CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Fuel Cell

Fuel cell is an electrochemical energy conversion device, which uses clean and efficient hydrogen as a chemical energy to produce electricity, with water and heat as by products (Figure 2.1). Using the hydrogen as a fuel source, the only emission will be pure water; absolutely no toxic emissions are produced. Fuel cell consists of an electrolyte medium sandwiched between two electrodes i.e. an anode and a cathode. The anode side facilitates electrochemical oxidation of fuel (H_2) whereas the cathode side promotes electrochemical reduction of oxidant (O_2). Ions generate during oxidation or reduction, as shown in equations 1–3, which are transported from anode to cathode through the ionically conductive but electronically insulating electrolyte. The electrolyte also serves as a barrier between the H_2 (fuel) and O_2 (oxidant). The H_2 was split into proton and electron at the anode during oxidation reaction, subsequently the electron pass through the external circuit to generate the electricity. The proton passes through the electrolyte to the cathode on the other side of the fuel. At the cathode, the proton and electron combine with O_2 to form water which flow out of the fuel cell. Many benefits of fuel cell that provide a very clean energy, high quality power, high power density, silent process, low operating temperature for quick startup, and low fuel consumption.

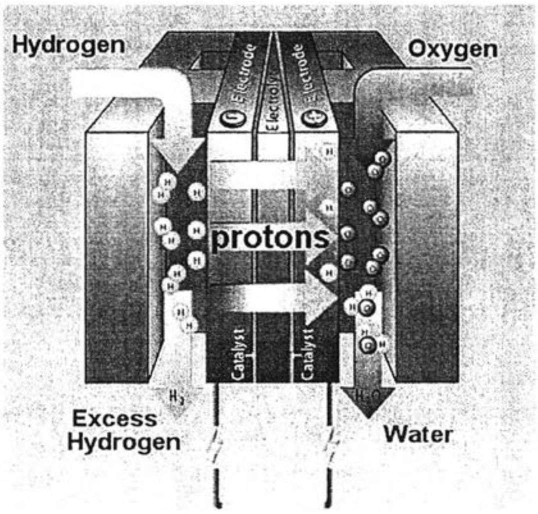

Figure 2.1 Fuel cell's diagram. (www.scientific-computing.com)

Anode reaction: $H_2 \longrightarrow 2H^+ + 4e^-$ (1)

Cathode reaction: $2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$ (2)

Overall reaction: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ (3)

Their electrolyte materials primarily classify fuel cells. The choice of electrolyte material also governs the operating temperature range in which the fuel cell operates. Fuel cell technology has been developed for both stationary and mobile applications. Table 2.1 lists the various types of fuel cells along with electrolyte used, operating temperature, maximum efficiency and some applications. A few of the most promising types are included Polymer Electrolyte Membrane (PEM), Phosphoric Acid (PA), Molten Carbonate (MC) and Solid Oxide (SO). Each type of fuel cells has its own advantages, disadvantages, limitations, and potential applications. The fuel cell, the most suitable tool used for transportation, is PEM fuel cell. This fuel cell type has a considerable potential for replacing conventional combustion engines because of their efficiency in converting hydrogen to electricity (work), quick startup, favorable power-to-weight ratio and their environmental-friendliness.

Table 2.1 Fuel Cell Comparisons

	PEMFC	**MCFC**	**PAFC**	**SOFC**
Electrolyte	Ion exchange membrane	Molten carbonate salt	Liquid phosphoric acid	Solid metal oxide
Operating Temperature (°C)	60-100	600-1000	150-200	600-1000
Oxidant	O_2/Air	CO_2/O_2/Air	O_2/Air	O_2/Air
Applications	Vehicle, medium to large scale stationary power generation	Large-scale power generation	Medium to large scale power generation	Medium to large scale power generation

PEM fuel cells are currently under intense developing as alternative energy conversion system for passenger vehicles, such as cars and buses. Besides stationary and automobile applications, the PEMFC is also a promising candidate as power supply for the future consumer electronics. PEMFC operates at relatively low temperatures of around 60–100°C. Low temperature operation allows them to quickly start (less warm-up time) resulting in less wear on system components and better durability. However, a requirement of noble-metal catalyst (Pt or Pt based alloys) for separating the hydrogen's electrons and protons at the anode cell also increases the system cost. Nevertheless, the Pt catalyst is extremely sensitive to CO poisoning and therefore needs an auxiliary fuel processor to convert alcohols or hydrocarbon fuels (commercial gasoline) into pure hydrogen before being fed into the PEM fuel cell. This poisoning effect is attributed to the strong adsorption of CO on the catalyst surface, thereby blocking the adsorption sites for hydrogen. The PEMFC performance dramatically reduces, as observed at a concentration above 25 ppm as shown in Figure 2.2. Subsequently, the CO concentration must be reduced to < 10 ppm by using an effective process to prolong the high PEMFC performance.

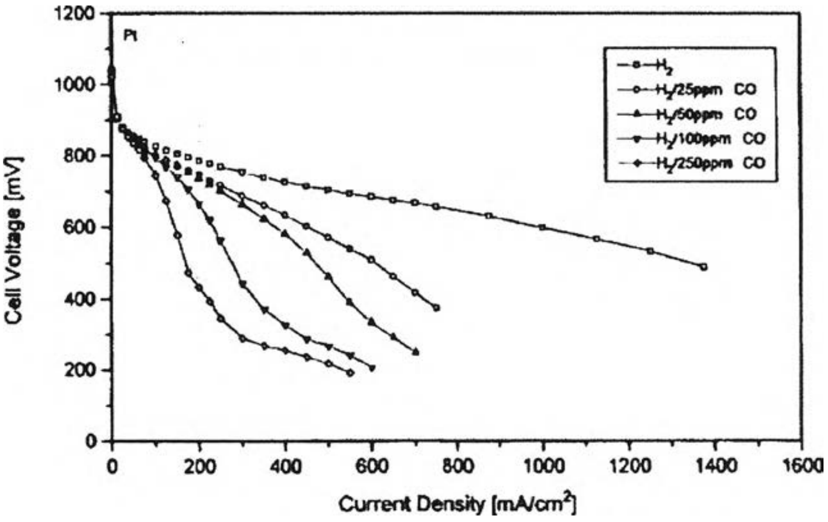

Figure 2.2 Performance of PEMFC decays under condition of CO poisoning. (Oetjen *et al.*, 1996)

Furthermore, the limitations of H_2 fuel are currently solved for the distribution, refueling system, and storage problems. These are posted serious challenges to the use of pure H_2 as a fuel for fuel cells. The infrastructure for its widespread distribution does not exist. Therefore, the on-board H_2 production has been extensively developed to supply a high quality H_2. Nowadays hydrocarbon fuels must be reformed in a series of steps to provide high purity hydrogen for use in PEMFC.

2.2 Method for generating hydrogen for fuel cells

The fuel cell is operated with the H_2 coming from various raw materials. Many methods of producing a H_2 rich gas were proposed to generate the H_2 fuel which fast and pure enough for supplying to the fuel cell i.e. steam reforming, partial oxidation, carbon dioxide reforming, and auto-thermal reforming.

- Methanol Steam Reforming

Steam reforming is the process where CH_4 and other hydrocarbons are converted into H_2 and CO by reacting with the steam at a temperature range of 700–1000°C, typically, over a Ni catalyst on a ceramic supports (Xu *et al.*, 1999; Li *et al.*, 2007). A widely studied hydrogen production process for an on-board fuel processor, using renewable energies (methanol), is the most promising candidate for the fuel options (Thomas *et al.*, 2000). In general, heavier hydrocarbon fuels have a slower reaction rate and a higher coke formation than lighter hydrocarbon fuels. Nowadays methanol reforming has been extensively studied because of having a high hydrogen/carbon ratio that can be converted into hydrogen at a moderate temperature (250–450°C). Moreover, the methanol can be produced from renewable source and does not contain carbon-carbon bonds, hence reducing the risk for coke formation (Manzoli *et al.*, 2004).

Methanol reforming takes place according to the reaction:

$$CH_3OH + H_2O \longleftrightarrow CO_2 + 3H_2 \qquad (4)$$

In Table 2.2, Ahmed *et al.* (1997) calculated the hydrogen concentration, which may be attained when using different fuels, and then compared these values with experimental results. From this table, it can be concluded that methanol have the highest hydrogen concentration when compare with others.

Table 2.2 Concentration of hydrogen in the product gas obtained with different hydrocarbons

Fuel	**H_2 concentration, % (dry)**		**H_2 Selectivity (%)**	**Temperature (°C)**
	Theoretical	**Experimental**		
Methanol	70	64	91	450
Ethanol	71	62	88	580
i-Octane	68	60	88	630
Cyclohexane	67	61	91	700
2-Pentene	67	58	88	670
Toluene	61	50	82	660

The typical catalysts have been the $Cu/ZnO/Al_2O_3$. Other alloy catalysts (Pt-Zn and Pd-Zn) have also been investigated. Among different metal oxide supports, ZnO plays a vital role in the development of high catalytic activity of catalyst for partial oxidation of methanol and steam reforming of methanol. The Brönsted base of ZnO support provides the enhanced activity of the catalyst. However, Cu-based catalysts deactivated rapidly and Pd-Zn catalysts have a high CO concentration in the reformate. Hence, the development of new catalysts is required more attention in order to replace Cu-based and Pd-Zn catalysts.

The methanol steam reforming process is usually operated with excess steam, to induce the water gas shift (WGS) reaction in the reformer and to lower the CO concentration in the reformate gas. However, this process produces not only H_2, but also CO, which poisons the PEMFC anode. The methanol conversion and the reformate composition depends on the activities of catalyst, space velocity, operating temperature and pressure. The methanol reforming is possible to yield a product gas containing up to 75% H_2. The diagram of steam reforming process is shown in

Figure 2.3. However, the methanol reforming process produces not only H_2, but also CO, which poisons the PEMFC anode. Consequently, the auxiliary units are required to remove the CO concentration in H_2 fuel to a level of less than 100 ppm.

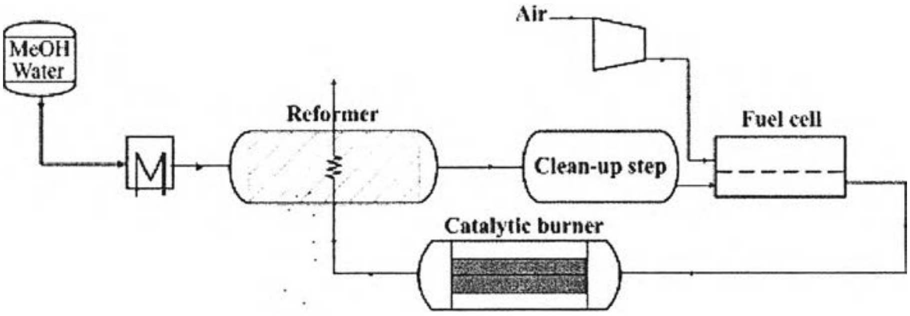

Figure 2.3 Methanol Reforming System. (Lindström *et al.,* 2002)

2.3 CO Removal Methods

Even with Pt-Ru catalysts in the PEMFC anode, a significant performance loss is still observed at a CO concentration above 100 ppm. Thus, the purification step of the reformate necessary to reduce the CO content may involve both high and low temperature water gas shifts (WGS), followed by preferential CO oxidation reaction (PROX of CO).

2.3.1 Water Gas Shift Reaction (WGSR)

The purpose of the WGS reaction is to increase H_2 yield by converting CO from the reformate gas to CO_2 coupled with water, as shown in equation 5.

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad (5)$$

The WGS reactor is an important auxiliary unit of the fuel processor. The water gas shift reaction is a reversible chemical reaction, in which CO and H_2 are favored at low temperature. The WGSR is a moderately exothermic chemical reaction ($\Delta H^o_{298} = -41$ kJ mol^{-1}) and hence its equilibrium constant decreases with the temperature, and high conversions are favored by low temperatures (Figure 2.4). Due to the thermodynamic limitation of water gas shift reaction at high temperatures and at low temperatures it is kinetically limited, normally performed in two steps. In industry, WGS reaction is carried out at two temperature regimes, high temperature (400–500°C) and low temperature (200–300°C) shift reactions. As well known, the metals like Pt and Pd are not work well in the WGS reaction because they are not easily oxidized by water. In general, the catalyst used in the water gas shift reaction is commercially available. The WGS reactors convert about 20% CO to 1% CO using the typical catalysts, which are Fe/Cr-based catalyst in the high temperature water gas shift reaction and $CuO/ZnO/Al_2O_3$ catalyst in the low temperature water gas shift reaction (LT-WGS).

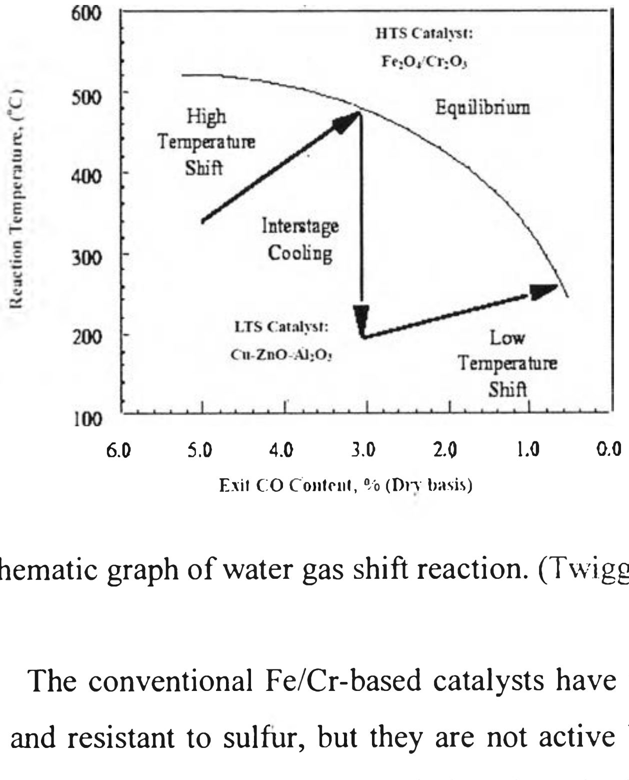

Figure 2.4 Schematic graph of water gas shift reaction. (Twigg *et al.*, 1989)

The conventional Fe/Cr-based catalysts have the advantages of low cost, long life and resistant to sulfur, but they are not active below 350°C (Trimm, 2005). Afterward, the H_2-rich stream has to induce into the low temperature water gas shift reactor further. Binary CuO–ZnO and ternary $CuO–ZnO–Al_2O_3$ and $CuO–ZnO–Cr_2O_3$ mixed oxide catalysts have been widely employed commercially in the low temperature water-gas shift reaction. However, after the LT-WGS reactor, the CO concentration in the H_2-rich stream which remains about 0.5–1%, is still too high for the PEMFC, thus the preferential CO oxidation reaction required to reduce CO is still needed for further study.

2.3.2 Preferential Oxidation or Selective Oxidation of CO

CO removal in the presence of a H_2-rich gas stream is well established to remove the undesired CO and prevent CO poisoning to the PEMFC anode. Among the various methods available for CO removal which are pressure swing adsorption, catalytic methanation, Pd membrane separation, and catalytic preferential CO oxidation reaction (CO PROX), the PROX of CO has been suggested to be a practical one. Many advantages of PROX have been reported, not only keeping the low operating cost, but also decreasing the CO content to the acceptance level (<10 ppm) without the excess hydrogen consumption that occurs during catalytic methanation before the H_2-rich fuel can be fed into PEMFCs. The catalyst for the PROX of CO must be effective in removing CO from a reformate gas, in which the main component is hydrogen, which is supplied to the fuel cell. The most important requirements for the PROX catalysts that have to be operated in the gas streams containing an excess amount of H_2 (Zhao *et al.*, 2007) are as follows:

- High CO oxidation rate at low temperatures
- High CO conversion (>99%) at a wide operating temperature range (80–200°C)
- High CO selectivity or the catalyst must not oxidize a significant quantity of H_2
- Good resistance to deactivation in the presence of H_2O and CO_2 in the reformate stream

Desired reaction: $CO + ½O_2 \longrightarrow CO_2 \quad \Delta H^o_{298} = -283\ kJ\ mol^{-1}$ (6)

Undesired reaction: $H_2 + ½O_2 \longrightarrow H_2O \quad \Delta H^o_{298} = -242\ kJ\ mol^{-1}$ (7)

The majority of researchers mainly focused on the improvement of the high performance catalyst for this process. The suitable catalyst should be active and very selective to convert CO to CO_2 at a relatively low temperature, while minimizing the hydrogen oxidation to water. Many different metal (Au, Pt, Ru, and Rh) catalysts have been studied for the PROX reaction. Pt-based catalysts are well known to effectively catalyze the preferentially oxidized CO to CO_2 at high temperatures (Avgouropoulos *et al.*, 2002), while Au-based catalysts present a great potential for achieving a high conversion at low temperatures, when the size of Au metal is smaller than 5 nm. (Kahlich *et al.*, 1999; Rossignol *et al.*, 2005; Avgouropoulos *et al.*, 2006). Previously, Haruta and coworkers reported that only nano-sized Au particles can catalyze the CO oxidation reaction (Haruta *et al.*, 1993). A few years later, Igarashi *et al.* (1997) investigated the Pt supported on zeolites for preferential oxidation of CO. Various zeolites, viz. A zeolite, mordenite, X zeolite, and alumina, were used as supports. The effect of the support was investigated on the selectivity for CO oxidation versus H_2 oxidation, as followed the order of A zeolite > mordenite > X zeolite > alumina. In 2003, Watanabe *et al.* proposed a new catalyst for the PROX reaction by using Pt-Fe/mordenite prepared by the conventional ion-exchange and the incipient wetness impregnation methods for doping Pt and Fe, respectively. The catalysts were investigated for the catalytic performance at various conditions compared to the Pt/mordenite. They found that the 2:1 Pt-Fe/mordenite ratio catalyst had a superior activity than the conventional Pt/Al_2O_3 catalyst which provided a complete removal of CO with 100% selectivity in the temperature range of 80–200°C. The nature of Fe was found to play an essential role to provide an alternative site for O_2 adsorption because Fe does not adsorb CO as extensively as O_2 (Schubert *et al.*, 1999; Liu *et al.*, 2002; Watanabe *et al.*, 2003). The Fe will be an intimate contact with Pt, facilitating CO oxidation because it creates a non-competitive dual site reaction mechanism instead of the typical competitive dual site reaction mechanism observed on unpromoted Pt catalysts (Fogler, 1999). Then, Rosso *et al.* (2004) developed the noble metal supported A zeolite catalysts employing 1 % of Pt, Pd and Ru as active metals and 3, 4 and 5-A as catalyst supports. The Pt catalysts showed a complete CO conversion and a remarkably high selectivity. Moreover, the selective CO oxidation on gold catalysts was studied by Kandoi *et al.*, 2004. Their results showed that Au and Cu provided more selective on CO than Pt at low temperatures. In the same year, Luengnaruemitchai *et al.* (2004) studied the effects of preparation methods (impregnation, co-precipitation and sol-gel) on PROX of CO in a simulated reforming gas to CO_2 over Au/CeO_2 catalysts. They found that the activity of Au catalyst depended very strongly upon the preparation method. Co-precipitation 1% Au/CeO_2 catalyst exhibited the highest activity and good selectivity at 110°C. From our previous results (Naknam *et al.*, 2007), the presence of Au in a Pt/A zeolite catalyst can slightly improve the catalytic activities. However, the temperature for the maximum CO conversion with higher CO selectivity was shifted to 40°C lower. If the addition of Au by co-impregnation yielded large Au particles, it would be unable to oxidize CO in the presence of H_2. A significant role of the catalyst support was found on the conversion, selectivity, and stability of the catalyst. For example, a ZnO catalyst support showed a high potential for used in the PROX reaction, reported by Iwasa *et al.* (2006). They investigated the catalytic activities of various supported Pd catalysts, and found that the catalytic activities significantly changed with the supports used. The Pd/ZnO catalyst prepared by the precipitation method exhibited the highest CO conversion. In the case of a Au-based catalyst, Au supported on ZnO has been investigated for the PROX (Zhang *et al.* (2003) and Wang *et al.* (2005)) and it was revealed that Au (1.5%wt)–Pt (1.0%wt) supported on ZnO displayed the best PROX activity, giving high CO conversion (97.5%), and the high stability for 500 h of testing. Hence, it can be expected that the performance of a Au catalyst can be enhanced by using ZnO as a catalyst support. In addition, there are many reports in literature about using FeO_x to promote the performance of Pt catalysts, e.g. Pt/Al_2O_3, Pt/CeO_2, and Pt/TiO_2 (Shou *et al.*, 2004). The role of reducible oxide supports have been described by the diffusion of oxygen from the lattice at the edge of the Au active sites for the CO oxidation reaction (Schubert *et al.*, 2001). It was thus interesting to study the effect of a mixed metal oxide support by adding Fe_2O_3 to a ZnO support.

For the current research activity, the low-temperature preferential CO oxidation in the presence of H_2 over Au/ZnO was initiated in an attempt to improve the performance for the PROX. Moreover, the catalytic activities of Au markedly depend on the preparation method, which brings about a great difference in the size of Au particles and the interaction with support. Deposition-precipitation method is the most promising method for preparing Au catalyst, which is effective to deposit Au with high dispersion. Haruta (1993) indicated that deposition-precipitation (DP) technique had the advantage over co-precipitation (CP), in that all active Au remained on the support surface and none of the active Au was buried within it. The simulated stream consisted of 1% CO, 1% O_2, and 40% H_2 balancing with He at a total flow rate of 50 ml min^{-1}. In addition, the realistic methanol steam reformate contains up to 25% CO_2 and 10–15% H_2O. Therefore, it is essential to investigate the influence of CO_2 and H_2O on the preferential CO oxidation reaction in order to evaluate whether the high activity and selectivity observed in simulated reformate are maintained under more realistic conditions. Moreover, the catalytic activity of the prepared catalysts was tested at constant temperature for 12 h to observe the stability with time-on-stream.

Moreover, the addition of a multi-staged PROX system offers better CO conversion and CO selectivity, which is considered as an alternative method to improve the performance of the preferential CO oxidation process. Igarashi *et al.* (1997) and Ahluwalia *et al.* (2005) suggested that the selectivity could be enhanced by fractionizing the oxygen addition to a multi-stages reactor, resulting in a large reduction of a total amount of oxygen to oxidize CO in the H_2-rich stream. This could be reduced to 0.7% by using a two-stage reactor. Srinivas and Gulari (2006) conducted the experiment of PROX reaction using two-stage system over 2%Pt/γ-Al_2O_3, and found that the two-stage system provided slightly higher CO selectivity (~49.72–49.94%) than the single-stage system (49.3%). The two-stage process performance can also be enhanced by several variables, such as reaction temperature of each stage; oxygen split ratio; catalyst amount of each reactor, etc. In addition, in order to avoid the presence of heat exchangers, the suitable operating temperature for the PROX process should be around 50–150°C. Finally, the selected catalyst was used in a two-stage reactor to monitor the process performance in simulated reformed gas (CO_2- and H_2O-free).

2.4 Fuel Processor

A fuel processor is a major system in a fuel cell power system. Fuel processing depends on both the raw material and the fuel cell technology. The innovative technologies have been extensively developed to achieve a high performance for the on-board fuel cell vehicle applications. The main limitation of using hydrogen in vehicle applications is due to its unfavorable storage properties. Moreover, nowadays, there is no existing extensive hydrogen infrastructure and no commercially viable H_2 storage technology for vehicles. The fuel processor systems based on the PEM fuel cell applications can employ an onboard fuel processor that has an ability to convert the fuels, such as gasoline, methane, or methanol, into H_2. Besides H_2, CO_2 and CO are also formed. Since CO is a serious poison for the anode catalyst in the PEMFC, the formed CO needs to be removed. Generally, the production of clean H_2 for the PEMFC from hydrocarbon feeds is accomplished by a series of catalytic steps including steam reforming, desulfurization, water gas shift, and CO removal by preferential CO oxidation as shown in Figure 2.5. The average operating temperatures of each process stage are indicated. The on-board fuel processor requires a compactable size, quick start-up time, and ability to operate at a wide condition range.

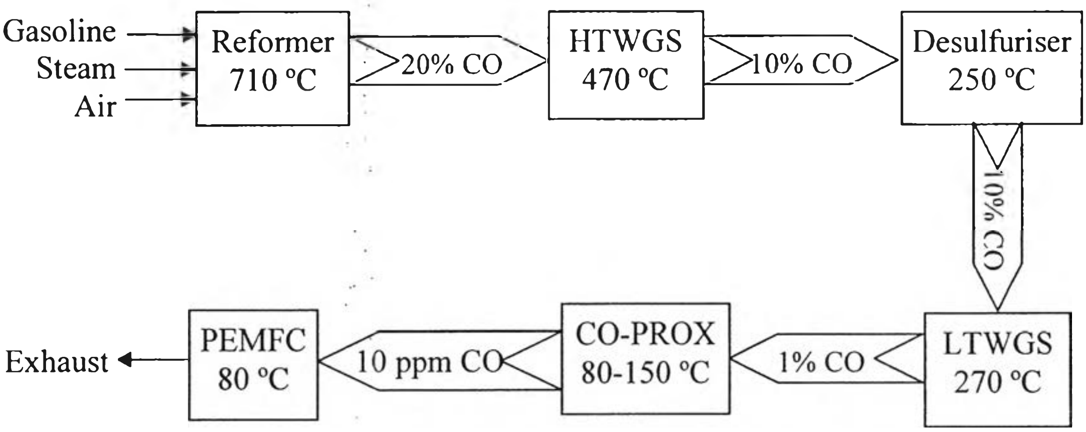

Figure 2.5 Schematic description of a gasoline processor for hydrogen production. (Rosso *et al.,* 2004)

Previously, our experiments were tested using several catalysts and the simulated stream. Finally, the fuel processing system, consisting of four major units in series i.e. evaporators, methanol steam reformer reactor, high and low temperature water gas shift reactors, and double-stage preferential CO oxidation reactors, was constructed to observe the catalytic activities in the real reformate. The methanol steam reforming process generates hydrogen. After evaporation of the fuel, a methanol-water mixture, the methanol and water react in the reformer over a Au/ZnO catalyst to produce H_2, CO_2, and CO. The products coming out the methanol steam reformer was passed to the high and low temperature water gas shift reactors. Consequently, the H_2-rich gas was introduced to the double-stage PROX reactors in order to eliminate the trace amounts of carbon monoxide in the H_2-rich stream to an acceptable level (<100 ppm), by oxidation with O_2 over a Au/ZnO catalyst. The clean H_2-rich gas is then used in a PEM fuel cell to generate electricity.