Steam and partial oxidation reforming options for hydrogen production from fossil fuels for PEM fuel cells

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Abstract Proton exchange membrane fuel cell (PEM) generates electrical power from air and from hydrogen or hydrogen rich gas mixtures. Therefore, there is an increasing interest in converting current hydrocarbon based marine fuels such as natural gas, gasoline, and diesel into hydrogen rich gases acceptable to the PEM fuel cells on board ships. Using chemical flow sheeting software, the total system efficiency has been calculated. Natural gas appears to be the best fuel for hydrogen rich gas production due to its favorable composition of lower molecular weight compounds. This paper presents a study for a 250 kW net electrical power PEM fuel cell system utilizing a partial oxidation in one case study and steam reformers in the second. This study has shown that steam-reforming process is the most competitive fuel processing option in terms of fuel processing efficiency. Partial oxidation process has proved to posses the lowest fuel processing efficiency. Among the options studied, the highest fuel processing efficiency is achieved with natural gas steam reforming system.

1. Introduction

Production of pure hydrogen for use in downstream polymer electrolyte membrane fuel cells (PEMFCs) for mobile applications is gaining increasing interest in recent years [1]. The PEMFC is an adequate system for the power sources of the zero-emission source of power, as its current density is higher compared to other types of fuel cells. The stack structure is rather simple, and there is no leakage or loss of electrolyte during the operation. Other advantages include rapid start-up and response, long endurance, and flexibility of fuel usage from pure hydrogen to methanol and natural gas. In addition, because of the various ranges of power, PEMFC can be used in various fields, such as power sources for stationary generators, space shuttles, road vehicles, and marine auxiliary applications. However, there are many disadvantages to be overcome. It cannot utilize waste heat and cannot be directly connected to the fuel processor, because the operating temperature of the PEMFC is too low. The platinum catalyst is very expensive and the CO tolerance limit for platinum is also too low. For the PEMFC to be commercialized in mobile and stationary power supplies, the above disadvantages have to be overcome first [1,2].

2. PEM fuel cell total system simulation model

The use of chemical flow-sheeting software has become an integral part of the evaluation of the performance of fuel cell systems. The steady state simulation computer code of the Aspen-HYSYS process modeling tool has been utilized along with conventional calculations for fuel cell systems.

Natural gas, gasoline and diesel type hydrocarbon mixtures have been studied as three different sources for hydrogen production. The average molecular weights are around 16.5 kg kmol^{-1}, 95 kg kmol^{-1} and 200 kg kmol^{-1} for the natural gas (CH_4), gasoline (C_6H_{12}) and diesel ($C_{12}H_{26}$) fuels, respectively [2,3]. All the simulations in this study are based on these compositions.

The investigated PEM fuel cell system consists of the following sections and their components:

Fuel processing and clean-up section
- Steam reforming or partial oxidation reformer (two cases investigated).
- High and low temperature shift reactors (HTS and LTS).
- Preferential oxidation reactor (PROX).

PEM fuel cell section
- Fuel cell stack.
- DC/AC converter.

Auxiliary units
- Pumps.
- Compressor.
- Expander.
- Heat exchangers.
- Heaters.
- Coolers.
- Burner.

Fuel processing consists of reforming and clean-up sections as shown in Fig. 1. The reforming section contains the reforming reactors: an auto-thermal (ATR) or two steam reforming units (PRE-SREF and SREF), or a partial oxidation (POX) reactor. The clean-up section is made up by high and low temperature shift reactors (HTS and LTS) and the preferential oxidation reactor (PROX).

For all cases, all reactors are simulated to operate under equilibrium conditions. The thermodynamic equilibrium system calculations are based on minimizing the Gibbs free energy. All reactor simulation calculations have been performed keeping "$T_{reactor}$" almost constant taking heats of reaction into account.

2.1. Overall description of a fuel processing and clean up sections

The fuel processing efficiency covers the section from the hydrocarbon feed section to the fuel cell including all reforming and clean-up reactors and auxiliary equipment.

The pressure is kept constant at 3 bars. The operation temperatures of reactors are changed parametrically to determine the best operation parameters. The limitations set by the catalysts and hydrocarbons involved are also considered. The simulation code is capable to calculate the steady state product compositions taking into account the incoming stream compositions under the defined operating conditions.

The aim is to convert as much as the hydrogen in the fuel into hydrogen gas at acceptable yields in an efficient manner while decreasing CO and CH_4 formation. Lower S/C ratios favor soot and coke formation, which is not desired in catalytic steam and auto-thermal reforming processes.
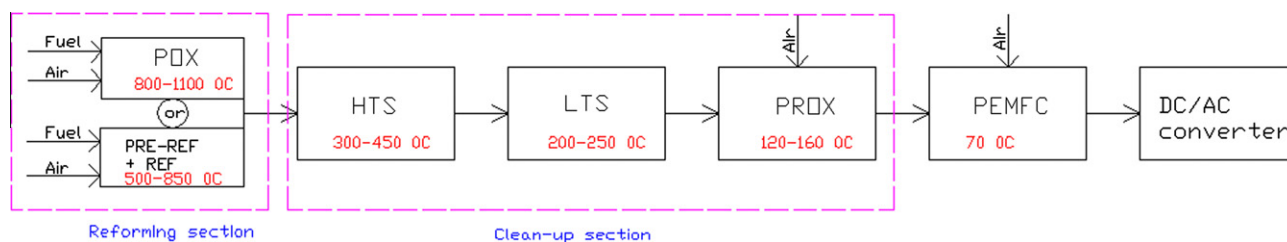
Figure 1   The investigated inlet and outlet stream temperature ranges for the reactors.

Fig. 1 presents the investigated range of the operation conditions for major fuel processing units (REF and POX, HTS, LTS, and PROX). This study presents the results for REF operating temperatures at 500 °C and 800 °C. The selection of these operating conditions are based on theoretical studies aiming at producing hydrogen rich and carbon monoxide poor mixtures in an efficient manner at acceptable conversions taking into account catalyst properties [2].

2.2. Chemical reaction scheme

The fuel processor is simplified to a reformer or partial oxidation reactor, two water gas shift reactors and a preferential oxidation reactor for the modeling purpose. The model includes detailed reactions associated with total oxidation reforming (TOR), partial oxidation reforming (POX) and steam reforming (SREF).

Steam reforming is a method of hydrogen production used on a large scale industrially, most notably in the production of ammonia. Steam reforming involves both the reforming reaction Eqs. (1) and (2) and the water–gas shift reaction Eq. (3). These are carried out at elevated temperatures over a supported nickel catalyst [4–6].

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

Steam reforming process requires two stages desulphurization and pre-reforming processes. Desulphurization process removes sulphur from the flow as sulphur acts as poison both to the fuel cell (platinum) and the steam reforming (nickel) catalysts. Therefore, its removal is the first step in any reforming system flow sheet. There are several desulphurization techniques, the most common is a two stage process known as hydrodesulphurization (HDS). Pre-reforming process, Eqs. (4) and (5) is required to reduce the concentration of higher hydrocarbons, which are much more reactive than methane and can lead to problems of coke formation. As these compounds are more reactive, they can be easily removed via a lower temperature adiabatic pre-reforming reactor. Generally pre-reforming catalysts tend to have a higher nickel percentage than traditional reforming catalysts and the reactor is run at temperature between 300 °C and 550 °C, depending on the gas composition. Removing these hydrocarbons can also lead to a reduction in the steam usage .This can lead to an increase in plant efficiency [7,8].

$$2CO \rightarrow C + CO_2 \tag{4}$$

$$CH_4 \rightarrow C + 2H_2 \tag{5}$$

Also methane may react with steam by partial oxidation (POX) as follows

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \tag{6}$$

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \tag{7}$$

In order to reduce the CO concentration out of the LTS, the preferential oxidation reaction (PROX) was performed [9,10].

$$CO + 1/2O_2 = CO_2 \tag{8}$$

$$H_2 + 1/2O_2 = H_2O \tag{9}$$

Thus, the model takes into account nine reactions (1)–(9) and seven gas species, i.e., methane (CH_4), oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), water (H_2O), hydrogen (H_2) and nitrogen (N_2).

2.3. Simulation of the Partial Oxidation reformer and steam reformer

Partial Oxidation is a less efficient than steam reforming method for converting natural gas to Hydrogen as demonstrated by Eqs. (6) and (7). When the catalyst temperature reaches about 800 °C, at which the partial oxidation reaction can be self-activated, the predetermined mixture of methane and air is fed to the reformer. Whilst this produces less hydrogen per a mole of methane feed, compared with steam reforming, it has proved advantageous for small scale operation where efficiency is not such an issue. Here the low overall cost, compactness and low operating temperatures are a real advantage [1,2]. In this study, partial oxidation and steam reforming reactors are modeled using HYSYS conversion reactors.

2.4. Simulation of water gas shift reactor

The CO content can be reduced to about 0.5% by reacting it with water at lower temperatures to produce additional hydrogen according to the WGS reaction (Eq. (3)). Commercial hydrogen plants generally perform the WGS in two stages: (i) High-temperature shift at 300–450 °C using an oxide catalyst, and (ii) low-temperature shift at 200–250 °C using copper zinc oxide. Heat exchangers are required between shift reactors to provide cooling, and the conversion in an adiabatic reactor is limited because the reaction is exothermic and the temperature increases as the reaction proceeds. In this study, WGS reactors are modeled using equilibrium reactor. By using equilibrium reactor, HYSYS will determine the composition of the

outlet stream and the value of equilibrium constant for each reaction [11–13].

2.5. Simulation of preferential oxidation reactor

Carbon monoxide is a poison to the precious metal catalyst in the anode of the PEM fuel cell. Preferential oxidation (PROX) is a reactive approach to destroy CO in the reformat composition. PROX of CO is typically used to reduce CO to the ppm levels required for the PEM fuel cell. The catalyst and conditions must be selected to minimize the oxidation of hydrogen. For the overall process model heat and material balance, 50% selectivity to CO oxidation is assumed, with the remainder of the oxygen reacting with hydrogen to form water. The PROX reactor was modeled in HYSYS as a conversion reactor based on two reactions to oxidize CO (Eqs. (8) and (9)). Fig. 2 shows the process and complete PEM fuel cell system scheme simulation studied by Aspen – HYSYS 3.2 taking into account selected balance plant of plant equipment.

As shown in Fig. 2, the hydrocarbon fuel is first pressurized (2), and then vaporized (5). The vaporized hydrocarbon fuel is divided into two streams. One stream (6) is directed to the burner where it is combusted to provide the necessary process heat. The other stream (7) is mixed in the air–fuel mixer (AFM) with the hot compressed air (9) from the compressor. The air fuel mixture (13) is heated with the hot combustion gases (40) from the combustor up to the required POX or PRE-SR temperature (35).

All of the chemical reactions are assumed to occur adiabatically under equilibrium conditions. The gases leaving POX reactor (14) are cooled (16) prior to entering the HTS reactor. The gases are further processed in LTS and PROX. The exit gases from the PROX (23) are fed to PEM fuel cell after cooling (25).

It is desired to maximize hydrogen concentration and to minimize carbon monoxide (CO) content considering the requirements of PEM fuel cells. The high and low temperature water- gas shift reactors (HTS and LTS) and the preferential oxidation (PROX) are used to decrease the CO concentration level of the POX reactor exit gas to the desired values.

The pressure of the fuel at 4.1 bar prior to the POX inlet continuously drops to 3.0 bars before entering the PEM fuel cell.

Air compressed to 5 bars is divided into 4 streams. One stream is directed to the air–fuel mixer (8) as POX reactant. Another stream is used in PROX (9). The third stream (10) supplies the cathode air of PEM fuel cell. The fourth air stream is the combustion air (11). Pressurized water (3) is converted to steam (4) to be used in HTS. Water is circulated (41–42) to cool down the PEM fuel cell.

Anode and cathode off-gases (26) of the PEM fuel cell are combusted together with the hydrocarbon fuel (6). The combustor off- gases are expanded after exchanging heat with the hydrocarbon fuels to heat them up prior to POX entrance to produce additional power. The final burner exit gases (40) are at 550.4 °C. The fuel cell stack is assumed to run under constant temperature and pressure, namely 70 °C and 3 bars. The PEM fuel cell characteristics are presented in Table 1.

The study assumes 88% utilization of hydrogen in the cells. The inlet air to the cathode is humidified to a relative humidity of 30%. The anode inlet stream is also humidified if necessary.

Table 2 summarizes the data of different auxiliary system components utilized in the simulation studies.

The thermal efficiencies of the POX, HTS, LTS and PROX reactors are η_{POX}, η_{HTS}, η_{LTS} and η_{PROX}, respectively. They are defined as the ratio of the heating values and mass flows of the exit and inlet streams Eqs. (11)–(14). The heating value of a stream is calculated by the multiplication of its lower heating

Table 1 The PEM fuel cell characteristics (e⁻: electron).

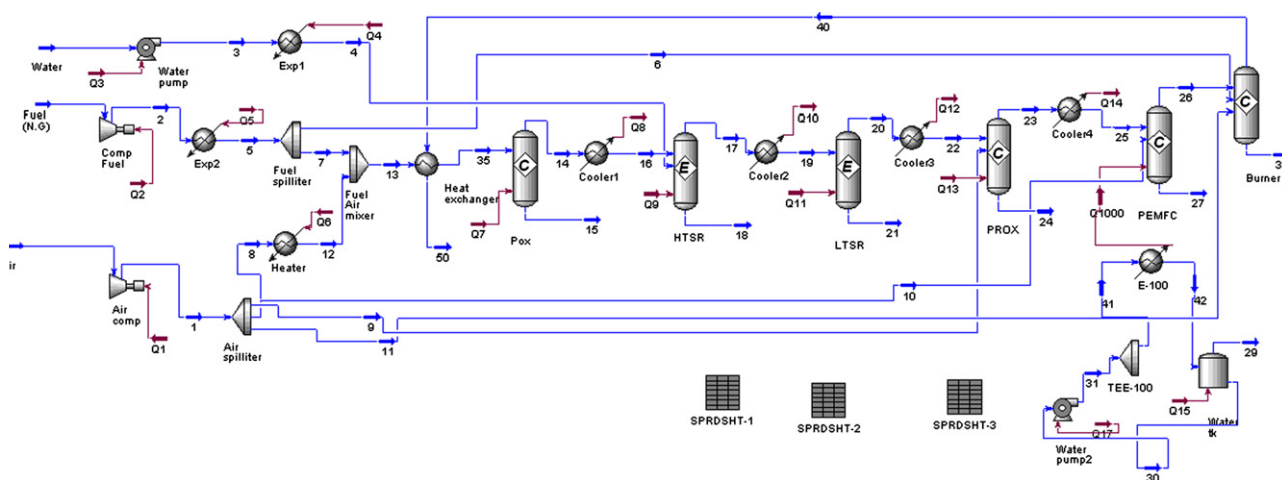|	
$2H_2 \rightarrow 4H^+ + 4e^-$	Anode reaction
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	Cathode reaction
88	Fuel utilization (%)
70	Fuel cell outlet tempera temperature (°C)
3	Pressure (bar)
750	Average cell voltage (mV)
Water	Stack cooling media

Figure 2 Actual POX Natural Gas PEM fuel cell system flow diagram simulated by Aspen HYSYS 3.2.

Table 2 Auxiliary system component data.

Component	Parameter	Value
Fuel pump	Adiabatic efficiency	75%
Water pump	Adiabatic efficiency	75%
Cooling water pump	Adiabatic efficiency	75%
Compressor	Adiabatic efficiency	70%
Expander	Adiabatic efficiency	75%
Burner	Outlet temperature	548 °C
DC/AC Converter	Conversion efficiency	98%

value (LHV) with its mass flow rate (m) in kg per hour. η_1 presents the fraction of the POX inlet stream heating value to the heating value of the total fuel feed to the system. The remainder is fed to the burner. The total fuel processing efficiency is the product of η_1, η_{POX}, η_{HTS}, η_{LTS} and η_{PROX} as shown in Eq. (15).

$$\eta_1 = (m_7 * LHV_7)/(m_F * LHV_F) \tag{10}$$

$$\eta POX = (m_{16} * LHV_{16})/(m_{35} * LHV_{35}) \tag{11}$$

$$\eta_{HTS} = (m_{19} * LHV_{19})/(m_{16} * LHV_{16}) \tag{12}$$

$$\eta_{LTS} = (m_{22} * LHV_{22})/(m_{19} * LHV_{19}) \tag{13}$$

$$\eta_{PROX} = (m_{25} * LHV_{25})/(m_{22} * LHV_{22}) \tag{14}$$

$$\eta_{FP} = \eta_1 * \eta_{POX} * \eta_{HTS} * \eta_{LTS} * \eta_{PROX} \tag{15}$$

The PEM fuel cell section consists of the following components:

- Fuel cell stack;
- DC/AC converter.

The PEM fuel cell module has been simulated using the PEM fuel cell characteristics presented in Table 1. All the characteristic figures are calculated for a fuel cell stack with 3300 cells.

The PEM fuel cell (η_{FC}) efficiency depends on hydrogen utilization ratio (Uf) which defines the percentage of hydrogen fuel reacted in the fuel cell, stack voltage, and DC/AC conversion efficiencies as shown in Eqs. (16)–(18)

$$\eta_{DC/AC} = 0.98 \tag{16}$$

$$\eta_{stack\ voltage} = V_{cell} * 0.8 \tag{17}$$

$$\eta_{FC} = \eta_{stack\ voltage} * \eta_{DC/AC} \tag{18}$$

Auxiliary units comprise pumps, compressor, expander, heat exchangers, heaters coolers and burner. The auxiliary system efficiency ($\eta_{Aux.}$) is calculated as follows:

$$\eta_{motor} = 0.90 \tag{19}$$

$$P_{parasitic} = (P_{P1} + P_{P2} + P_{P3} + P_C)/\eta_{motor} \tag{20}$$

$$\eta_{Auxiliary} = 1 + (P_E - P_{par})/P_{PEM\ AC} \tag{21}$$

Extensive heat integration is sought within the present study to achieve acceptable overall system efficiency levels. The overall system efficiency ($\eta_{net.el}$) is calculated as the product of fuel processing (η_{FP}), PEM fuel cell (η_{FC}) and auxiliary (η_{Aux}) system efficiencies.

$$\eta_{net.el} = \eta_{FP} * \eta_{FC} * \eta_{Aux} \tag{22}$$

3. SREF based fuel processing, fuel cell, auxiliary and overall system efficiencies

The following results obtained from the reforming of natural gas, gasoline, and diesel fuel systems. Fig. 2 shows an example of the reforming process using Natural Gas fuel for PEM fuel
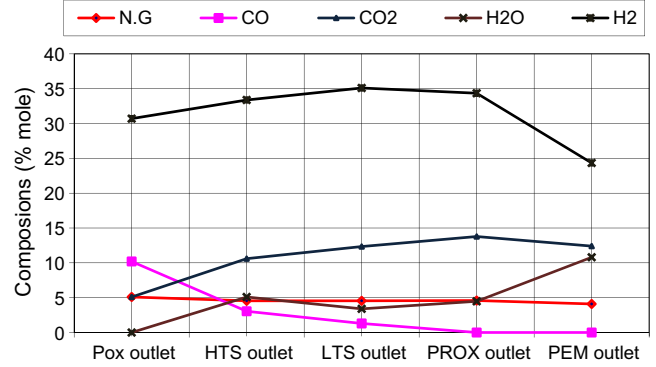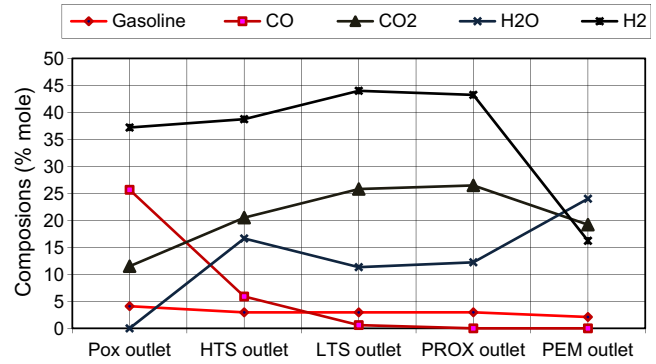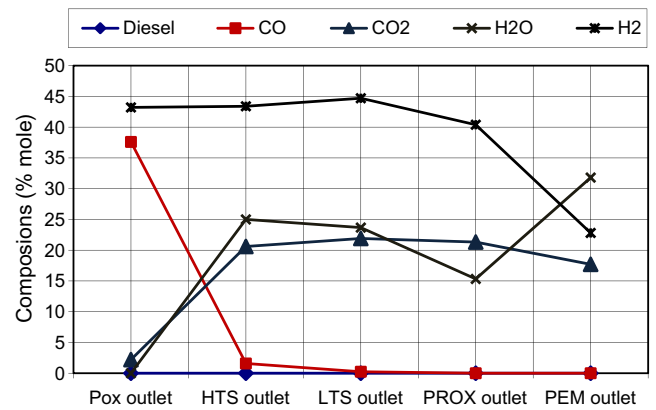
Figure 3 Product compositions of natural gas fuel preparation reactors.

Figure 4 Product compositions of gasoline fuel preparation reactors.

Figure 5 Product compositions of diesel fuel preparation reactors.

Table 3 Simulation results for selected system points calculated under the prescribed operating conditions applied in this study.

Stream	Fuel	Air	Water	5	6	13	8	10	11
Temperature (°C)	25	20	25	200	200	209.4	242.3	242.3	242.3
Pressure (kPa)	120	100	170	170	170	170	500	500	500
Mass flow(kg/h)	33.6	1200	5e-4	33.63	1.3	52.33	20	40	1140
Stream	35	14	17	19	20	22	23	25	40
Temperature (°C)	500	850	350	100	250	120	150	70	550.4
Pressure (kPa)	170	170	168	170	170	163	163	300	170
Mass flow (kg/h)	52.3	40.23	40.23	40.2	40.2	40.2	40.2	40.2	1222

Table 4 SREF based fuel processing, fuel cell, auxiliary and overall system efficiencies.

Fuel	η_{FP}	η_{FC}	η_{Aux}	$\eta_{net.el}$
Natural gas	96.05	53.54	91.7	47.156
Gasoline	94.05	53.54	90	45.318
Diesel	87.17	53.54	90.5	42.37

cell. The components results for partial oxidation case are shown in the following Figs. 3–5 .With the developed system models, which are implemented in the HYSYS 3.2 process simulator, effluents from all reactors are known.

Fig. 3 shows the molar fractions of all components in the effluent of all reactors in the natural gas fuel processor system. In this case, 100% methane is converted to produce 30.7% hydrogen, 5.1% CO_2 and 10.2% CO. Also, under these conditions, oxygen is 100% consumed.

The molar fractions of all components in the effluent of all reactors in the gasoline gas fuel processor system are shown in Fig. 4. In this case, 100% methane is converted to produce 37.2% hydrogen, 11.5% CO_2 and 25.6% CO.

Fig. 5 shows the molar fractions of all components in the effluent of all reactors in the diesel fuel processor system. In this case, 100% diesel is converted to produce 43.2% hydrogen, 2.2% CO_2 and 37.6% CO. Also, under these conditions, oxygen is consumed.

The second case in this study includes steam reforming for Natural gas, gasoline, and diesel fuels using HYSYS simulation. The results for Natural gas system for the selected system points calculated under the prescribed operating conditions applied in the second study are shown in Table 3.

Fuel processing and net electrical efficiencies of natural gas and gasoline/diesel fuels for the investigated fuel reforming options are presented in Table 4. The simulation results indicate that the fuel processing efficiencies decrease in the order of steam reforming greater than partial oxidation for both gasoline and diesel fuels. Steam reforming appears as the most promising fuel reforming option based on fuel processing efficiencies. Only minor differences have been observed in terms of efficiencies of the selected gasoline and diesel fuels.

So, the presented results of natural gas show higher fuel processing efficiencies than the liquid fuels, and also higher overall system efficiencies. The highest fuel processing efficiency is achieved for the steam reforming of natural gas, namely 96.05%. The same option gives a maximum net electrical efficiency at 47.156% as calculated in Table 4. Hence,

the natural gas with steam reforming is about 14% more efficient than its liquid fuel counterparts based on steam reforming.

For the first case of partial oxidation for natural gas, gasoline, and diesel fuels HYSYS simulation systems, the results of the simulation studies show no major efficiency differences regarding the average molecular weights of the investigated hydrocarbon fuels. The obtained efficiency level at 30% is higher than those of Otto engines and lower than those of diesel engines. So, the second case of steam reforming will further increase the system efficiency than the first case.

4. Conclusions

1. PEM fuel cells generate electrical power from air and from hydrogen or hydrogen rich gas mixtures. Therefore, there is an increasing interest in converting current hydrocarbon based transportation fuels such as Natural gas, gasoline, and diesel into hydrogen rich gases acceptable by PEM fuel cells on board ships.
2. Natural gas appears to be the best fuel for hydrogen rich gas production due to its favorable composition from lower molecular weight compounds. Steam reforming and auto-thermal reforming appear as the most competitive fuel processing options in terms of fuel processing efficiencies. POX shows the lowest fuel processing efficiency level. Among the options studied the highest fuel processing efficiency is achieved with natural gas steam reforming at about 96.05%. The obtained total system efficiency level is at 30% and 47.15% for natural gas POX and steam reforming systems respectively.
3. High PEMFC system efficiency levels can be achieved only with intensive heat integration within the PEMFC systems. Hence, heat integration system studies are of utmost importance along with the development of novel reforming catalysts, clean-up systems and PEMFC components if on-board hydrogen production is desired.

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