Autothermal reforming as a hydrocarbon fuel processing option for PEM fuel cell

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Abstract

In this paper, we discuss the results of a preliminary systematic simulation study: the effect of operating parameters on the product distribution and conversion efficiency of high and low molecular weight hydrocarbon mixtures in autothermal reforming (ATR). The HYSYS simulation software has been utilized for the simulations and calculations of the fuel processing reactions. It is desired to produce hydrogen-rich reformate gas with as low as possible CO formation, which requires different combinations of T_{ATR}, S/C and O/C ratios. Fuel properties only slightly effect the general trends.
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1. Introduction

Efficient and zero-emission vehicles are of utmost importance for the future in terms of sustainable development. Low-temperature fuel cell systems are considered for powering future automobiles in an efficient and low-emitting manner. Within this frame, proton exchange membrane (PEM) and direct methanol (DM) fuel cells (FC) have been developed. PEMFC and DMFC systems operate on hydrogen or methanol, respectively. Hence, there is great interest in converting current hydrocarbon based transportation fuels such as gasoline and diesel into fuels acceptable by fuel cells as the on board fuel for vehicles. PEMFC systems are being studied in our group.

PEMFC generates electric power from air and hydrogen or from a hydrogen-rich gas. Water and waste heat are the only by-products. Hydrogen-rich gas can be produced from conventional transportation fuels via various reforming technologies. Steam reforming, partial oxidation and autothermal reforming (ATR) are the three major reforming technologies consisting of similar steps. First, the fuel is vaporized. It is desired to maximize the hydrogen content while decreasing the carbon monoxide and methane formation. Then this gas mixture is further processed in two shift reactors. In these reactors, carbon monoxide is reacted with steam to produce additional hydrogen by the water gas shift reaction. The remaining carbon monoxide can be further converted into carbon dioxide by selective oxidation. The hydrogen-rich fuel containing carbon monoxide at ppm levels is ready to be fed to the PEMFC [1].

Steam reforming shows the highest hydrogen production efficiencies. However, the required heat input due to endothermic reactions is considered as a major drawback for automotive applications. Partial oxidation needs external cooling in general. Autothermal reforming promises better dynamic response than both of the before mentioned reforming processes.

This study presents the performance of ATR for two different average molecular weight hydrocarbon fuel mixtures containing no sulphurous compounds under selected operation conditions. In the ATR fuel processor, vaporized hydrocarbon fuel, air and water (steam) are fed at controlled conditions to the reactor to produce the reformate gas mixture in an autothermal way. The reformate gas mixture containing the desired hydrogen must be processed further to convert carbon monoxide to carbon dioxide. The hydrogen-rich gas has to be cooled and humidified to desired fuel cell inlet conditions. The quality of the raw reformate (i.e. CO, CO_2, CH_4 and other hydrocarbons, H_2O, and N_2 contents) is strongly affected by the reforming conditions. The ATR fuel processor efficiency is defined as the ratio of the lower heating value (LHV) of the total amount of hydrogen in the reformate exit to the LHV of the hydrocarbon fuel fed into the fuel processor [2].

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Table 1
The parameters and their ranges studied in the presented simulations

O/C															
600 °C[a]				700 °C				800 °C				900 °C			
2[b]	2.5	3	3.5	2	2.5	3	3.5	2	2.5	3	3.5	2	2.5	3	3.5
HHCM (16 kg/h)															
0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
LHCM (16 kg/h)															
0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50

[a] T_{ATR}.
[b] S/C ratios.

It should be noted that the concentration of the H_2 in the reformate influences the performance of the fuel cell stack. Higher hydrogen concentrations show better fuel cell performance. Moreover, the chemical composition of the raw reformate determines the extent of subsequent processes required, primarily in terms of CO reduction. Additional or extensive processing steps are not desired due to their adverse effects on the volume, weight and cost of the fuel processing system to be utilized for transport applications.

Hydrocarbon reforming, water gas shift reaction, selective/preferential oxidation and, if necessary, desulphurisation steps, all require specific catalysts. The feed streams have to be compatible with the catalyst, so are the operation conditions. This paper does not take the constraints imposed by catalysts into consideration.

2. Methodology

The HYSYS simulation software has been utilized for the simulations and calculations of the fuel processing reactions. The solutions are based on equilibrium conditions.

The thermodynamic equilibrium in a reformer reactor depends on the following parameters [3–5]:

- chemical composition of the fuel;
- preheat temperatures of the reactor feed air, steam and fuel;
- relation of S/C and O/C ratios;
- heat loss/gain of the reactor;
- pressure inside of the reactor.

In this study, one lower molecular weight hydrocarbon (LHCM) and one higher molecular weight hydrocarbon

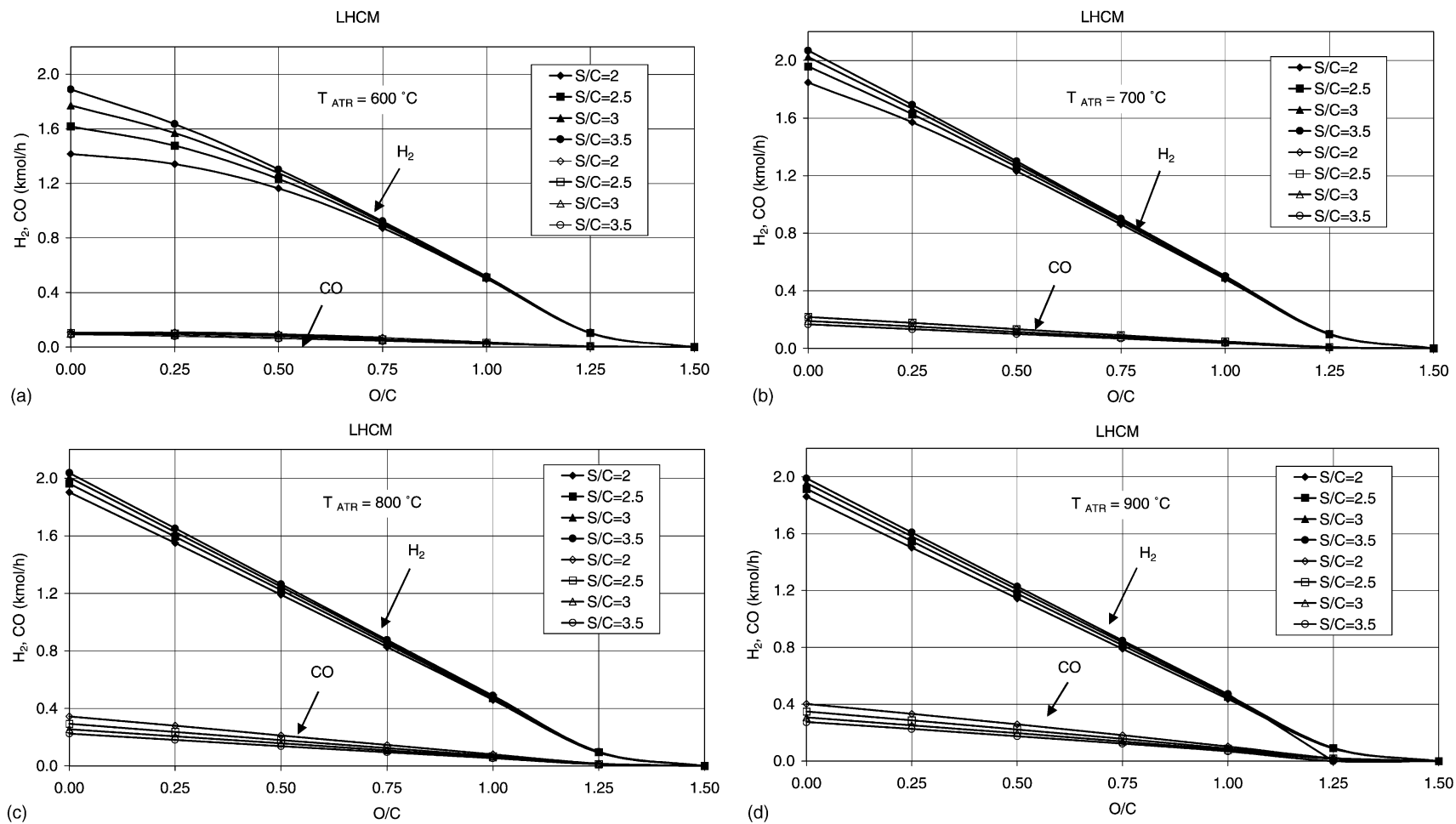
Fig. 1. The schematic of the simplified reforming system.

Fig. 2. (a–d) The effect of isothermal equilibrium temperature, O/C ratio an S/C ratio on H_2 and CO production for LHCM.

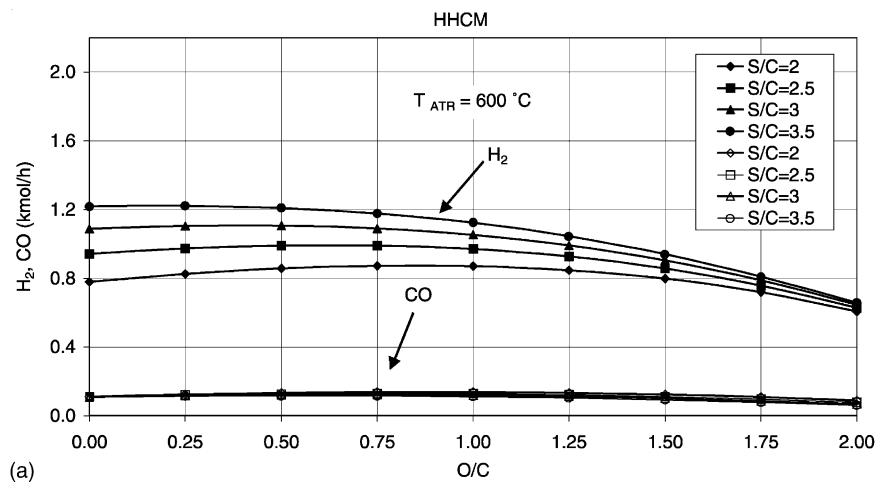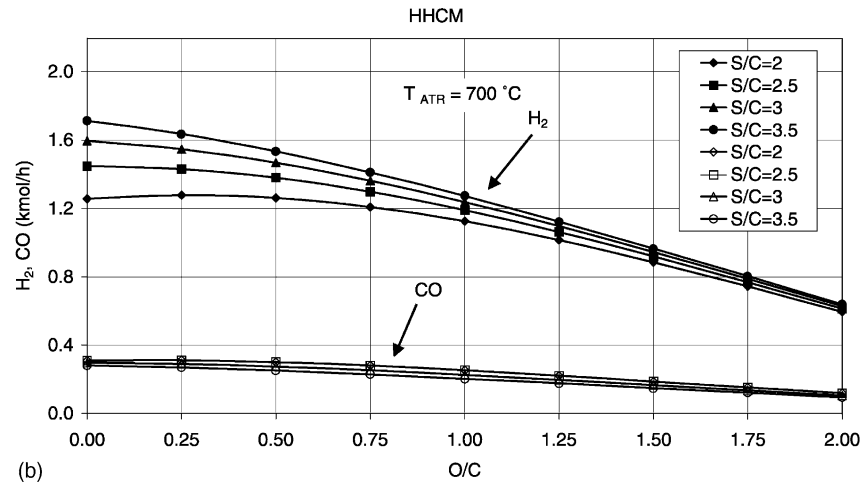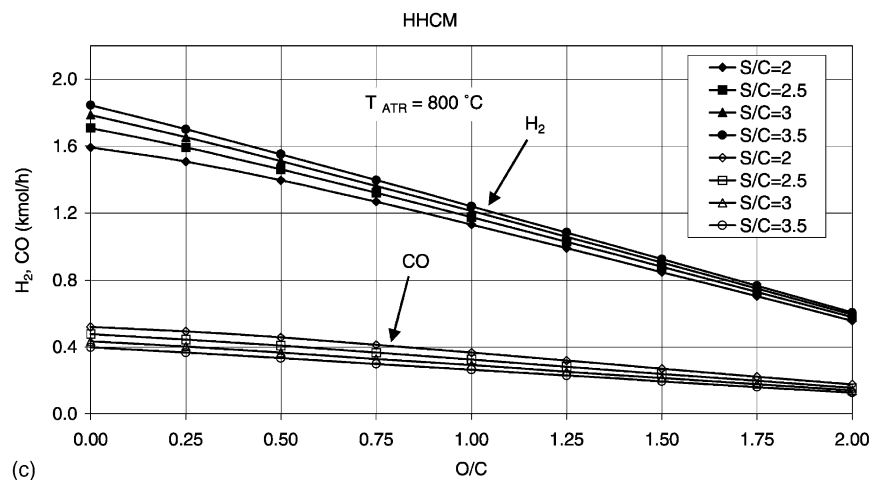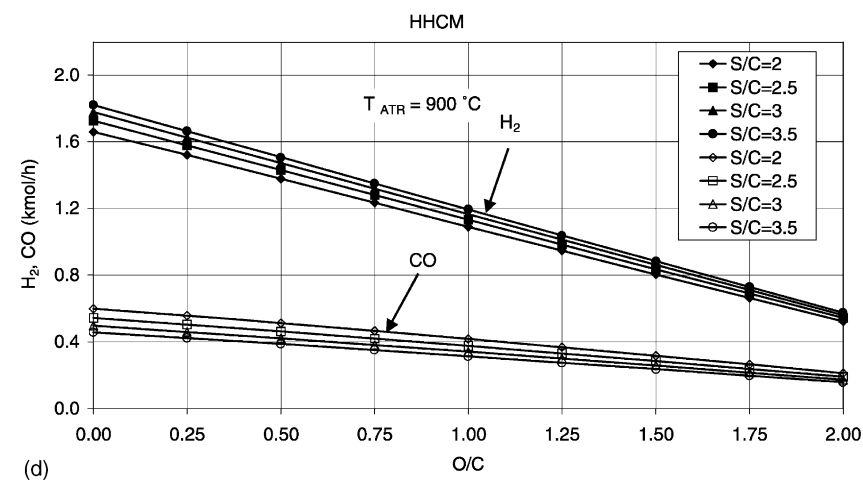Fig. 3. (a–d) The effect of isothermal equilibrium temperature, O/C ratio and S/C ratio on H_2 and CO production for HHCM.
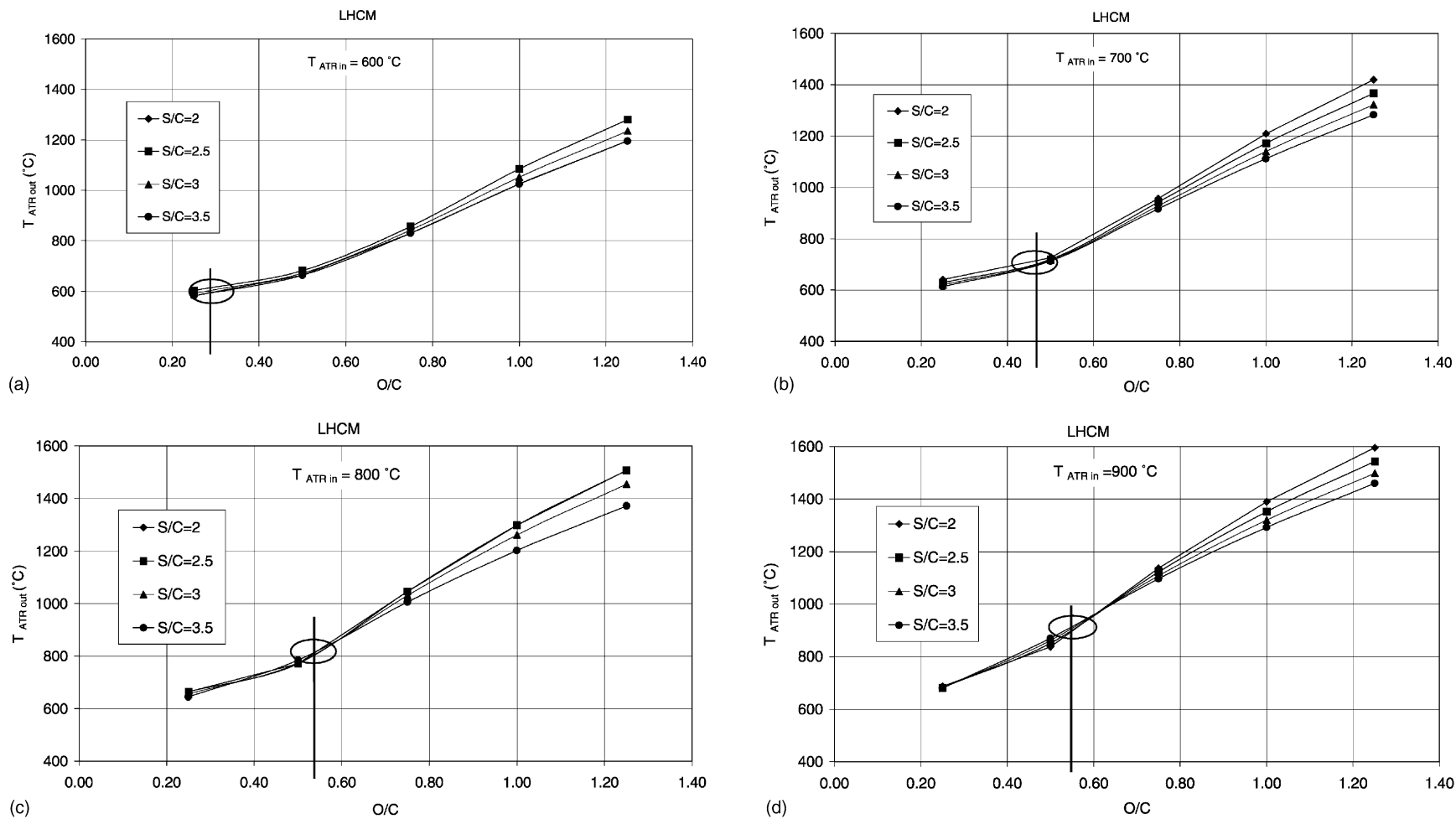
Fig. 4. (a–d) The relationship among adiabatic equilibrium temperature, O/C ratio and S/C ratio and LHCM.
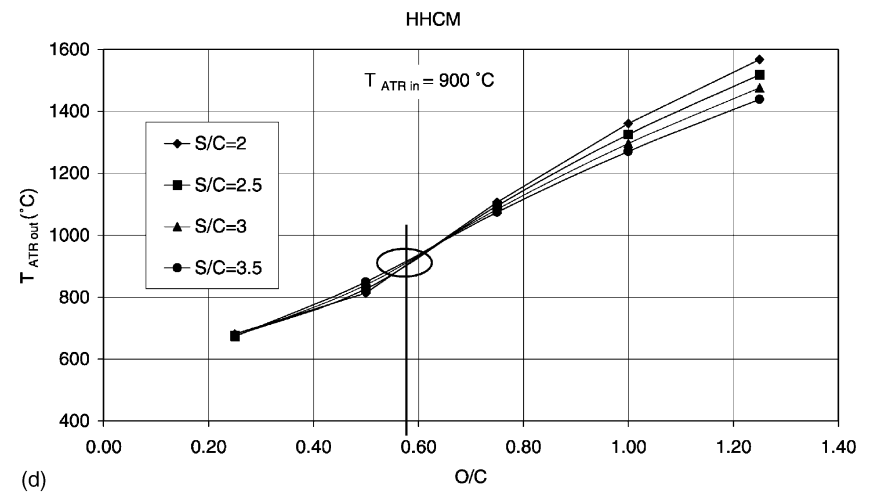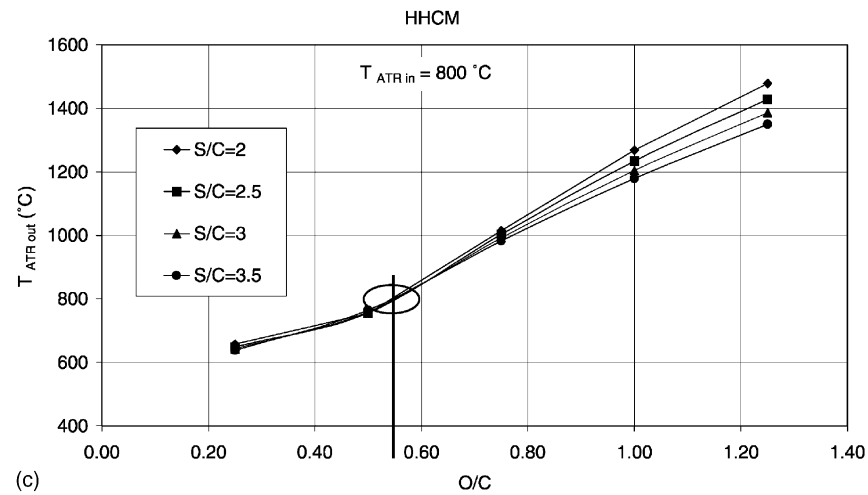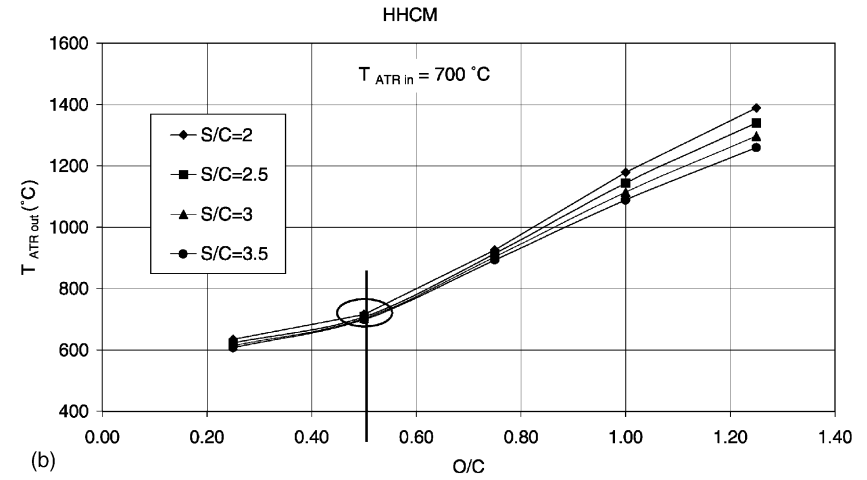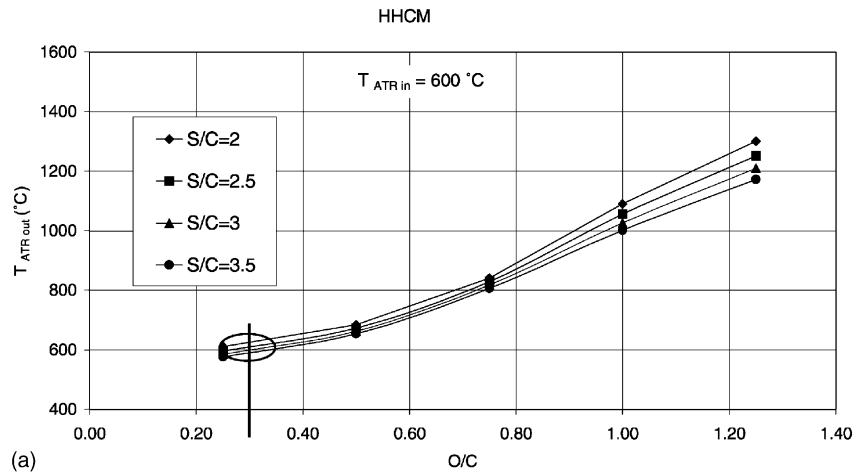
Fig. 5. (a–d) The relationship among adiabatic equilibrium temperature, O/C ratio and S/C ratio for HHCM.

(HHCM) mixtures were studied. LHCM consists of 33.6% hexane (C_6H_{14}), 28% hexene (C_6H_{12}) and 38.4% xyol (C_8H_{10}), similar to gasoline. The molecular weight of the assumed gasoline is 95 kg/kmol. The molecular weight of the selected HHCM ($C_{12}H_{26}$) is around 200 kg/kmol.

In this study, the selected primary operating variables in ATR system are fuel composition, temperature of the pre-heated fuel/air/steam mixture, steam-to-carbon (S/C), oxygen-to-carbon (O/C) ratios and reforming temperature (T_{ATR}). The pressure is taken constant as 3 bar. Table 1 summarizes the parameters and their ranges studied in the presented simulations.

In this study, the aim is to convert as much as the hydrogen in the fuel into hydrogen gas and while decreasing CO and CH_4 formation. Lower S/C ratios favor soot and coke formation, which is not desired in catalytic operations. Although the catalytic reaction is not analyzed in detail here, a considerably wide S/C ratio (2.0–3.5) range has been selected to see the effect on hydrogen yield. The catalytic properties will after all limit applicable

operational parameter ranges such as S/C and temperatures.

First, simulation calculations have been performed under adiabatic conditions. Under adiabatic conditions, the fuel–gas mixture (fuel/steam/air) is fed into the ATR at the selected T_{ATR}. The temperature of the exit product stream is determined by the extent of the endothermic and exothermic reactions in the reactor due to adiabatic conditions. For each fuel composition and selected T_{ATR} and S/C ratio there is a specific O/C ratio range that enables operation at almost isothermal reaction conditions. These ranges have been studied in detail and compared with results from isothermal reaction condition studies.

In isothermal reaction condition studies, the preheated fuel/air/steam mixture temperature (T_{ATR}) is assumed to be equal to that in the reformer (T_{ATR}). Depending on the extent of endothermic and exothermic reactions heat supply/removal may be necessary.

The thermodynamic equilibrium system calculations are based on minimizing the Gibbs free energy. In real opera-
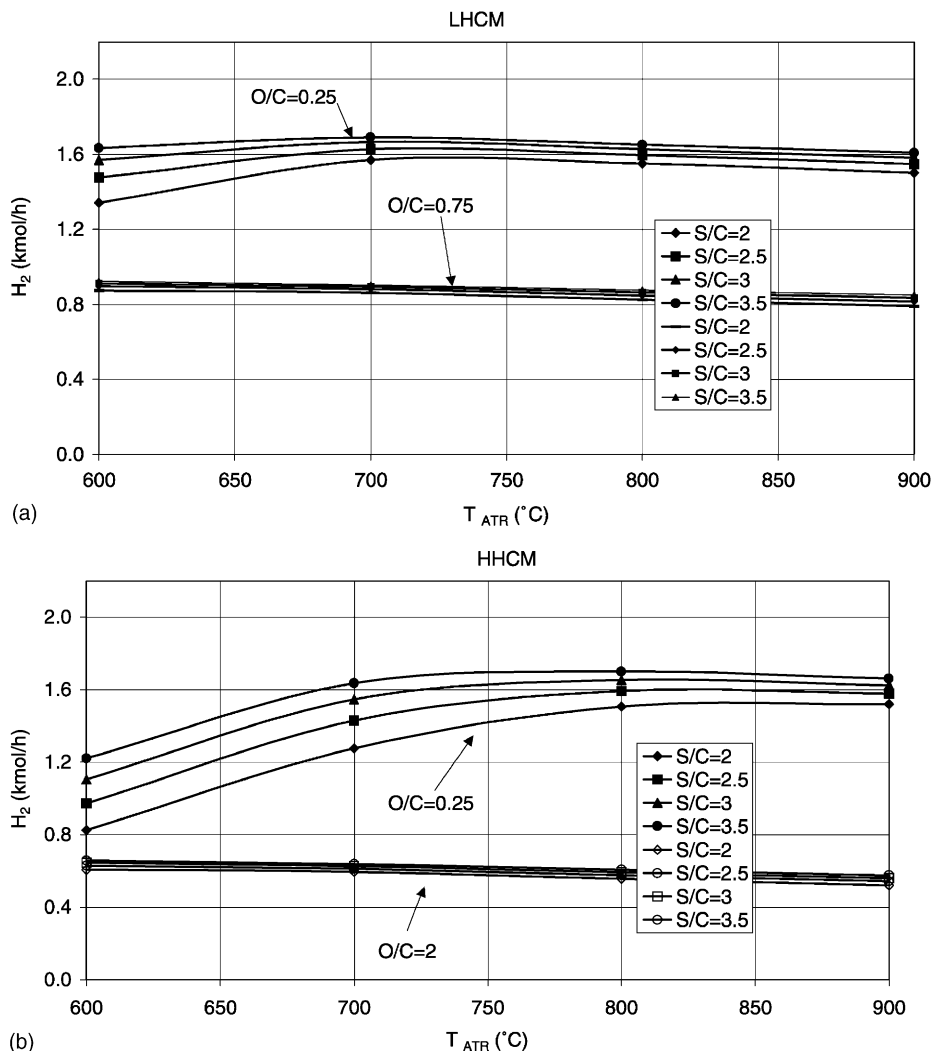

Fig. 6. (a and b) Temperature effect on hydrogen production at selected O/C and S/C ratios for LHCM and HHCM.

tions, the upper T_{ATR} limit is determined mainly by three parameters, namely catalyst, fuel composition and desired product composition.

The schematic of the simplified reforming system utilized in the simulation studies is given in Fig. 1.

3. Results and discussion

The study aims to determine the desired process conditions for a high hydrogen and low CO containing reformate mixture at moderate temperature with the minimum amount of external energy supply needs for two selected hydrocarbon fuels. The major chemical difference of the selected lower and higher hydrocarbon fuels is based on their average molecular weights as explained in the previous section.

The results of this study indicate very similar behavior for both of the investigated fuels in general. The trends are almost the same; the numerical values are slightly different.

The major operational parameters, which effect the reformate gas composition for a given fuel composition are O/C and S/C ratios and process temperature.

Figs. 2 and 3 show the effect of O/C, S/C and operation temperature on hydrogen and CO production rate for LHCMs and HHCMs at isothermal conditions, respectively.

Increasing O/C ratios decrease hydrogen and CO formation. Above a certain O/C ratio, hydrogen production is almost diminished. This effect is observed at lower O/C ratios for LHCM. The effect of S/C on hydrogen is more pronounced at lower O/C values. Increase of S/C favors hydrogen formation. CO formation is depressed at higher S/C values especially at higher operation temperatures. Higher operation temperatures enhance CO formation while decreasing hydrogen formation. Hence, the results indicate that there should be an optimum temperature and S/C and O/C ratios for a given fuel.

Autothermal reforming of both the LHCM and HHCM fuels have been analyzed under adiabatic conditions for four different inlet temperatures (Figs. 4 and 5, respectively) at
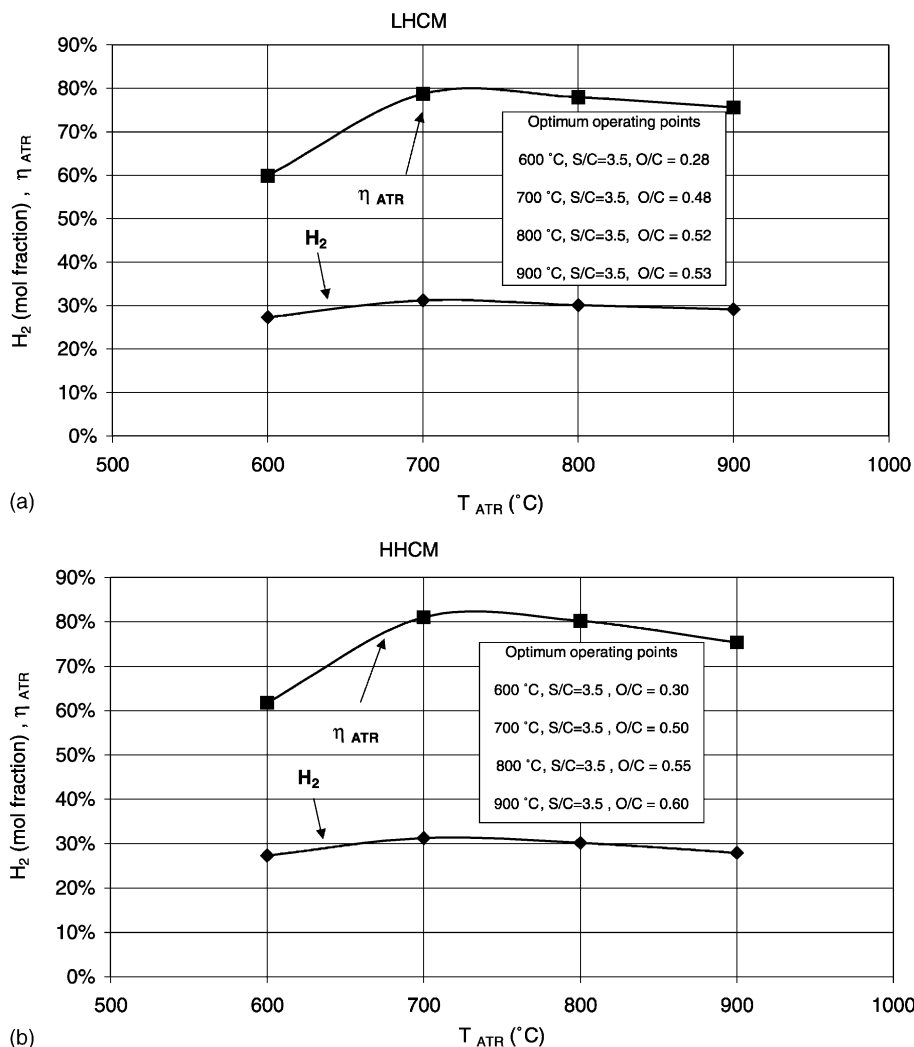

Fig. 7. (a and b) The efficiency of ATR at optimum T_{ATR}, O/C and S/C ratios for LHCM and HHCM.

selected O/C and S/C conditions. For each temperature the O/C and S/C ratios, which simulate almost isothermal adiabatic operation, have been determined. Higher inlet temperatures appear to necessitate higher O/C ratios to achieve the desired conditions for both fuels.

Fig. 6 presents the change in hydrogen production as a function of isothermal process temperature at selected O/C and S/C ratio combinations for LHCM and HHCM fuels. At lower O/C conditions, which favor hydrogen, production the effect of temperature is more pronounced.

The selection of the right operation parameters is very important in terms of the ATR efficiency and the hydrogen content of the ATR off-gases (Fig. 7). The differences observed for both fuels are due to their different molecular structures.

4. Concluding remarks

Special operation conditions towards efficient production of hydrogen-rich reformate gas with as low as possible CO formation require different combinations of T_{ATR}, S/C and O/C ratios.

Fuel properties slightly affect the operation conditions. In general, the trends are similar for similarly made up hydrocarbon mixtures as illustrated for the investigated LHCM and HHCM fuels.

References

[1] EG&G Services Parsons Inc. Science Applications International Corporation, Fuel Cell Handbook, fifth ed., US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, October 2000.

[2] E. Danial Doss, R. Kumar, R.K. Ahluwalia, M. Krumpelt, Fuel processor for automotive fuel cell system: a parametric study, J. Power Sources 102 (2001) 1–15.

[3] D. Ju Moon, K. Sreekumar, S.D. Lee, B. Gwon, H.S. Kim, Studies on gasoline fuel processor for fuel cell powered vehicle application, Appl. Catal. 215 (2001) 1–9.

[4] C. Pereira, R. Wilkenhoener, S. Ahmed, M. Krumpelt, Liquid Fuel Reformer Development, Electrochemical Technology Program, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, 2 July 1999.

[5] A. Docter, A. Lamm, Gasoline fuel cell systems, J. Power Sources 84 (1999) 194–200.