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Thermal Analysis of PROX reactor with shell and tube type heat exchanger

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Abstract — *The PROX reaction process occurring in the reactor with 1%(wt) platinum based on iron hydroxyphosphate was analyzed between temperature range of 80 ^0C and 120 ^0C in hysys software. A shell and tube type heat exchanger was designed and analyzed for temperature control for PROX reaction, containing copper tubes. The temperature profile suggests the expected temperature rise in the PROX reactor and temperature drop in the heat exchanger. The heat exchanger was able to bring down the temperature of gases from 2100 C to 1130 C successfully. The gas composition sent to the PROX reaction process was 40% H_2, 1% CO, 9% CO_2, 0.5% O_2, and 49.5% Ar. The result suggests that the removal of heat from the gases increases the CO selectivity and conversion.*

I. INTRODUCTION

The increment in the requirement of electricity has forced us to find new and better energy source for the same. The conventional energy sources like coal and petroleum fuels are not sufficient enough to produce electricity as they are restricted by maximum efficiency of Carnot cycle. In addition to that use of coal and petroleum products as fuel produces harmful gases like NO_x, CO, SO_2 etc. These limitations of conventional fuels lead us to find non-conventional energy sources which are more efficient and do hardly any harm to the environment.

Fuel cells are promising new alternatives for the generation of electricity. They use hydrogen as fuel and produce electricity. They are the electrochemical device with efficiency almost double of Carnot fuel cycles. The emission due to the fuel cells is much lower than the conventional methods. Their higher power to weight ratio make them more effective way to produce electricity. Figure 1 shows basic PEM fuel cell working.

II. FUEL PROCESSING

The hydrogen required for the fuel cell cannot be provided to the plant via pipes or transportation because it's really hard to handle the hydrogen because of its explosive nature. The only way to provide hydrogen is to produce it at the required point. Mainly the hydrogen is produced from the traditional hydrocarbon products like gasoline. They can be reformed into the hydrogen rich stream which s than supplied to the fuel cell. Unfortunately the stream contains carbon monoxide with them which is needed to be removed as it reduces efficiency and working life span of the fuel cell.

Typically, the carbon monoxide is removed from the gas by water gas shift method. But it can remove the carbon monoxide up to 99% and the fuel cell requires the gas with less than 1ppm of carbon monoxide.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

The additional filter of the gases is done by three methods: (1) Methanation (2) Membrane Separation (3) PROX reaction

Methanation process uses 3 moles of H_2 with 1 mole of CO which is not efficient enough.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

Membrane process uses high cost membrane and very high pressure to separate H_2 from the gases.

So the only economical way to produce carbon monoxide free gas stream is PROX reaction.

III. PROX REACTION

PROX reactors use catalysts to reduce the concentration of CO by selectively oxidizing CO into CO_2. The gas stream exiting the WGS typically contains 40% H_2 and only 1% CO. Oxidation of CO is a rapid reaction but the high concentrations of H_2 in the PROX inlet gas mean that some H_2 oxidation is inevitable. The CO and H_2 oxidation reactions are shown in equations (3) and (4) respectively.

$CO + ½ O_2 \rightarrow CO_2$ $\Delta H_{298} = -283$ kg/mol (3)

$H_2 + ½ O_2 \rightarrow H_2O$ $\Delta H_{298} = -242$ kg/mol (4)

Fortunately, catalysts are being developed that are capable of preferentially oxidizing CO in the presence of H2 [2-6]. In certain temperature ranges, these catalysts favor CO absorption on their surface, thereby allowing CO to be oxidized selectively. The correct temperature range is critical for proper PROX performance.

The performance of PROX reactors is generally described by CO conversion (XCO) and CO selectivity (SCO) at a given gas hourly space velocity (GHSV) in the reactor. CO conversion and selectivity are defined by equations (5) and (6).

$$X_{co} = \frac{\text{(moles of CO at inlet) - (moles of CO at outlet)}}{\text{Moles of CO at inlet}} \quad (5)$$

$$S_{co} = \frac{CO\ converted \times 100}{Total\ conversion} \quad (6)$$

GHSV is defined by equation (7) and it is the ratio of the volume flow rate of the gas to the volume of the reactor. GHSV tells the residence time of the gas stream in the reactor. High GHSV represents short residence time.

V = reactor volume
Q = volume flow rate/hr

GHSV = V/Q

Maintaining the PROX reactor in the optimal temperature range is difficult because the oxidation of CO and H2 are both highly exothermic reactions (enthalpy of formations for the reactions are shown in equations (3) and (4)). As CO is converted, heat is released and the temperature rises in the reactor. Sufficient heat must be removed to compensate for the heat released during the reaction or else the temperature rises to undesirable levels and PROX performance drops. Micro channel reactors have been shown to effectively manage heat generation by conduction through the reactor framework [7]. Micro channel reactors, however, must be scalable to meet the volume flow requirements of transport vehicles. The scaled up reactor must also be lightweight and compact. Another method of heat removal is to insert heat exchangers into the reactor bed. In this case, the reactor consists of a tube filled with catalyst supported by a substrate. Examples of substrate supports are alumina pellets, ceramic monoliths, and metal foams. A small amount of catalyst is coated over the surface of the support material. As the gas stream flows through the reactor the temperature will rise in the catalyst bed. Heat exchangers inserted into the bed will remove the unwanted heat out of the reactor by means of a coolant fluid.

IV. PREVIOUS PAPER REVIEW

A PROX silicon microreactor developed by Ouyang et al. [7] closely simulates an isothermal reactor. The microreactor is a single channel (500 _m width x 470 _m depth x 4.5 cm length) in a silicon chip capped with PyrexTM glass. A thin film of Pt/Al2O3 catalyst was deposited on the channel walls. Each point within the reactor was maintained at the same temperature because the generated heat was quickly conducted through the reactor walls. Experimental data displays near 100% CO conversion and 40% CO selectivity achieved at temperatures between 180 and 220 °C.

A working multistage PROX reactor reported by Pan et al. [18] demonstrates the feasibility of thermal integration and high thermal efficiency.

Dudfield et al. [19] compared the performance of three PROX reactor designs that all feature active heat removal from the reaction zone. A shell and tube heat exchanger was filled with porous micro spheres coated with catalyst.

Brooks et al. [21] reported a multi section reactor similar to the one developed by where heat exchangers are placed between catalyst sections for temperature control. A total of four catalyst chambers where used with flat panel microchannel heat exchangers inserted between each bed.

V. OBJECTIVE

Objective of the study is to provide a PROX reactor 1% (wt) with platinum based on iron hydroxyphosphate which reduces the carbon monoxide level up to 0.001%.

Second objective of the project is to provide a heat removing equipment that can keep the temperature of the gases in allowable range.

VI. METHODOLOGY

The proposed reactor design uses metal foam as a catalyst support and shell and tube type heat exchangers for PROX reaction. Metal foams are effective supports for catalysts in PROX reactors because of their high surface area per unit volume, low density, low pressure drop, high thermal conductivity, and irregular passageways. Panels are inserted between sections of catalyst coated foam. Catalysts used are 1% (wt) platinum based on iron hydroxyphosphate.

High heat transfer per unit volume and weight make the shell and tube type heat exchangers superior to other products appropriate for this application. The goals of this project include proving that these heat exchangers are effective in controlling the temperature in the PROX reactor that the control of temperature results in a high performance PROX reactor capable of rapid CO conversion and high selectivity at high space velocities**.**

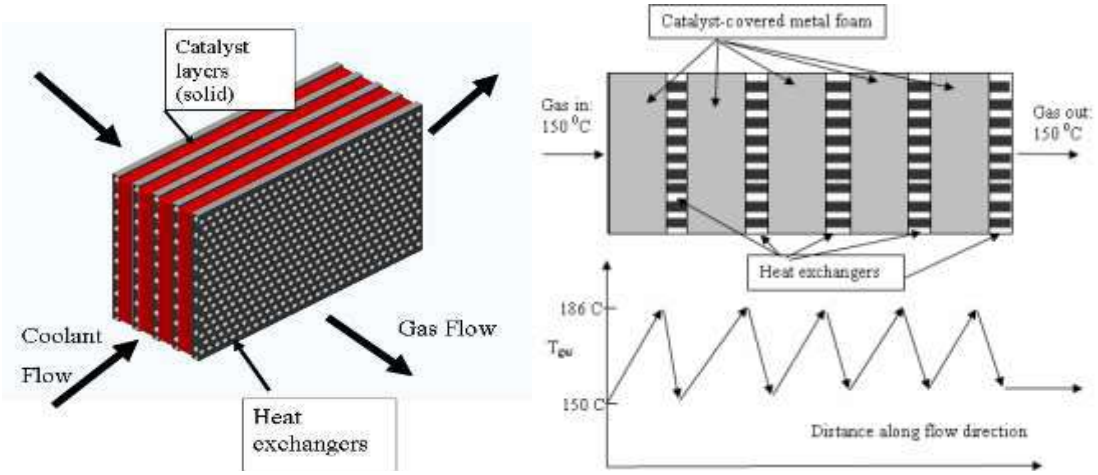

Figure: Reactor concept with micro heat exchangers and a saw tooth axial temperature profile.

VII.PROX REACTION ANALYSIS

Composition of Reaction Gases (stream 1)

Components	Molar Flow	Mole Fraction	Mass Flow	Mass Fraction
	(kg*mole/hr)		(kg/hr)	
Co2	0.00	0.00	0.00	0.00
CO	100	1.00	2801	1.00
Oxygen	0.00	0.00	0.00	0.00
H20	0.00	0.00	0.00	0.00
H2	0.00	0.00	0.00	0.00

Oxygen composition (stream 2)

O2	50	1.00	1600	1.00

Reaction Gases Properties:

Temperature (C)	110
Pressure (kPa)	101.3
Molar flow (kg*mole/hr)	100.0
Mass Flow (kg/hr)	2801.
Heat Capacity (kJ/kg*C)	1.248
Thermal Conductivity (W/m*K)	0.030

Oxygen properties

Temperature (C)	110
Pressure (kPa)	101.3
Molar Flow (kg*mole/hr)	50
Mass Flow (kJ/hr)	1600
Heat Capacity (kJ/kg*C)	0.942
Thermal Conductivity (W/m*K)	0.033

Outlet Composition without cooling (stream 3)

Temperature (C)	2657
Pressure (kPa)	101.3
Molar Flow (kg*mole/hr)	120.9
CO_2 Molar Flow Fraction	0.4814
CO molar Flow Fraction	0.5186

Outlet composition with cooling (stream 3)

Temperature (C)	112
Pressure (kPa)	101.3
Molar Flow (kg*mole/hr)	100
CO2 Molar Flow Fraction	1.000
CO molar Flow Fraction	0.000

VIII. HEAT LOAD

The model described in the literature review section was used to design the heat exchangers for the PROX reactor. The model requires several inputs including fluid mass flow rates, inlet temperatures, heat load, fluid properties, and panel geometry. The amount of heat that must be removed by the heat exchangers is equal to the heat released during the oxidation reactions in equations (3) and (4). The heat released in a PROX reactor depends on the size of reactor needed for a fuel cell. The heat exchangers are conservatively sized to absorb a load calculated by assuming all oxygen is consumed by the more exothermic CO oxidation reaction (ΔHr, 298K = -283 kJ/mol). Assuming a surplus of CO is present, the heat release depends on the molar flow rate of O2 consumed as described in equation (14). The flow rate of O2 consumed is multiplied by 2 in equation (14) because the energy release is per mol of CO or per ½ mol of O2.

8.1 Heat addition (Q) = ΔHco(kJ/mol) * O_2(consumed)

= -283 (kJ/mol) * O_2(consumed)

8.2 Temperature rise:

Q = m*Cp*ΔT

m = mass of gases (kg)
Cp = Specific heat of gases (kJ/kg*K)
ΔT = Temperature rise

So,

$$\Delta T = \frac{-283\ (kJ/mol) * O2(consumed)}{Mass * Cp}$$

8.3 Heat addition due to reaction:

R = $\bar{R}$/M
= 8.314/22.36
= 0.372 kJ/kg*K

ρ = P/R*T
=101.32/0.372*400

= 0.680 kg/m3

With the flow rate of 13 L/min (i.e. V= 0.000219 m3/s).

8.4 Mass flow rate (m) = ρ * V
= 0.680 * 0.000291
= 0.000198 kg/s

8.5 Heat capacity (C) = m * Cp
= 0.000198 * 1.248
= 0.000247 kW/K

And the molar flow rate of O_2 is:

ηO_2 = 0.005 * 0.000198 * 1000 / 22.36

= 4.438*10-5 mol/s

Heat addition

Q = ΔH_{co}(kJ/mol) * O_2(consumed)

= -283 (kJ/mol) * O_2(consumed)

= -283 * 4.43*10-5 *2

= -25.06 W

Therefore, the heat exchanger must be capable to remove 25.06 W heat from the gases.

Temperature rise

$$\Delta T = \frac{Q}{Mass * Cp}$$

$$= \frac{25.06\ W}{0.000198\ kg/s * 1.248\ kJ/kg*K}$$

= 101.5 K

Assuming the gas temperature entering the catalyst bed is 110 °C then the temperature leaving the bed will be 210 °C. The gas temperature will return to 110 °C after passing through the heat exchanger designed to remove 25 W from the gas stream flowing at 13 L/min (at 298 K) with an upstream gas temperature of 210 °C.

IX. HEAT EXCHANGER

A heat exchanger was designed according to the heat load discussed above. Copper tubes of 10 mm inner diameter and 12 mm outer diameter was used in a 4*4 formation fixed between two iron plats of 72mm*72mm and boxed with another iron plats.

The above design of heat exchanger was analyzed in Ansys software for its performance and it showed that it is able to remove the heat of 25 Watt with effectiveness of 0.87.

According to the design a heat exchanger was fabricated and its effectiveness was tested. The results of the experiments are as below:

Experiment:

As shown in figure hot air at 100 ^{o}C was taken from the heater and through pipe it was passed through the copper tubes of heat exchanger. The metal box was filled with water around the tubes.

Figure: Experimental setup

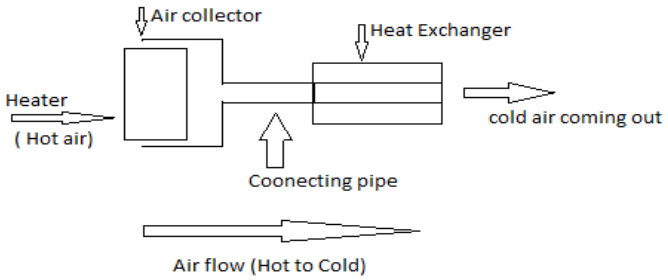

Figure: Schematic Diagram of the Experiment

The table containing data of outlet temperature and calculation of the effectiveness of the heat exchanger is as below:

9.1 Effectiveness of the Heat Exchanger

$\varepsilon = m_a * c_p * (T_{h,i} - T_{h.o}) / m_w * c_{pw} * (T_{h,il} - T_{c.i})$

$m_a = 0.200$ kg/s
$c_{pa} = 1$ kJ/kg * ^oC
$T_{h,i} = 100\ ^oC$
$m_w = 0.00234$ kg/s
$c_{pw} = 4.2$ kJ/kg * ^oC
$T_{c.i} = 20\ ^oC$

Reading Table

Reading No.	$T_{h,o}$ (^oC)	ε
1	57	0.84
2	59	0.86
3	60	0.87
4	61	0.89
5	65	0.92
Average	60	0.87

Same experiment was conducted with air as coolant and the outlet temperature was 80 ^oC. So according to the outlet temperature with no heat exchanger, with heat exchanger and air as coolant and then water as coolant, a chart was developed as below:

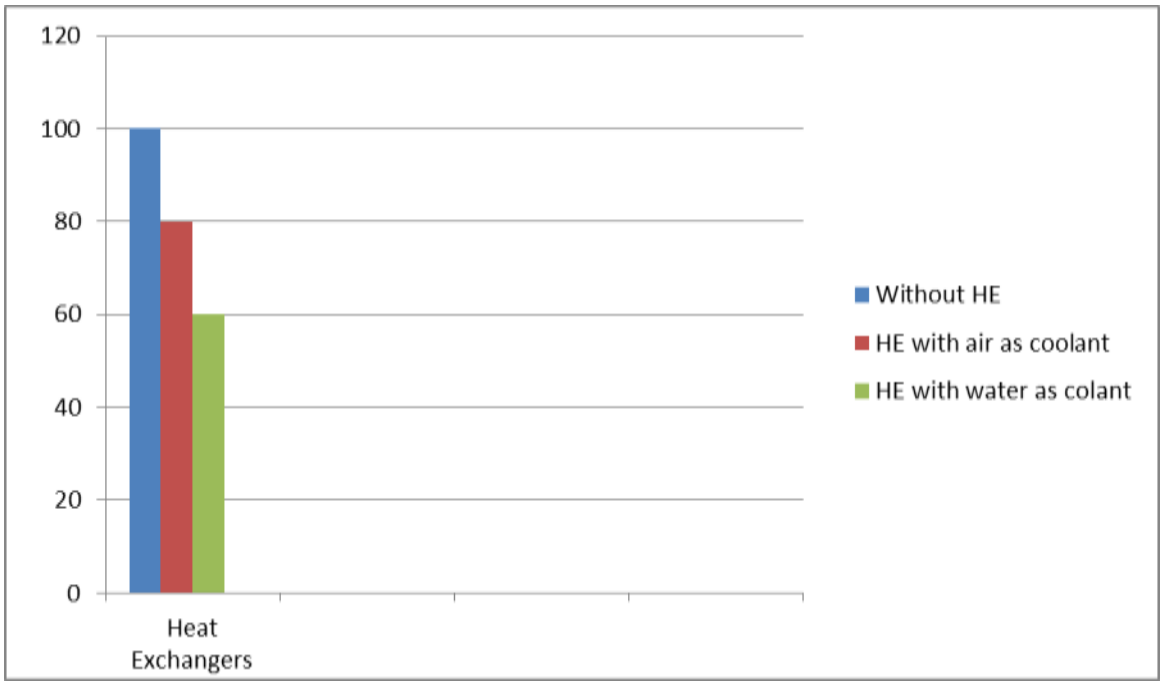

Figure: Outlet Temperature of the heat exchanger with different coolants.

X. CONCLUSION

As the reading table suggest the heat exchanger is able to bring down the temperature of air to 60 ^oC from 100 ^oC with water as coolant. Thus the effectiveness of the heat exchanger is derived to 0.87 which is exactly as much as required for cooling of the gases in the PROX reactor.

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