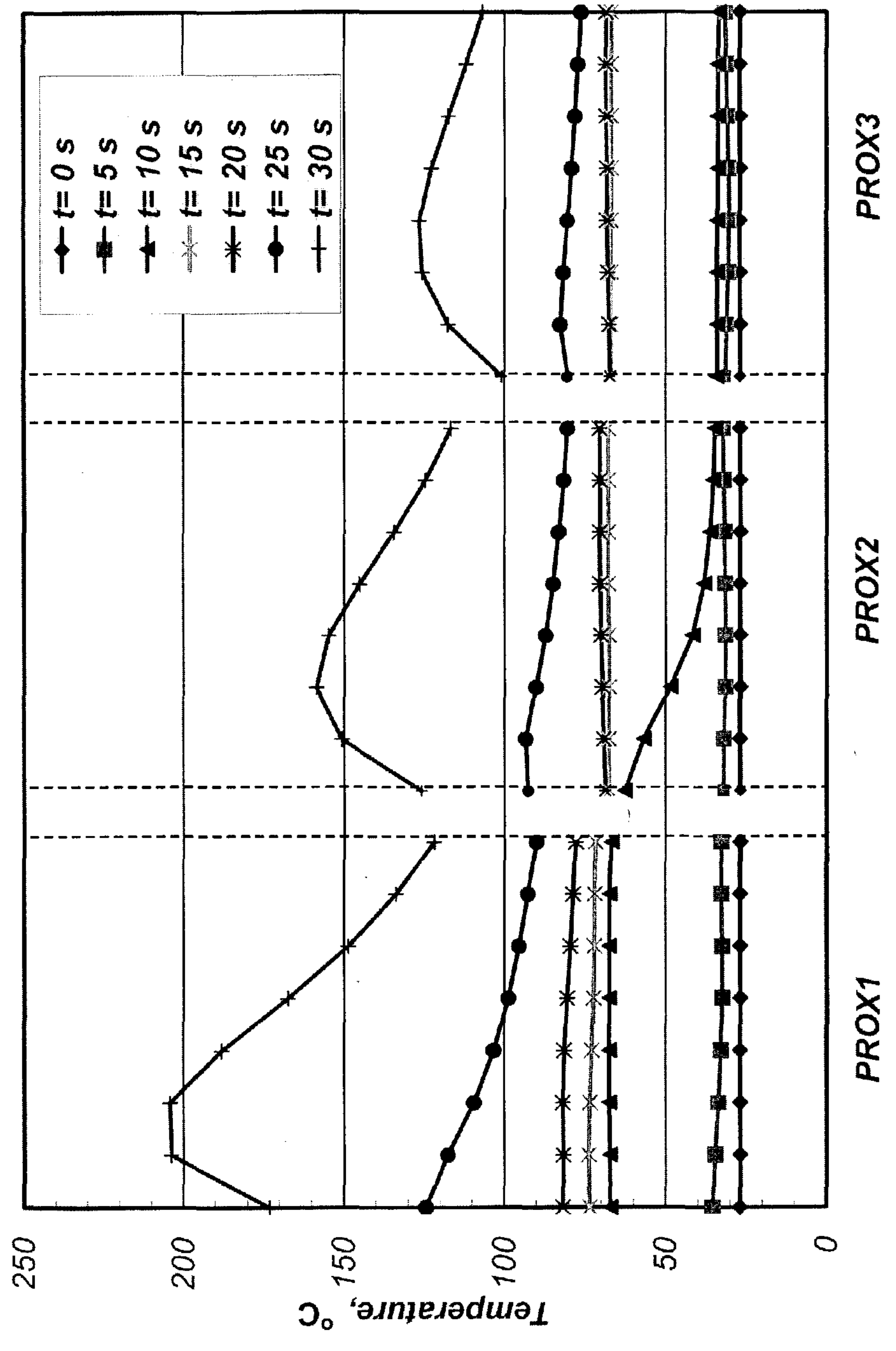

t= 0 s
t= 5 s
t= 10 s
t= 15 s
t= 20 s
t= 25 s
t= 30 s
250
200
150
100
50
0
Temperature, °C
PROX1
PROX2
PROX3

Figure 7

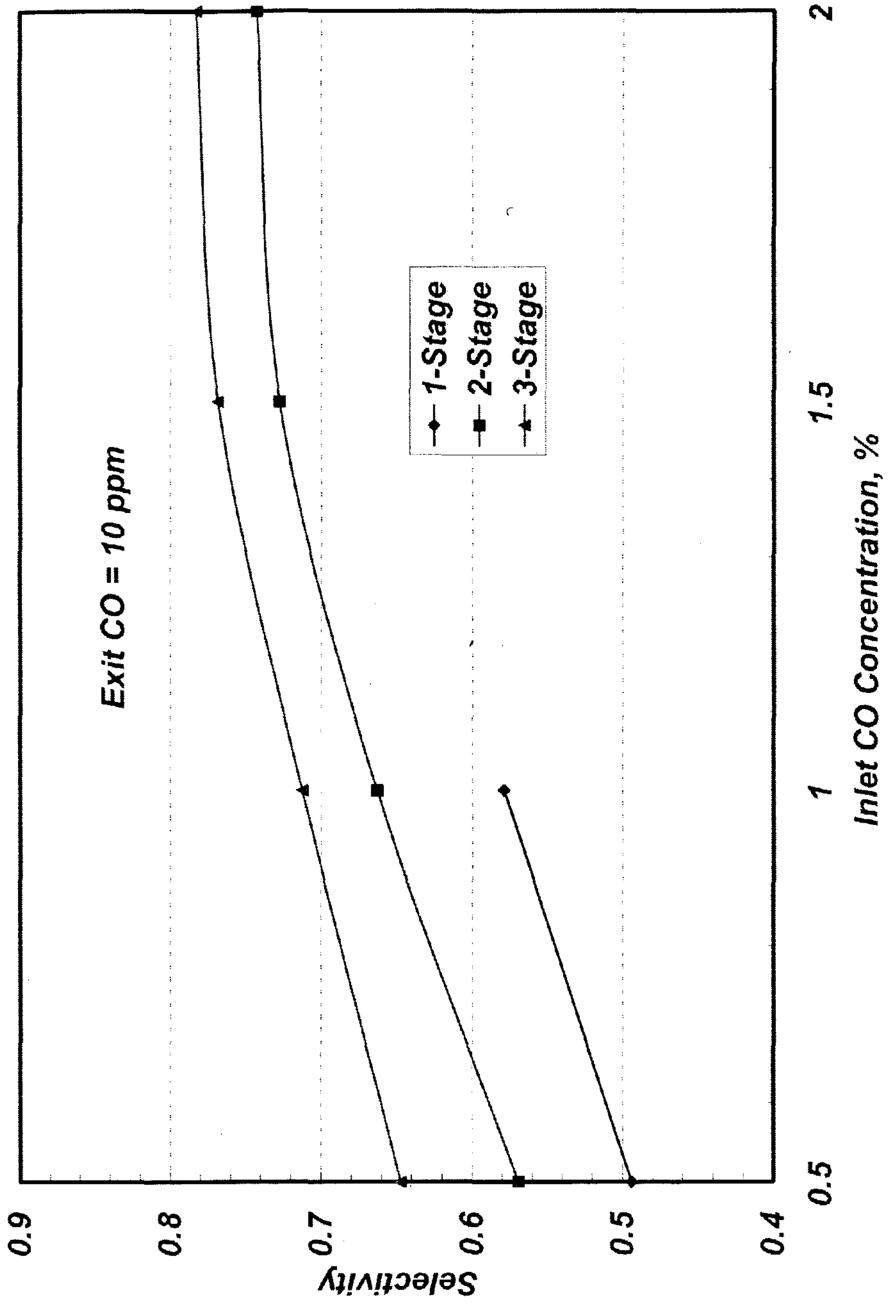

Exit CO = 10 ppm
1-Stage
2-Stage
3-Stage
Selectivity
0.9
0.8
0.7
0.6
0.5
0.4
0.5
1
1.5
2
Inlet CO Concentration, %

Figure 8

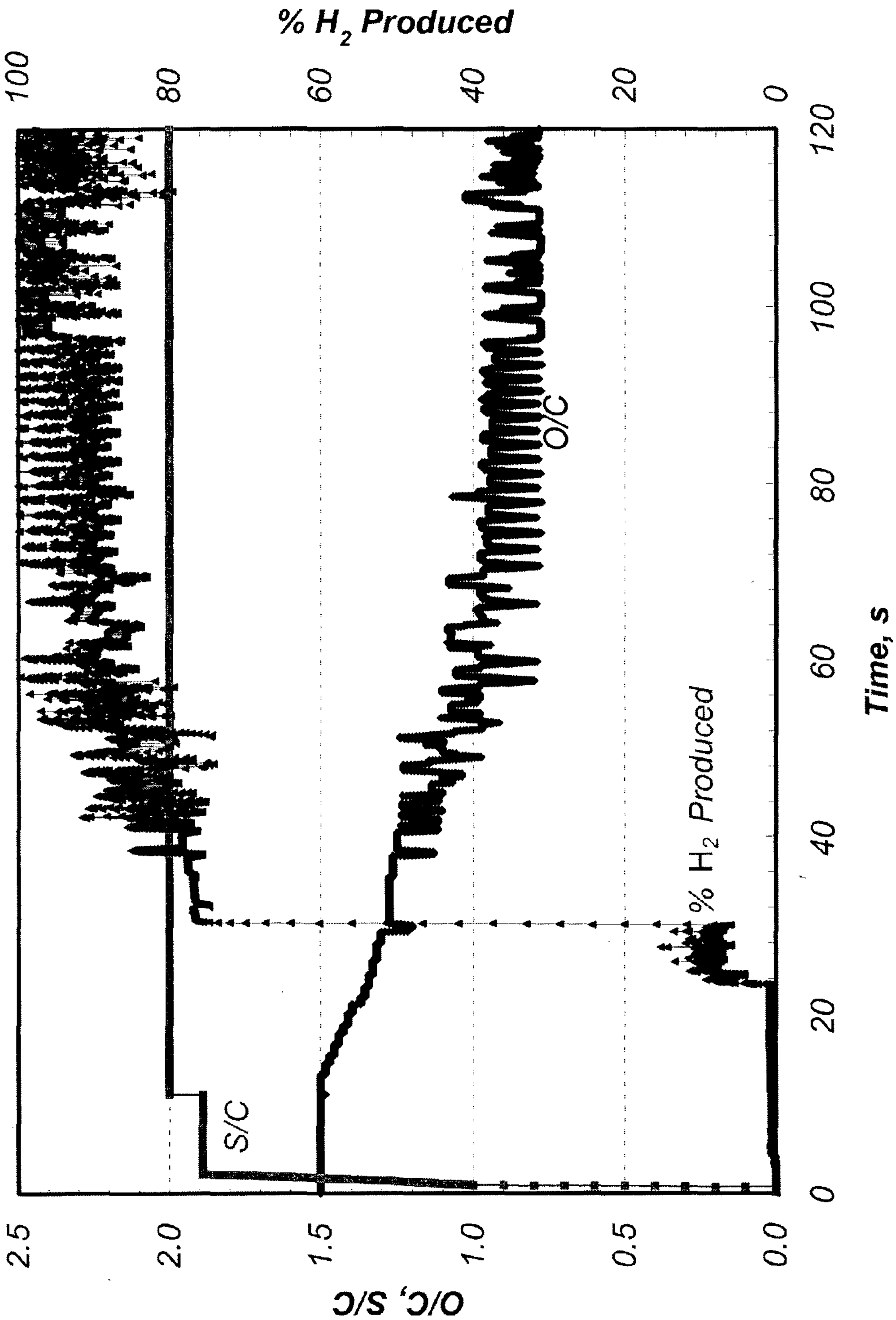

% H_2 Produced
100
80
60
40
20
0
O/C, S/C
2.5
2.0
1.5
1.0
0.5
0.0
Time, s
0
20
40
60
80
100
120
S/C
O/C
% H_2 Produced

Figure 9

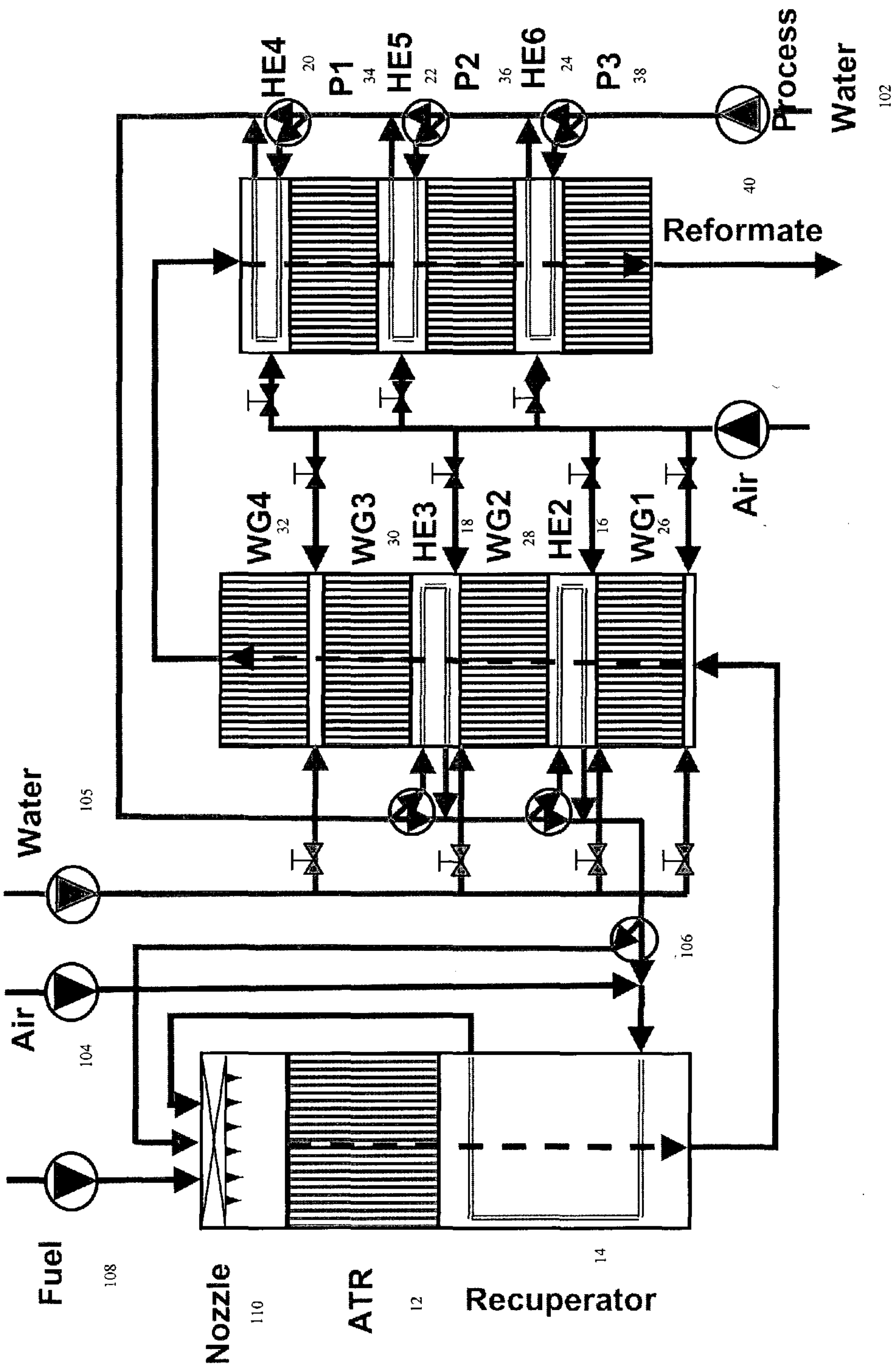

HE4
20
P1
34
HE5
22
P2
36
HE6
24
P3
38
Process
Water
102
40
Reformate
WG4
32
WG3
30
HE3
18
WG2
28
HE2
16
WG1
26
Air
Water
105
106
Air
104
Fuel
108
Nozzle
110
ATR
12
Recuperator
14

Figure 10

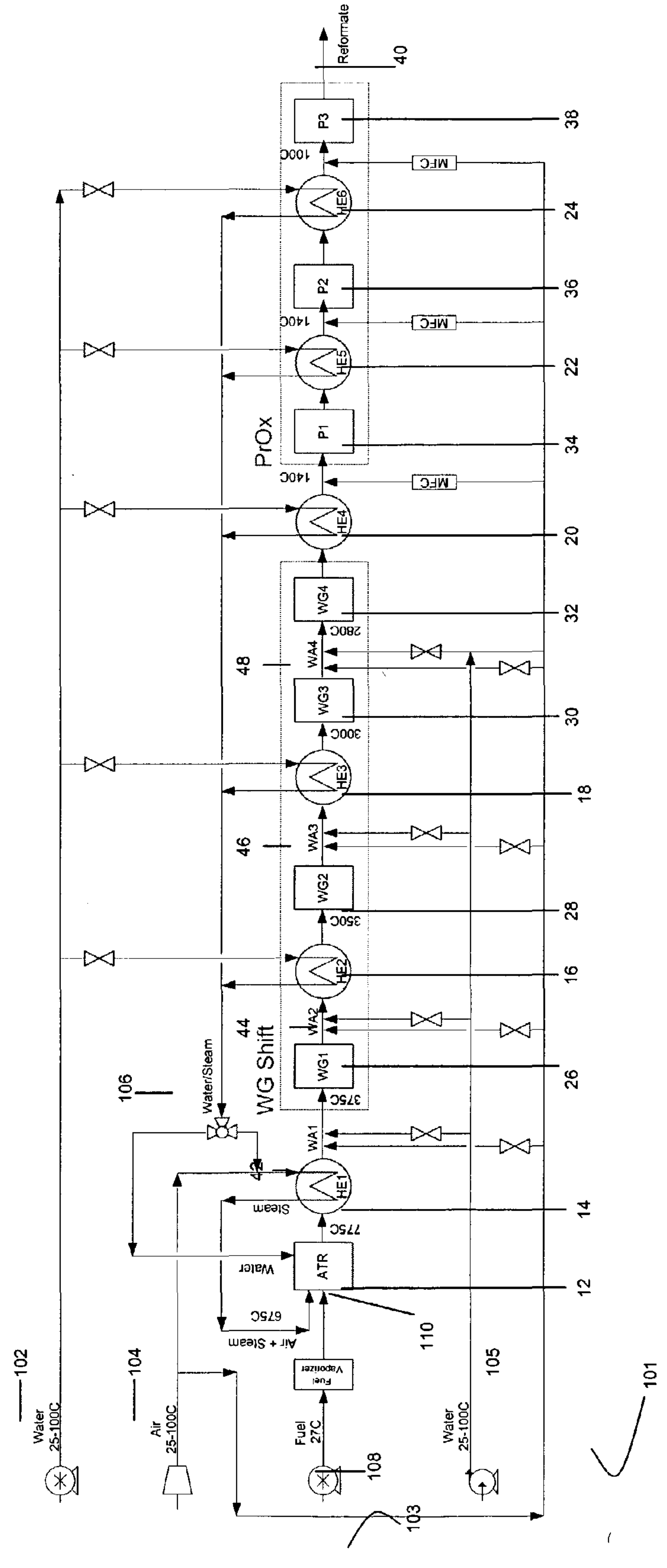

Reformate
40
P3
38
100C
MFC
HE6
24
P2
36
140C
MFC
HE5
22
PrOx
P1
34
140C
MFC
HE4
20
WG4
32
280C
WA4
48
WG3
30
300C
HE3
18
WA3
46
WG2
28
350C
HE2
16
WA2
44
WG Shift
WG1
26
375C
WA1
Water/Steam
106
42
HE1
14
Steam
775C
ATR
12
Water
675C
Air + Steam
110
Fuel Vaporizer
Water 25-100C
102
Air 25-100C
104
Fuel 27C
108
Water 25-100C
105
103
101

Fig. 11

FUEL PROCESSOR FOR PRODUCING HYDROGEN FROM HYDROCARBON FUELS

[0001] The United States Government has certain rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy and The University of Chicago representing Argonne National Laboratories.

FIELD OF THE INVENTION

[0002] The present invention relates to fuel cells that use autothermal reforming. More specifically this invention relates to fuel processor systems having a dynamically controlled thermal integration mechanism that enables the fuel processor to maintain the temperature profile that yields the maximum efficiency and fast transient response during cold starts and during load changes.

BACKGROUND OF THE INVENTION

[0003] Autothermal reforming has been espoused for the conversion of hydrocarbon and alcohol fuels to hydrogen in fuel processors for fuel cell system applications that have constraints on system size and weight, and require rapid start-up and load following capabilities. The idealized form of the autothermal reforming reaction can be written as: $C_nH_mO_p+x(O_2+3.76N_2)+(2n-2x-p)H_2O=nCO_2+(2n-2x-p+m/2)H_2+3.76xN_2$ (1) where, x is the oxygen-to-fuel molar ratio. The corresponding oxygen-to-carbon (O/C) and steam-to-carbon (S/C) ratios are represented as 2x/n and (2n−2x−p)/n, respectively. Actual reformers produce significant amounts of carbon monoxide (CO), which requires that the reformer be followed by water gas shift reaction ($CO+H_2O=CO_2+H_2$) zones and preferential oxidation zones ($CO+1/2O_2=CO_2$). When the fuel contains sulfur species, all sulfur-containing species must be removed prior to the catalyst that is poisoned by it. This means locating appropriate sulfur traps within the fuel processor.

[0004] It has been established that the maximum efficiency of the fuel processor is achievable at the thermoneutral point—the operating point where the oxygen-to-carbon (O/C) and steam-to-carbon (S/C) ratios lead to a zero heat of reaction ($\Delta H_r=0$). In the absence of waste heat available from sources outside the fuel processing system, the efficiency, which is defined as the lower heating value of the hydrogen in the reformate as a percentage of the lower heating value of the fuel fed to the fuel processor, of the fuel processor can approach this theoretical limit by using thermal integration. That is by heat exchange between the reactants (being heated) upstream of the reformer, and the products (being cooled) downstream of the reformer. Thermal integration provides the energy needed to generate steam and to preheat the steam and air before they are fed into the reformer. It has been shown that the ability to operate at high preheat temperatures, while at low O/C ratios and achieving high conversions of the fuel to hydrogen and carbon dioxide favors high hydrogen concentrations in the reformate, and thus high fuel processing efficiencies. High S/C ratios favor effective conversion of CO in the shift reactor, and lead to potentially smaller and lighter fuel processors.

[0005] Fuel processors for fuel cell systems need to balance many requirements and constraints, the particulars of which are application specific. In general, the fuel processors should be small, lightweight, efficient, capable of rapid start, capable of dynamic response at varying processing rates and inexpensive among other desirable attributes. Fuel processors currently have several constraints and limitations. A fuel processor's efficiency drops at part load. Also, fuel processors are known to be sluggish in responding to step-up transients. Problems arise due to the unavoidable heat losses from the fuel processor and the inability to maintain the reactors at set temperatures at part load, since at reduced flow rates the heat exchangers are oversized. This is particularly true during later shift zones, causing the desired CO conversion to not be achieved.

[0006] The fuel processor represents a series of unit operations and processes through which the primary fuel (e.g., hydrocarbon, alcohol, etc.) is converted to a hydrogen-rich gas that is suitable for the fuel cell. The low temperature polymer electrolyte fuel cell usually requires that the hydrogen-rich gas contain less than 10 to 100 parts per million (ppm) carbon monoxide, and there are other tolerance limits known in the art for chemical species such as sulfur and ammonia, as well.

[0007] Thus, a fuel processor for applications with constraints discussed above is needed such that it achieves the desired conversion of the feed streams through the shortest path and yet offers the flexibility to accommodate the control algorithms during various steady and transient operating modes such as start-up, steady-state, ramp-up, ramp-down, shutdown, and other various operating modes.

SUMMARY OF THE INVENTION

[0008] Fuel cells, especially those that operate at low temperatures, operate on high purity hydrogen. If a hydrogen supply is unavailable, the fuel cell system includes a fuel processor to convert available hydrocarbon or alcohol fuels into a hydrogen-rich gas that can be used by the fuel cell.

[0009] The present invention relates to a novel fuel processor system based on a thermal integration mechanism that enables the fuel processor to maintain the temperature profile that yields the maximum efficiency and dynamic response. With electronic chips determining the "optimal temperature profile" for a given operating load, the thermal integration is continuously adjusted such that the specified "optimal temperature profile" is achieved in the shortest possible time and maintained dynamically as the fuel processing rate varies over time. The present invention further relates to a new process for the conversion of a hydrocarbon fuel into a hydrogen-rich gas, based on autothermal reforming followed by the shift reaction and the preferential oxidation reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] **FIG. 1** is a schematic of an Integrated Fuel Processor with Temperature Control, with Coolant Water Streams in Series;

[0011] **FIG. 2** is a schematic of water flow through a Thermally Integrated Fuel Processor during Startup;

[0012] **FIG. 3** is a chart depicting the temperatures along the length of the autothermal reformer after light-off;

[0013] **FIG. 4** is a chart of temperatures for Water Gas Shift Reactors **1**, **2**, **3**, and **4** after set time intervals;

[**0014**] **FIG. 5** depicts a Thermally Integrated Fuel Processor during reforming operations with the water flowing through all designated flow paths;

[**0015**] **FIG. 6** is a chart depicting a Water Gas Shift Reactor and Preferential Oxidation Reactor temperatures and concomitant H_2 and CO concentrations as controlled with intermediate heat exchangers or water quench;

[**0016**] **FIG. 7** is a chart depicting Preferential Oxidation Reaction heatup at set intervals of time;

[**0017**] **FIG. 8** is a chart of CO Selectivity from Multi Stage Monolith-Supported Preferential Oxidation Reactors;

[**0018**] **FIG. 9** is a chart depicting Fuel processor production of 75% of rated H_2 after the 30-s startup period; and

[**0019**] **FIG. 10** shows a fuel processor that dynamically controls the coolant water flow path and quantity through the heat exchangers.

[**0020**] **FIG. 11** is a schematic of an Integrated Fuel Processor with Temperature Control, with Coolant Water Streams in Parallel

DETAILED DESCRIPTION OF THE INVENTION

[**0021**] The present invention relates to a new process for the conversion of a hydrocarbon fuel into a hydrogen-rich gas, based on autothermal reforming followed by the shift reaction and the preferential oxidation reaction. As shown in **FIG. 1**, a preferred embodiment provides a compact (>1000 W/L), inexpensive ($10/kW) and a lightweight (>1000 W/kg) fuel processor **101** with a greater than 80% efficiency based on lower heat value, that is capable of rapid startup (<30 seconds from a cold start) and turn down. The target for transient response is one second for 10% to 90% power. This preferred embodiment consists of an autothermal reformer **12**, a heat exchanger **14** which is a steam/air superheater-recuperator, water/air injectors **42**, **44**, **46**, **48**, heat exchangers **16**, **18**, **20**, **22**, **24**, catalytic zones comprising water gas shift reactors **26**, **28**, **30**, **32**, and preferential oxidation reactors **34**, **36**, **38**, and balance-of-plant items such as pumps, valves, pipes, sensors and etc. Each of the catalytic zones comprises a separate catalytic stage.

[**0022**] The process includes specifying the desired temperature at several, ideally four to ten, intermediate locations in the reformate flow path and expressly controlling those temperatures. This feature achieves the desired conversion with the least amount of catalyst, which contributes to the compact, lightweight, and inexpensive fuel processor **101** of **FIG. 1**. With accurate temperature control at these intermediate locations, the fuel processor **101** can maintain desired product quality and high efficiencies at any processing rate within its capacity range as well as during transients. In a preferred embodiment, all of the reformate is cooled by a process water **102** (used in the chemical reactions). The air, which also needs to be preheated, is used as a coolant only in the heat exchanger **14** (also referred to as a recuperator heat exchanger). This is done to reduce the pressure drop and thereby limit the power demand on the air blower/compressor. The present invention may utilize a Fast-Start protocol dependant on bringing the reactors to temperature without having to heat the heat exchangers **14**, **16**, **18**, **20**, **22**, **24** during the start-up period. For the Fast-Start protocol, the process water **102** bypasses the second through sixth heat exchangers. During Fast-Start, the process water **102** also bypasses the heat exchanger **14** and directly enters the autothermal reformer **12** via a nozzle **110**.

[**0023**] The temperatures at these locations are controlled by varying the fraction of coolant **102**, for example the process water **102**, flowing through the heat exchangers **16**, **18**, **20**, **22**, **24**. The temperatures at these locations are further controlled by direct injection of liquid, preferably water, into the reformate stream **40**. For example, the on-off control function may be accomplished by having the process water **102** bypass the heat exchangers **16**, **18**, **20**, **22**, **24** if the reformate temperature is below a set temperature point. Conversely, if the reformate temperature is above a set temperature point, then process water **102** would not bypass the heat exchangers **16**, **18**, **20**, **22**, **24** and water quenching could also be utilized by injecting water into the reformate at the water/air injectors **42**, **44**, **46**, **48**. The fuel processor **101** may be designed such that the flow path of the coolant **102** through, or bypassing, the heat exchangers **16**, **18**, **20**, **22**, **24** and the preferential oxidation reactors **34**, **36**, **38** is continuously adjusted to maintain a desirable temperature at each of the critical zones (each critical zone is a region where the temperature impacts the efficiency of the fuel processor **101**) in a fuel processing train **103**. These flow rates also can be continuously adjusted to maintain a desirable temperature at each critical zone in the fuel processing train. In addition, the flow paths can be controlled by 3-way on/off valves. The total process water **102** flow rate can be adjusted with the water pump, while the flow rates through each of the heat exchangers **16**, **18**, **20**, **22**, **24** can be adjusted with proportional 3-way valves. The fuel processor **101** can be designed such that the temperature is lowered to the desired value by injecting liquid water through a sparger, such that the endothermic phase change of the injected water leads to cooling of the gas stream. Furthermore, the fuel processor **101** can be designed where the temperature is raised to the desired value by injecting oxygen-containing gas (e.g. air) through a sparger, such that the oxygen reacts with the combustible gases to generate heat. Alternatively, a duty cycle can replace an on-off control system. Thus, it is possible to operate at a steady state with the flow path of process water **102** varying in time.

[**0024**] In accordance with the present invention, the fuel processor **101** has been designed that can convert fuels, such as hydrocarbons and alcohols, into a hydrogen-rich gas stream that is suitable for a polymer electrolyte fuel cell. The fuel processor **101** is based on autothermal reforming, because of the many benefits associated with this reaction. Examples of these benefits include: (1) the ability to dynamically control the heat of reaction by varying the O/C ratio; (2) the ability to control the reforming temperature with the O/C ratio and the S/C ratio; (3) when compared to partial oxidation reformers, the ability to operate the autothermal reformer at lower temperatures and being less likely to form carbonaceous deposits; (4) having the fuel processing rate in autothermal reformers not heat transfer limited. The result is a more efficient and faster production of hydrogen. **FIG. 9** illustrates the production of hydrogen at set time intervals during start-up.

[**0025**] **FIG. 1** shows a simplified schematic of the fuel processor **101** reported in the present invention. **FIGS. 5 and 11** further illustrate fuel processor systems. The fuel processor **101** of **FIG. 1** contains the autothermal reformer **12**, the heat exchanger **14**, the water/air injector **42**, the first water gas shift reactor **26**, the water/air injector **44**, the heat exchanger **16**, the second water gas shift reactor **28**, the water/air injector **46**, the heat exchanger **18**, the third water gas shift reactor **30**, the water/air injector **48**, the fourth water gas shift reactor **32**, the heat exchanger **20**, the first preferential oxidation reactor **34**, the heat exchanger **22**, the second preferential oxidation reactor **36**, the heat exchanger **24**, and the preferential oxidation reactor **38**. In this embodiment of the present invention, the steam and air are preheated to a temperature that approaches the autothermal reformer **12** exit temperature, approximately 775° C. is an optimum temperature for the autothermal reformer **12** for gasoline. This steam and air mixture mixes with the fuel stream in the autothermal reformer **12**.

[**0026**] To prevent any pyrolysis or thermal cracking of the fuel components, the fuel stream enters the autothermal reformer **12** at preferably less than 350° C. The reformate from the autothermal reformer **12** is cooled in the heat exchanger **14**, for example ideally to 380° C., by the air **104** and water/steam feeds **106** going into the autothermal reformer **12**. The reformate temperature at each subsequent catalyst zone inlet is cooler than that of the preceding zone. The reformate then passes through multiple water gas shift reactors **26**, **28**, **30**, **32**. FIG. **1** illustrates the fuel processor **101** system with four zones, each containing one of the water gas shift reactors **26**, **28**, **30**, **32** and each separated by one of the heat exchangers **14**, **16**, **18**, and/or one of the water/air injectors **42**, **44**, **46**, **48**. **FIG. 4** is a chart of the water gas shifts reactors' **26**, **28**, **30**, **32** temperatures during start-up. The heat exchanger **14** can utilize a coolant stream **106** and **104** that is a mixture of air and water. The air and water can be mixed prior to entering the autothermal reformer **12** to provide longer contact time, a larger cooling capacity, greater turbulence to increase heat transfer and lower oxygen concentrations, thus reducing hot spots in the autothermal reformer **12**. The temperatures in the fuel processor **101** may be efficiently controlled such that the temperature is lower at each successive critical zone. **FIG. 6** is chart depicting the water gas shift reactors' **26**, **28**, **30**, **32** and the preferential oxidation reactors' **34**, **36**, **38** temperatures as controlled with intermediate heat exchangers or water quench.

[**0027**] Ideally the autothermal reformer **12** is maintained at between 700-950° C., by adjusting the O/C and S/C ratios, and the inlet temperatures of the fuel, air, and steam feeds entering the autothermal reformer **12**. Furthermore, the temperatures of the air and steam feeds into the autothermal reformer **12** may be raised to $T_{exit}-T_{approach}$ (temperature at exit minus temperature at approach), where T_{exit} is the reformate gas temperature and $T_{approach}$ is the difference in temperature between the reformate gas as it enters the heat exchanger **14** and the coolant **102** as it exits the heat exchanger **14**. The water/air injectors, **42**, **44**, **46**, **48** increase the concentration of steam in the reformate gas and therefore accelerate the kinetics of the water gas shift reaction which results in greater conversion of CO to additional hydrogen. The water added with the water/air injectors **42**, **44**, **46**, **48** raises the effective H_2O/C ratio of the fuel processor **101** to greater than 1.8, preferably in the range 1.8-2.5.

[**0028**] The superheated air/steam mixture coming out of the heat exchanger and flowing into the nozzle at the tip of the reformer **14** is helpful in vaporizing the fuel when the fuel vaporizer is not effective. The heat exchanger **14** may be designed such that $T_{approach}$ is maintained to less than 150 centigrade degrees, and preferably to less than 5 centigrade degrees. The exact approach temperature to be used is to be decided on the basis of optimization between the fuel processor **101** weight, volume, pressure drop, cost, and system efficiency. The average temperature in the autothermal reformer **12** is maintained between 700-950° C., preferably between 750-850° C., by adjusting the O/C ratio of the feeds entering the autothermal reformer **12**, which is maintained between 0.5-1.0, preferably between 0.6-0.8. Furthermore, the average temperature in the autothermal reformer **12** is maintained at the desired temperatures by adjusting the H_2O/C ratio of the feeds entering the autothermal reformer **12**, which is maintained in the range 1.3-2.5, preferably between 1.5-2.3. The use of an anode gas burner where the combustible gas present in the fuel cell anode effluent is oxidized to generate heat, which energy is then transferred to the autothermal reformer reactant streams, such that the fuel processor **101** can be operated at a higher thermal efficiency.

[**0029**] For optimum efficiency, the catalytic zones **26**, **28**, **30**, **32**, **34**, **36**, **38** preferably operate in a narrow range of temperatures. TABLE 1 describes the target temperature for gasoline in the embodiment of the present invention illustrated in **FIG. 1**.

TABLE 1

	Optimum Temperatures for Catalytic Reactors							
PHASE	ATR	WG1	WG2	WG3	WG4	P1	P2	P3
TARGET TEMPERATURE	775° C.	375° C.	350° C.	300° C.	280° C.	140° C.	140° C.	100° C.
OPTIMUM TEMPERATURE RANGE	700–800° C.	360–400° C.	330–370° C.	280–320° C.	260–300° C.	100–150° C.	100–150° C.	90–120° C.

[**0030**] For highest efficiency, the air **104** and the process water **102** should be preheated as close to the autothermal reformer **12** temperature as possible. Optimum O/C and S/C are determined by the approach temperature, as seen in TABLE 2.

TABLE 2

Approach Temperature's Effect on O/C and S/C

ATR Temperature	775° C.	775° C.	775° C.	775° C.
Recuperator Approach Temperature	25° C.	100° C.	150° C.	200° C.
S/C in ATR	1.7–1.8	1.8–1.9	1.9–2.0	2.0–2.1
O/C in ATR	0.71	0.75	0.77	0.81
Equilibrium CO at LTS	0.9%	0.7%	0.6%	0.5%
FP Efficiency (%)	85.2–85.9	83.9–84.8	83.6–84.5	82.9–83.7
Theoretical FP Efficiency	86.2%	85.6%	85.0%	84.6%

[0031] **FIG. 2** illustrates the startup mechanism whereby the water **102** and the water/steam **106** feeds bypasses some of the heat exchangers **14, 16, 18, 20, 22, 24**. This allows for a substantially increased performance of the fuel processor **101** during first 30 seconds following startup. **FIG. 10** is a chart depicting fuel processor production of 75% of rated H_2 after the 30-second startup period. The Fast-Start strategy consists of use of the autothermal reformer **12** for exothermic fuel conversion (partial oxidation reformer, where no water is injected) with O/C>1 to produce hydrogen, carbon monoxide, and other light hydrocarbon gases such as methane, etc. The shift reactors **26, 28, 30, 32** are operated as preferential oxidation reactors by injecting air through the water/air injectors **42, 44, 46, 48**. As the autothermal reformer **12**, the water gas shift reactors **26, 28, 30, 32** and the preferential oxidation reactors **34, 36, 38** begin to heat up, water is introduced gradually to control the peak temperature. The water gas shift reactors **26, 28, 30, 32** and the preferential oxidation reactors **34, 36, 38** are heated in parallel by distributed combustion of H_2 and CO. In the device depicted by **FIG. 1**, the heating priority is: first, the water gas shift reactor one **26**; second, the water gas shift reactor two **28**; third the water gas shift reactor three **30**; fourth the preferential oxidation reactor one **34**; fifth the preferential oxidation reactor two **36**; sixth the preferential oxidation reactor three **38**; and seventh the water gas shift reactor four **32**. In fact, the water gas shift reactor four **32** need not be brought to operating temperature, nor is it essential to fully heat up the water gas shift reactor three **30**. To further facilitate the Fast Start protocol, process water **102** may bypass all of the heat exchangers **14, 16, 18, 20, 22, 24**, during start-up. During and immediately after start-up the O/C ratio is >0.75.

[0032] The fast start protocol consists of rapidly bringing the autothermal reforming reactor **12** to a design temperature. The autothermal reformer **12** is started as a partial oxidation reactor having an O/C ratio of 1.5. A fuel **108**, such as gasoline, is fed to the nozzle **110** as a liquid until the fuel vaporizer is heated above 150° C. Water is introduced gradually to control a peak reactor temperature. Water is also fed together with gasoline until the quality is 1. The O/C ratio is relaxed toward 0.75 after S/C reaches 2.0. Once S/C reaches 2.0, the reactor temperature is controlled by varying O/C.

[0033] The water gas shift reactors **26, 28, 30, 32** are started up by heating them in parallel with distributed combustion of H_2 and CO generated by the autothermal reformer **12**. Oxidation air is fed to the water gas shift reactors **26, 28, 30, 32**, at the water/air injectors **42, 44, 46, 48** in the preferred embodiment illustrated in **FIG. 1**. If the peak temperature anywhere in a stage exceeds its allowable maximum, the air supply for that stage is cut off. Allowable maximum temperatures for the four stages of the device of **FIG. 1** are 450, 450, 400, and 400° C. respectively. The flow path of process water **102** is controlled dynamically. The process water **102** bypasses the heat exchangers **14, 16, 18, 20, 22, 24** unless the gas temperature at the inlet to the catalytic zone following it exceeds its design value. The process water **102** bypasses the heat exchanger **14** until it boils off completely in the remaining heat exchangers.

[0034] The preferential oxidation reactors **34, 36, 38** are started by bringing them up to temperature using the sensible heat in the reformate leaving the last stage of the water gas shift reactors **26, 28, 30, 32** (i.e. the 4th stage in the preferred embodiment) and by oxidizing the CO present in the reformate gas. If necessary the heatup of the preferential oxidation reactors can be accelerated by injecting additional oxygen to oxidize hydrogen that may be present in the reformate gas The preferential oxidation reactors **34, 36, 38** units include air injectors. **FIG. 7** is a chart depicting Preferential Oxidation Reactor heatup at set intervals of time during start-up. Combustion air is fed equally to the stages of the preferential oxidation reactors **34, 36, 38**, three in the preferred embodiment. If the peak temperature anywhere in a stage exceeds its allowable maximum, the air supply for that stage is reduced or cut off, and the process water is allowed to flow through the respective upstream heat exchanger to maintain the desired temperature. Allowable maximum temperatures in the preferred embodiment are 250, 225 and 150° C. and **FIG. 9** is a chart of Multi Stage Monolith-Supported Preferential Oxidation Reactors.

[0035] After the start-up has completed, the system transitions from start-up mode to reforming mode, the supply of combustion air to the water gas shift reactors **26, 28, 30, 32** is terminated. Air feed to the preferential oxidation reactors **34, 36, 38** is determined by the fuel processing rate, the inlet CO concentration and specified stage stoichiometry. Process water **102** bypasses the heat exchanger **14** until it is completely boiled off in the heat exchangers **16, 18, 20, 22, 24**. If the reformate temperature at the inlet to the first water gas shift reactor **26** exceeds the set point (375° C. for the example in Table 1), then liquid water must be added at water/air injector **42** to quench the gas mixture down to the set point. The flow path of process water **102** continues to be adjusted dynamically to control the bed temperatures. The S/C ratio is fixed at the specified value (2.0 for the example in Table 2) while O/C is varied to control the autothermal reformer **12** temperature, as represented in TABLE 2.

[0036] The heat exchangers **14, 16, 18, 20, 22, 24** are sized to ensure that at the rated operating capacity, the process water **102** cools the reformate stream **40** to the temperature specified for entry into the next catalyst zone **26, 28, 30, 32, 34, 36, 38**. At other throughput rates, if the process water **102** flow through the heat exchanger **14, 16, 18, 20, 22, 24** results in excessive cooling, the water flow can be bypassed intermittently to maintain the reformate temperature within a small range around the value specified for that location. If however, the reformate is not cooled to the specified temperature even with the process water **102** flowing through the heat exchangers **14, 16, 18, 20, 22, 24**, then liquid water can be injected directly into the reformate stream **40** for evaporative cooling.

[0037] There is no heat exchanger before the last shift zone (for example, the fourth water gas shift reactor **32** in the preferred embodiment) and cooling is achieved entirely by liquid water injection. This is because at these relatively lower temperatures (less than 300° C.), it is advantageous to accelerate the kinetic rates for the shift reaction by increasing the concentration of steam in the reformate stream **40**. The reformate from the last water gas shift zone then enters the first of the preferential oxidation reactor **34**, **36**, **38** zones. Before entering each successive of the preferential oxidation reactors **34**, **36**, **38** zones, the reformate is cooled through the heat exchangers **20**, **22**, **24**.

[**0038**] The nozzle **110** has a dual function. It serves as an atomizer and, for example, in one embodiment it must be capable of atomizing mixture of liquid gasoline and water of between 0-100% gasoline. Gasoline is fed to the nozzle **110** as a liquid until the fuel vaporizer is heated to above 150° C. During the start-up period, water is fed together with gasoline. Further, the nozzle **110** must be able to function as a mixer. During typical reforming mode, the nozzle **110** most preferably should mix gasoline vapor with the mixture of air and superheated steam.

[**0039**] The size of the water gas shift reactors **26**, **28**, **30**, **32** is determined by the S/C and the CO concentrations at inlet and exit (desired), as demonstrated in TABLE 3. It is preferable to minimize the size of the water gas shift reactors **26**, **28**, **30**, **32**, while maximizing their efficiency and productivity.

[**0040**] The performance of the preferential oxidation reactors **34**, **36**, **38** can be optimized, as illustrated by TABLE 4. TABLE 4 is based on Los Alamos National Laboratory data at 100° C. rather than the 140/140/100° C. recommended in this application. The CO selectivity increases with CO concentration. The preferred design as reflected in TABLE 4 is conservative. Two stages may suffice, but with lower selectivity.

TABLE 4

Optimized Performance of Preferential Oxidation Reactor

Stage	1	2	3	At FP Exit	Overall
CO	1.0%	0.2%	0.07%	10 ppm	
Stoichiometry	1.03	1.05	2.27		1.40
CO Selectivity	0.77	0.64	0.42		0.71
ghsv (1/h)	37,00	37,00	37,00		12,300

[**0041**] TABLE 5 illustrates the catalyst requirements for a 10 kWe fuel processor designed in accordance with the present invention.

TABLE 3

Size of Water Gas Shift Reactors is Determined by S/C and Exit CO Concentration

Approach	25° C.			100°			150°		
Outlet CO	1.2%	1.1%	1.0%	1.1%	1.0%	0.9%	0.9%	0.8%	0.7
FP Efficiency	85.2	85.6	85.9	83.9	84.4	84.8	83.6	84.0	84.5
ATR									
S/C	1.75	1.70	1.66	1.94	1.89	1.83	2.01	1.95	1.89
O/C	0.71	0.71	0.71	0.75	0.75	0.75	0.77	0.77	0.77
Stage 1									
Inlet CO	11.3	11.6	11.8	10.0	10.3	10.5	9.5%	9.7%	10.0
H_2O/CO	1.8	1.7	1.6	2.3	2.2	2.1	2.5	2.4	2.3
ghsv, (1/h)	54,00	53,49	53,00	59,67	59,05	58,44	62,45	61,74	61,08
Stage 2									
Inlet CO	5.2%	5.5%	5.8%	4.2%	4.4%	4.6%	3.8%	4.0%	4.2
H_2O/CO	2.8	2.5	2.3	4.2	3.8	3.4	4.9	4.4	4.0
ghsv	27,86	27,60	27,35	32,31	31,98	31,65	36,02	35,63	35,24
Stage 3									
Inlet CO	3.4%	3.7%	3.9%	2.6%	2.7%	2.9%	2.3%	2.4%	2.6
H_2O/CO	3.7	3.3	2.9	6.2	5.5	4.9	7.4	6.6	5.8
ghsv	10,34	10,30	10,20	12,15	12,02	11,90	13,65	13,34	13,30
Stage 4									
Inlet CO	2.1%	2.3%	2.6%	1.5%	1.6%	1.7%	1.3%	1.4%	1.5
H_2O/CO	7.3	6.4	5.6	12.6	11.0	9.7	15.2	13.3	11.7
ghsv	6,230	4,170	2,450	17,81	10,00	6,310	16,47	9,410	5,720
WGS, kg	4.6	5.8	8.2	2.9	3.5	4.4	2.8	3.5	4.6

TABLE 5

Catalyst Requirements for a 10 kWe Fuel Processor

	GHSV (1/h)	Volume	Weight
ATR	74,000	250	0.150
WGS	6308	3590	2.450
WG1	66,000	380	0.235
WG2	41,000	570	0.375
WG3	22,000	1040	0.690
WG4	13,600	1600	1.150
PrOx	12,333	2130	0.870
P1	37,000	710	0.290
P2	37,000	710	0.290
P3	37,000	710	0.290
Totals	3951	5970	3.470

[0042]

TABLE 6

Re-optimization of WGS Space Velocities

FP Efficiency	84.4	84.4	84.4	84.4	84.4	84.4
Stage 4 Inlet	250°	250°	260°	270°	280°	290°
Outlet CO Conc.	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%
ATR						
S/C	1.89	1.89	1.93	1.97	2.01	2.05
O/C	0.75	0.75	0.75	0.75	0.75	0.75
Stage 1 WGS						
Inlet Co Conc.	10.3	10.3	10.1	9.9%	9.7%	9.5%
H2O/CO	2.2	2.2	2.3	2.4	2.5	2.5
ghsv, 1/h	5905	6211	6340	6476	6608	6734
Stage 2 WGS						
Inlet Co Conc.	4.4%	4.4%	4.3%	4.1%	4.0%	3.8%
H2O/CO	3.8	3.8	4.0	4.3	4.1	4.0
ghsv, 1/h	3198	3613	3766	3923	4082	4227
Stage 3 WGS						
Inlet Co Conc.	2.7%	2.8%	2.7%	2.6%	2.5%	2.4%
H2O/CO	5.5	5.4	5.8	6.3	6.7	7.2
ghsv, 1/h	1202	1387	1634	1926	2230	2347
Stage 4 WGS						
Inlet Co Conc.	1.6%	1.7%	1.6%	1.6%	1.6%	1.5%
H2O/CO	11.0	10.6	10.8	10.8	11.0	11.3
ghsv, 1/h	1000	9250	1130	1299	1364	1206
WGS, kg	3.5	3.4	3.0	2.6	2.5	2.6

[0043] One of the main problems that the present invention overcomes is size, weight, and dynamic response requirements of fuel processors. This is accomplished by enabling precise control of the temperature and temperature profiles at all times, thereby ensuring that the necessary conversions are always achieved within very small catalytic zones. The present invention allows for dynamic control of temperature at critical points. This dynamic temperature control improves the transient response of the fuel processor **101**, thus allowing for substantially instantaneous transient response. Dynamic temperature control also allows for a fast start by bringing the reactors to their desired temperatures without having to heat exchangers **14**, **16**, **18**, **20**, **22**, **24** during start-up. Another benefit of the dynamic temperature control is that the heat exchangers **14**, **16**, **18**, **20**, **22**, **24** do not need to be precisely sized. This is significant because in many applications the fuel-processing rate is not constant and is rarely at the maximum capacity.

[0044] From the foregoing teachings, it can be appreciated by one skilled in the art that a new, novel and nonobvious method and device for the conversion of a hydrocarbon fuel into a hydrogen-rich gas, based on autothermal reforming followed by the shift reaction and the preferential oxidation reaction has been disclosed. It is to be understood that numerous alternatives and equivalents will be apparent to those of ordinary skill in the art, given the teachings herein, such that the present invention is not to be limited by the foregoing description but only by the appended claims.

What is claimed is:

1. A fuel processor comprising a dynamically controlled thermal integration mechanism, wherein the thermal integration mechanism maintains the fuel processor temperature within a predetermined temperatures range.

2. A fuel processor for converting a fuel into a reformate, which is a hydrogen-rich gas, having a reformate temperature, comprising:

a coolant stream having a variably controllable flow path;

an air feed having an air feed temperature;

a water feed having a water feed temperature;

a steam feed having a steam feed temperature;

the reformate having a reformate temperatures, an oxygen to carbon ratio, a steam to carbon ratio;

a fuel processing train having an autothermal reformer, at least one heat exchanger adapted to utilize the coolant stream, at least one water/air injector, at least one water gas shift reactor for controlling the CO and H_2 concentration in the reformate, at least one preferential oxidation reactor and at least one critical zone, and at least one means for dynamically controlling the temperature of the fuel processor; wherein the dynamic control means provides for maintenance of the temperature of the at least one critical zone within a predetermined temperature range.

3. The fuel processor of claim 2, wherein the coolant stream comprises a mixture of air and water to be fed into the autothermal reformer.

4. The fuel processor of claim 2, wherein the reformate temperature at each successive critical zone is lower than in the preceding zone.

5. The fuel processor of claim 2, wherein the temperature of the autothermal reformer is maintained by adjusting the oxygen to carbon ratio, the steam to carbon ratio, and the temperatures of the fuel, air and water feeds entering the autothermal reformer.

6. The fuel processor of claim 2, wherein the controlling means are selected from the group consisting of heat exchangers, liquid injection ports, liquid injection spargers, air injection ports and air injection spargers.

7. The fuel processor of claim 2, wherein the at least one critical zone is located downstream of the reformer in the fuel processing train.

8. The fuel processor of claim 2, having a flow path of the coolant streams that is continuously adjusted to maintain a desirable temperature at each critical zone in the fuel processing train.

9. The fuel processor of claim 2 wherein flow rates of the coolant streams flowing through or bypassing the heat exchangers in the fuel processing train are continuously adjusted to maintain a desirable temperature of the reformate at the at least one critical zone in the fuel processing train.

10. The fuel processor of claim 2, wherein the reformate temperature is lowered to the desired value by injecting liquid water through a sparger, such that the endothermic phase change of the injected water leads to cooling of the gas stream.

11. The fuel processor of claim 2, wherein the reformate temperature is raised to the desired value by injecting oxygen-containing gas through the sparger, such that the oxygen reacts with the combustible gases to generate heat.

12. The fuel processor of claim 2, wherein autothermal reformer temperature is maintained by adjusting the temperatures of the fuel, air, and steam feeds entering the autothermal reformer.

13. The fuel processor of claim 2, wherein the average temperature in the autothermal reformer is maintained by adjusting the steam to carbon ratio and oxygen to carbon ratio of the fuel, air, and steam feeds entering the autothermal reformer.

14. The fuel processor of claim 2, wherein the temperatures of the air and steam feeds into the autothermal reformer are raised to $(T_{ATR\_exit}-T_{approach})$.

15. The fuel processor of claim 2, having an anode gas burner where a combustible gas present in a fuel cell anode effluent is oxidized to generate heat, which energy is then transferred to the autothermal reformer, such that the fuel processor can be operated at a higher thermal efficiency.

16. The fuel processor of claim 2, wherein an electronic chip determines an optimal temperature profile.

17. The fuel processor of claim 2, wherein the at least one water gas shift reactor and the at least one preferential oxidation reactor are heated in parallel by distributed combustion of H_2 and CO.

18. A method of heat exchange between fluids entering and leaving an autothermal reformer comprising the steps of:

mixing air and water feeds prior to entering a heat exchanger;

providing longer contact time between air and water/steam;

providing a greater cooling capacity in the heat exchanger;

providing greater turbulence in the heat exchanger to improve heat transfer; and

lowering the concentration of oxygen in a resulting mixture.

19. The method of claim 18 further comprising the additional step of water bypassing the heat exchanger unless a gas temperature at a stage following it exceeds its design value.

20. The method of claim 18 further comprising the additional step of cutting off air supply for a stage when the temperature for the stage exceeds a predetermined maximum.

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