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A thermodynamic analysis of the reformer sponge iron cycle

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Abstract

A mathematical model of the reformer sponge iron cycle (RESC) is presented. The model is based on a thermodynamic analysis of the process, simulating the complete hydrogen production cycle including the hydrocarbon reformer, the sponge iron reactor (SIR) and the auxiliary devices required to operate the process. A parametric process analysis is performed in order to investigate the effect of different levels of operating temperature and different recycle rates on the RESC system performance. A number of gaseous and liquid hydrocarbons are investigated as candidate fuels for applications requiring an on-site hydrogen production capacity. Hydrocarbon to hydrogen conversion efficiencies are presented, along with a full analysis of mass and energy balances. An additional hydrocarbon burner unit running with the same fuel as the RESC hydrogen production cycle is considered as heat source for the endothermic conversion process of hydrocarbon fuel into hydrogen. The mathematical RESC model provides a sound base for further developments of the system, and will be applied in theoretical studies performed in parallel to investigations with a laboratory-scale unit operated at Graz University of Technology.

Keywords: RESC; Sponge iron cycle; Reformer; Hydrogen production

1. Introduction

The use of fossil fuels in transportation applications contributes a considerable share to the overall emissions of greenhouse gases [1]. Introducing fuel cells running on hydrogen into vehicle power trains is one of the most promising approaches in reducing emissions of the transportation sector, and providing clean and emission-free on-board power in mobile applications. One of the major issues that has to be addressed in the early stages of hydrogen fuel cell vehicle introduction is the development of a cheap and efficient way of supplying and/or generating hydrogen fuel in decentralised filling stations. On-site production of hydrogen is particularly interesting in early fuel cell vehicle applications, because the existing infrastructure can be utilised (e.g. a supply with natural gas or other hydrocarbons readily available with a regular filling station) without having to install a designated hydrogen pipeline or an expensive supply with liquid and/or gaseous hydrogen from a central hydrogen production facility. These on-site hydrogen production plants could be replaced with advanced technology in later stages of the introduction of hydrogen, or they could just as well be converted to operate with other fuels derived from regenerative sources (e.g. bio-methanol or bio-ethanol). The latter could be easily achieved with RESC technology, requiring only minor adaptations to modify the system from operating with fossil hydrocarbon fuels to alcohols derived from regenerative sources, for instance.

The reformer sponge iron cycle (RESC) is currently being investigated as innovative process for converting hydrocarbon fuels into pure hydrogen [2]. The RESC is based on the well-known steam iron process [3,4]. This process was utilised to produce large quantities of hydrogen gas at the beginning of the last century, mainly for applications in the field of aerial navigation [5]. Combining the simple, but limited operational capabilities of the sponge iron reaction with the possibilities of a hydrocarbon reformer-based system provides an innovative means of producing hydrogen. The RESC process essentially enables the conversion of hydrocarbons, alcohols, or virtually any kind of solid, liquid, or gaseous fuel, that can be converted into a hydrogen- and/or carbon monoxide-rich gas, into pure

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Abbreviations: LHV, lower heating value; HEX, heat exchanger; HHV, higher heating value; LPG, liquid petroleum gas; RESC, reformer sponge iron cycle; SIR, sponge iron reaction

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hydrogen. Thus, fossil sources (e.g. natural gas, liquid petroleum gas, diesel) as well as regenerative sources (e.g. bio-gas, bio-methanol, bio-ethanol) could be utilised as fuel for the RESC hydrogen production process.

2. Overview of the RESC hydrogen production process

2.1. Principle of the RESC

The central element of the RESC is the sponge iron reactor (SIR), a reactor filled with porous iron pellets. The SIR is discontinuously supplied with reformer output gas and steam. Reformer output gas reduces the pellets from magnetite (Fe_3O_4) and wuestite (FeO) into iron metal (Fe) if the gas contains sufficient fractions of hydrogen and/or carbon monoxide. Laboratory investigations performed in a previous research project at Graz University of Technology revealed, that traces of hydrocarbons (e.g. methane), that are fed into the SIR with the reformer outlet gases, do not contribute a considerable share to the reduction of iron oxides. Thus, a high content of hydrogen and/or carbon monoxide has to be available with the SIR input gases. Once all of the magnetite and wuestite inside the reactor has been reduced, the supply with reformer outlet gases can be stopped, and hot steam is fed into the reactor. The iron pellets are thus re-oxidised back into the wuestite and magnetite stages in the presence of the hot steam atmosphere, converting a fraction of the steam into pure hydrogen. Hydrogen produced by the SIR offers a very high purity and does not contain significant amounts of carbonaceous species due to the fact that steam is the sole input species in the oxidation cycle. This is of special importance with respect to carbon monoxide catalyst poisoning effects reported for low-temperature polymer electrolyte membrane fuel cells [6,7]. SIR offgas in oxidation mode can thus be directly stored in a high pressure storage vessel after removing the steam. No extensive measures for gas clean-up are required.

Fig. 1 shows a strongly simplified schematic of the RESC system layout. Operating the RESC in oxidation mode is a straight-forward process converting steam into a mixture of steam and hydrogen, as outlined above. Operation in reduction mode is governed by the recycling of a certain fraction of SIR offgas, and by the addition of fresh hydrocarbon fuel into this stream of partially oxidised gas. The advantage of this partial recycling of offgas is two-fold: firstly, SIR offgas still contains considerable quantities of hydrogen and carbon monoxide. A fraction of these gases can be utilised with the reduction process of iron pellets by re-feeding the gases back into the SIR. The second key advantage is, that no additional steam has to be generated for the hydrocarbon reforming reaction. The hot SIR offgas contains sufficient quantities of steam and carbon dioxide to enable a full conversion of the hydrocarbon fuel over a wide range of SIR offgas recycling rates. The fraction of SIR offgas that is not recycled is combusted with ambient air in a burner unit, and this heat is subsequently used to evaporate and heat the fresh hydrocarbon species supplied to the system.

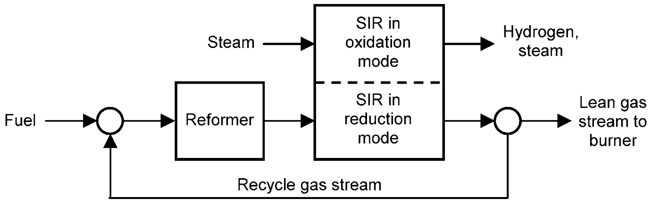

Fig. 1. Strongly simplified schematic of the RESC process.

Start-up procedures of the RESC system essentially include the heating of the SIR and the main reformer up to about 700 °C. Heating of these temperature-sensitive elements of the system could be achieved by combusting hydrocarbon input species in the lean gas burner unit and feeding the hot gases through the RESC system. Thermal inertia of the system suggests a continuous operation over the course of weeks or months when the thermal energy can be efficiently generated from the SIR offgas.

2.2. Key RESC process parameters

The RESC process essentially has three key parameters that determine design, operation and efficiency of the process: the choice of fuel, the choice of the RESC process temperature and the SIR offgas recycle rate. Operating the RESC process with different hydrocarbon fuels is not only an interesting aspect with respect to the ability to adapt the process to specific fuel options, but also with respect to key design criteria. Designing a RESC plant operating with higher hydrocarbons (e.g. pure liquid hydrocarbons such as heptane or a mixture of different hydrocarbons such as diesel, for instance) requires a different plant layout including additional components such as a hydrocarbon evaporator and a pre-reformer unit that are not required with the basic RESC design that is operated directly with methane (or natural gas, respectively) as fuel. SIR process temperatures and recycle rates have to be optimised for a specific application in order to derive a plant layout that is efficient, but yet small enough to be installed into the existing infrastructure of a regular filling station.

2.3. Aim of the mathematical model

The basic feasibility of the RESC concept has been proven with a laboratory-scale test unit that has been successfully operated at Graz University of Technology with different hydrocarbon fuels. The next step in the investigations was thus to develop a mathematical model of the complete hydrogen production plant in order to analyse the possibilities and the limitations of the process in different applications and scenarios. Key performance parameters were to be computed, investigating mass and energy balances of the individual components as well as of the complete process. The model is thus based on a thermodynamic analysis of the system, computing the thermodynamic limits of an idealised process. The performance figures presented in the following can thus be referred to as ideal thermodynamic limits of the process. The actual performance of a real-world RESC plant would be worse than the figures derived for the idealised process considered with the model development, particularly if a small laboratory-scale unit is considered. The model nevertheless provides a very good insight into governing aspects of RESC design, operation and efficiency.

3. Mathematical modelling of the RESC plant

The mathematical model of the RESC essentially consists of a hydrocarbon reformer model that is capable of calculating mass and energy balances for an isothermal hydrocarbon reforming reaction, a mathematical model of the SIR in oxidation and in reduction mode and an integration model where these two sub-models are implemented along with simplified models of heat exchangers, burners and gas mixing units. Derivation and implementation of the individual component models is briefly discussed in the following. Calculations presented within this paper are based on a model implemented in MATLAB Release 14 and running on a standard personal computer with a Pentium IV microprocessor.

3.1. Mathematical modelling of the hydrocarbon reformer

3.1.1. Introduction to mathematical modelling of the hydrocarbon reformer

The first component model discussed in the following is the hydrocarbon reformer unit model. This mathematical model is utilised to compute the reformer output gas concentrations as well as the thermal energy balance of the reformer for a specific input gas composition supplied to the reformer. Governing equations of the reformer model are presented below, along with a brief overview of mathematical implementation and model performance. The full RESC model is based on applying a pre-reformer unit – if higher hydrocarbons are considered – and a main reformer unit. Both reformers are mathematically described with the same set of equations, allowing a manual assignment of the operating temperature levels of either reformer unit.

3.1.2. Governing equations of the reformer model

The governing equations describing the reforming reaction of a hydrocarbon fuel with steam and/or carbon dioxide are written in Eqs. (1) and (2). Reforming of hydrocarbons is usually performed at elevated temperatures under the presence of catalyst materials, converting the hydrocarbon fuel into a hydrogen- and/or carbon monoxide-rich reformer output gas. The water–gas shift reaction written in Eq. (3) has also got to be considered with a complete thermodynamic analysis of a hydrocarbon reformer.

Hydrocarbon reforming reaction:

$$C_nH_m + nH_2O \leftrightarrow nCO + (n+m/2)H_2 \tag{1}$$

$$C_nH_m + nCO_2 \leftrightarrow 2nCO + (m/2)H_2 \tag{2}$$

Water–gas shift reaction:

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

The reforming reactions (1) and (2) and the water–gas shift reaction (3) proceed very rapidly at temperatures of 500 °C and above in the presence of catalyst materials. It can thus be assumed that the synthesis is close to equilibrium at the reformer outlet, presuming a sufficient dwell time of the gas in the reformer bed. Rostrup-Nielsen [8–10], Barin and Neuschütz [11] and Christensen [12] came to the same conclusions in their analyses.

3.1.3. Implementation of the hydrocarbon reformer model

The hydrocarbon reformer model implemented with the RESC simulation is based on the assumption of an isothermal reforming reaction. Thus, the reformer has to be heated by the lean gas burner unit in order to avoid a reduction in operating temperature along the gas flow direction due to the proceeding of the endothermic reforming reaction. The heat flux between reformer unit and ambient is neglected. Output gas compositions are furthermore assumed to be in full thermodynamic equilibrium for the specified reformer temperature.

Equilibrium compositions of the synthesis gas at a specified temperature and pressure are determined by applying the concept of minimising Gibbs energy. This method was developed at NASA [13] and has been demonstrated for thermodynamic equilibrium computations of numerous chemical systems. The main advantage of the Gibbs minimisation technique is its great flexibility and modularity. The governing principle of this method is the fact, that the Gibbs energy reaches a minimum if a system is in thermodynamic equilibrium. The Gibbs energy G (J) of a system containing a number of NS species is a function of temperature T (K), pressure (Pa) and system composition, where n_i is the number of moles of species i as shown in Eq. (4)

$$G = f(T, p, n_1, \ldots, n_{NS}) \tag{4}$$

It is thus necessary to compute the global minimum of function (4) for the solution of the Gibbs minimisation problem. If system temperature and pressure are assumed to be known and constant, the Gibbs energy is solely a function of system composition as shown in Eq. (5). Thus, the minimisation problem is simplified to finding the gas composition with the smallest Gibbs energy. Thermodynamic data for the reformer model calculations was taken from tables presented in Barin [14]

$$G = f(n_1, \ldots, n_{NS}) \tag{5}$$

3.1.4. Example calculation of the hydrocarbon reformer model

Fig. 2 shows an example output plot of the hydrocarbon reformer model, assuming an input flux of 1 mole of methane,

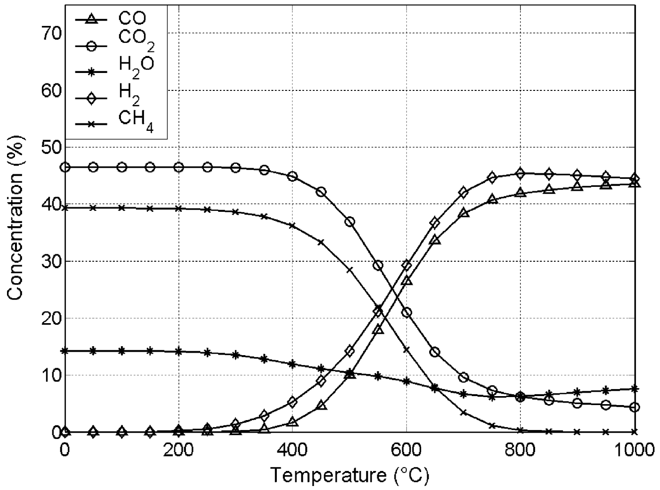

Fig. 2. Example output plot of the reformer model; input gas composition: 1 mole CH_4, 1 mole of CO_2 and 1 mole of H_2O.

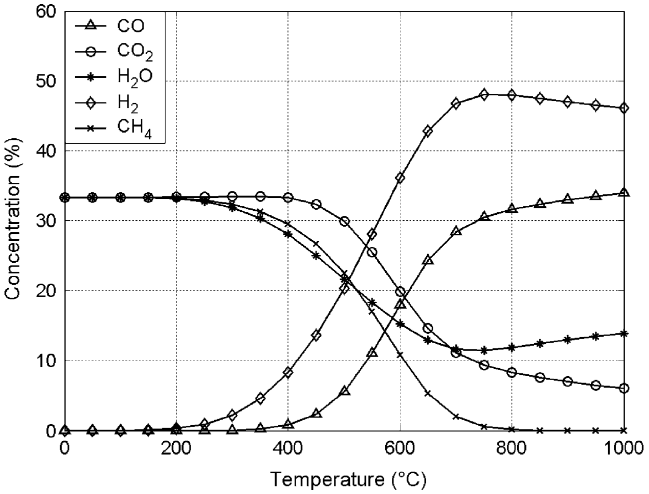

Fig. 3. Example output plot of the reformer model; input gas composition: 1 mole of C_7H_{16}, 5 moles of CO_2 and 5 moles of H_2O.

steam and carbon dioxide, respectively. Fig. 3 shows the equilibrium gas compositions for a supply with 5 moles of steam and 5 moles of carbon dioxide for each mole of heptane. The output gas composition (mol%) is shown as a function of the reformer equilibrium temperature. Assuming a reformer output temperature in the range of 800 °C – which is a normal RESC process temperature – heptane is completely converted, and only minor traces of methane remain in the reformer output gas. These traces are combusted in the lean gas burner, and thus utilised for heating purposes within the RESC.

3.2. Mathematical modelling of the sponge iron reactor (SIR)

3.2.1. Introduction to the sponge iron reaction

The sponge iron reaction is utilised as core hydrogen production mechanism of the RESC by reducing and subsequently re-oxidising iron pellets (the so-called contact mass) between the magnetite/wuestite/iron stages. Mathematical modelling of the SIR is based on determining the equilibrium gas concentrations of hydrogen and steam as well as of carbon monoxide and carbon dioxide as a function of temperature, input gas concentrations and initial oxidation stage of the pellets. Other gaseous components, particularly hydrocarbons, are assumed to pass through the reactor without oxidising and/or reducing the pellets. Measurements performed with the laboratory-scale RESC unit at Graz University of Technology demonstrated that this assumption is valid, and that the outlet gases can be considered as being in full equilibrium with the range of temperatures investigated for potential RESC operation. Reduction of the pellets is assumed to proceed with hydrogen and carbon monoxide in parallel, achieving a full equilibrium with either species. A selectivity between the oxidation of hydrogen and carbon monoxide with the contact mass has not yet been verified with experimental analyse. Some of the carbon monoxide will certainly not react directly, but rather participate in a water–gas shift reaction producing additional quantities of hydrogen. The current SIR model does not consider this indirect oxidation of carbon monoxide, but assumes the direct oxidation with the contact mass, only.

Wuestite is not considered in the stoichiometric ratio (FeO) but rather as $Fe_{0.947}O$, which represents a common composition of wuestite.

3.2.2. Governing equations of the sponge iron reactor model

The first governing equation of the SIR is the reaction between magnetite and wuestite, written in Eq. (6), producing 3 moles of wuestite out of 0.947 moles of magnetite. A total of 0.788 moles of hydrogen are converted into steam by this reaction. The same reaction can also proceed with carbon monoxide as reducing species according to Eq. (7), producing 0.788 moles of carbon dioxide as gaseous reaction product, respectively.

Magnetite–wuestite reaction:

$$0.947Fe_3O_4 + 0.788H_2 \leftrightarrow 3Fe_{0.947}O + 0.788H_2O \qquad \Delta H = 78.7\,\text{kJ mole}^{-1} \tag{6}$$

$$0.947Fe_3O_4 + 0.788CO \leftrightarrow 3Fe_{0.947}O + 0.788CO_2 \qquad \Delta H = 37.3\,\text{kJ mole}^{-1} \tag{7}$$

The second reaction considered with the SIR model is the conversion of wuestite into iron metal according to Eq. (8). This reaction produces 0.947 moles of iron metal out of 1 mole of wuestite by converting 1 mole of hydrogen into steam. Conversion of wuestite into iron metal can also proceed with carbon monoxide as reducing species according to Eq. (9).

Wuestite–iron reaction:

$$Fe_{0.947}O + H_2 \leftrightarrow 0.947Fe + H_2O \qquad \Delta H = -241.8\,\text{kJ mole}^{-1} \tag{8}$$

$$Fe_{0.947}O + CO \leftrightarrow 0.947Fe + CO_2 \qquad \Delta H = -282.9\,\text{kJ mole}^{-1} \tag{9}$$

The haematite (Fe_2O_3) to magnetite equilibrium was considered with initial investigations of the SIR hydrogen production cycle. Laboratory investigations revealed, that this oxidation stage can be neglected with a repeated cycling of the pellets because the pellets could not be re-oxidised back into the haematite stage again once they were reduced. Haematite is therefore not included with this thermodynamic analysis of the RESC process.

The Baur–Glaessner diagram shown in Fig. 4 provides an overview about the correlation between iron, wuestite and magnetite, and the respective equilibrium gas concentrations of carbon monoxide/carbon dioxide and hydrogen/steam. The equilibrium gas concentrations y^* (%) are derived from the individual gas concentrations y (%) according to Eqs. (10) and (11)

$$y^*_{H_2O} = \frac{y_{H_2O}}{y_{H_2} + y_{H_2O}} \tag{10}$$

$$y^*_{CO_2} = \frac{y_{CO_2}}{y_{CO} + y_{CO_2}} \tag{11}$$

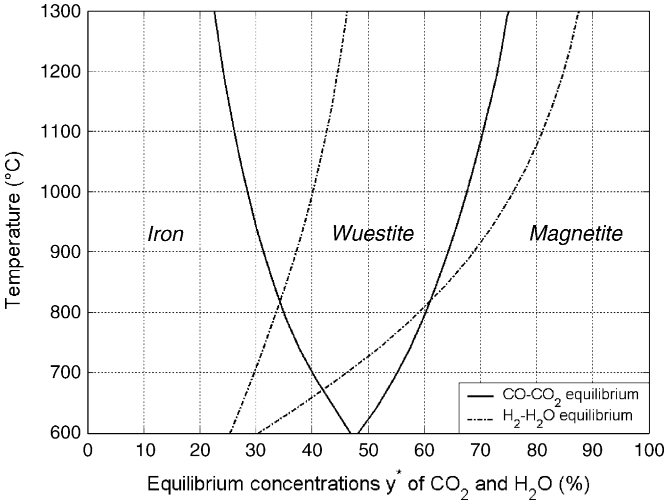

Fig. 4. Baur–Glaessner diagram.

The Baur–Glaessner diagram shows the respective equilibrium concentrations, with the steam/hydrogen equilibria shown as dash–dot lines, and the carbon monoxide/carbon dioxide equilibria shown as solid lines. The two leftmost equilibria lines shown in the plot of the Baur-Glaessner diagram represent the iron metal/wuestite equilibria, whereas the two rightmost lines represent the wuestite/magnetite equilibria. The Baur–Glaessner diagram provides two key properties describing the interaction between solid and gas phase in the REDOX reactions: Firstly, the equilibrium gas concentrations calculated for reactions of the investigated gaseous species with different iron oxides can be directly derived from the equilibrium lines shown in the diagram. Secondly, the relative position of the SIR input gas concentrations indicates which equilibrium can be achieved with a certain reaction temperature. Assuming a temperature of 800 °C, for instance, the equilibrium gas concentrations achieved with a reduction from magnetite to wuestite would be 40.9% H_2/59.1% H_2O, and 39.7% CO/60.3% CO_2, respectively. An input gas containing less than 40.9% H_2 and less than 39.7% CO will therefore not reduce magnetite. The same considerations can also be applied with the iron metal/wuestite equilibria. An input gas can only reduce wuestite if it contains more than 66.4% H_2 and/or more than 65.1% CO, otherwise the gas will not be able to reduce the wuestite into iron metal. Equilibrium concentrations also govern the oxidation of pellets from iron metal into wuestite and magnetite. A full oxidation into magnetite is achieved with a supply of pure steam.

Thus, the equilibrium gas concentrations can be directly derived from the Baur–Glaessner diagram as a function of reaction temperature if the SIR input gas compositions are known.

3.2.3. Implementation of the sponge iron reactor model

Implementation of the SIR model is based on a computation of the equilibrium gas concentrations for the iron metal/wuestite and the wuestite/magnetite equilibria for a pre-defined stream of input gas supplied to the reactor. In this, the following assumptions are applied:

- Hydrocarbons are assumed to be inactive within the SIR, and thus do not participate in the reduction and oxidation process of the pellets.
- Reduction of the pellets is assumed to proceed with hydrogen and carbon monoxide in parallel, achieving a full equilibrium with either species.
- SIR output gases are assumed to be in the full equilibrium with the respective iron(-oxides).
- Iron(-oxide) pellets are assumed to be present as either wuestite, magnetite, or iron metal.
- The SIR is computed as an isothermal process.

The SIR can be considered as an isothermal process if the amount of heat consumed and/or produced by the reaction of iron pellets with the gas phase is fully transferred into or transported out of the reactor, respectively. A RESC plant configuration where at least two individual SIRs are operated in parallel with one SIR in oxidation mode and the other SIR in reduction mode therefore suggests itself. Thus, the heat produced by the reactor with the exothermic reaction could be directly transferred into the other reactor operated with an endothermic reaction by means of thermal conduction. The inevitable difference between the operating temperatures of the SIR operated in reduction and the one operated in oxidation mode is neglected with this initial investigation of RESC performance. Thermodynamic data was again taken from tables presented in Barin [14]. Once the output gas concentrations have been derived, the thermal balance of the SIR is computed. This thermal balance is based on the aforementioned assumption of an isothermal process. The heat flux required to maintain a constant SIR operating temperature with the individual reactor is calculated. The change in enthalpy for the reactions from magnetite into wuestite, and from wuestite into iron metal is computed from the respective values of the enthalpy of formation.

3.3. Mathematical modelling of the complete RESC plant

3.3.1. Auxiliary devices required in a RESC plant

A number of auxiliary devices are required to handle the gas streams and to transfer heat between the different gas streams within the RESC plant. Evaporators are installed to transfer liquid hydrocarbon fuels into the gas phase before they are mixed with the recycle gas stream in reduction mode, and to produce steam from liquid water in the oxidation mode. These evaporators are considered with the thermodynamic analysis by calculating the heat flux required to achieve the change in enthalpy required with the evaporation of the species. Heat exchangers are utilised to transfer heat from the lean gas into the input gases, and are calculated in the same way. Burner units are required to combust the lean gas, and to provide an additional heat source in the RESC oxidation mode. These burner units are again considered with a thermodynamic analysis utilising air as oxidiser. Two components are of special importance with the reduction mode: gas mixer and recycle valve. The fraction of SIR off-gas, that is recycled and added to the fresh hydrocarbon fuel, is determined by the recycle valve. The hot recycle gas stream is added to the cold stream of hydrocarbon fuel in the gas mixing

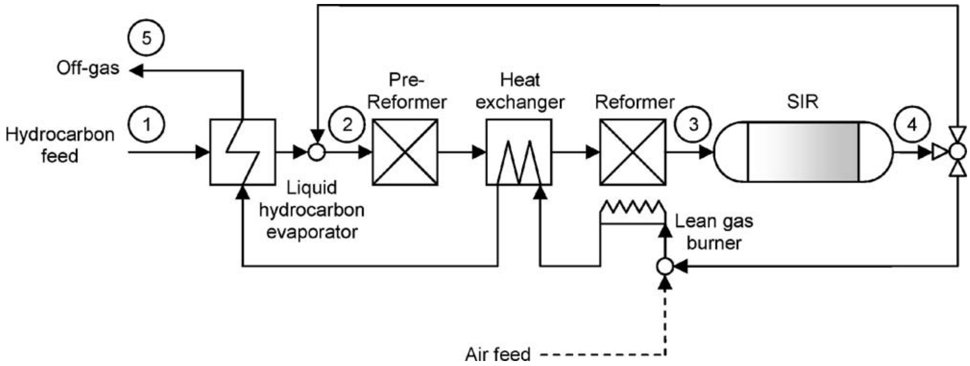

Fig. 5. Schematic of the RESC process in reduction mode.

unit. Both elements are considered with a straight-forward mass and energy balance. Pumps and compressors required for driving species through the plant are neglected. The whole plant is assumed to be operated at ambient pressure.

3.3.2. *Overview of the RESC process in reduction mode*

Fig. 5 shows a schematic of the RESC plant operated in reduction mode. Hydrocarbon fuel is supplied to the system as input species. An optional evaporator unit is included if liquid hydrocarbons are utilised as fuel. The hot recycle gas stream is added to this flux of input hydrocarbons before the mixture of gases is heated to process temperature and supplied to the isothermally operating reformer unit. The hydrocarbon reformer (or the main hydrocarbon reformer in case a pre-reformer unit is installed) is assumed to be operated at RESC process temperature. The pre-reformer is operated with significantly lower temperatures than the main reformer unit, and is also heated by the hot offgas coming from the lean gas burner unit. The pre-reformer heat exchanger is not shown in the schematic for the sake of simplicity. Reformer and SIR are operated at the same temperature level, which strongly simplifies thermal management of the system and contributes to a high conversion rate of the hydrocarbon fuel within the reformer due to the elevated reforming temperatures. SIR offgas is divided into a fraction that is recycled and added to the input gas stream, and the remaining fraction, the so-called lean gas, that is fed into the burner unit. Lean gas is thus combusted with ambient air, and the thermal energy is utilised to heat the hydrocarbon feed and the reformer input gases.

3.3.3. *Overview of the RESC process in oxidation mode*

Operating the RESC in oxidation mode requires less auxiliary components than operation in reduction mode. Fig. 6 shows a simplified schematic of the RESC plant layout in oxidation mode. Liquid water is supplied to the RESC at ambient temperature. This water is evaporated and heated to process temperature before it is fed into the SIR. The hot SIR offgas is utilised to heat the input water in the evaporator and in heat exchanger 1 (HEX1), whereas heat exchanger 2 (HEX2) is installed to add additional heat coming from an optional hydrocarbon burner unit. This hydrocarbon burner unit is assumed to be operated with the same hydrocarbon fuel that is also used with the RESC hydrogen production process. If an integrated RESC plant is considered where at least one SIR is operated in oxidation mode, with another SIR operated in reduction mode, the installation of an additional hydrocarbon burner unit considered with the oxidation layout could be avoided by injecting additional quantities of hydrocarbon fuel into the lean gas burner unit. Thus, the additional thermal energy could be supplied to the system without installing two separate burner units. Energy balance and efficiency of the overall process are identical in both cases.

3.3.4. *Hydrocarbon fuel options considered with the RESC simulation*

The RESC can essentially be operated with a wide range of different fuels produced from fossil as well as from regenerative sources. The only requirement is, that the fuel can be converted into a hydrogen and/or carbon monoxide-rich synthesis

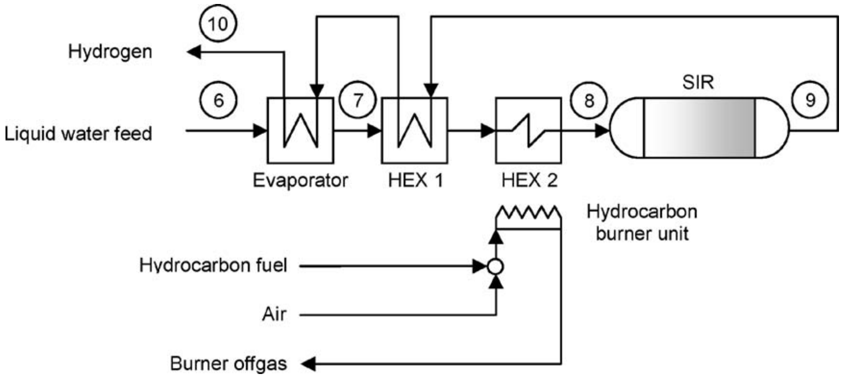

Fig. 6. Schematic of the RESC process in oxidation mode.

Table 1
Overview of hydrocarbons investigated with the current work

	Hydrocarbon	Standard state
CH_4	Methane	Gaseous
C_3H_8	Propane	Gaseous[a]
C_4H_{10}	Butane	Gaseous[a]
C_7H_{16}	Heptane	Liquid
C_8H_{18}	Octane	Liquid

[a] Can be liquefied at ambient temperature with small pressures.

gases. Performance of the RESC operated with the hydrocarbon fuel options presented in Table 1 is investigated within this paper. Three categories of hydrocarbons are considered: methane (CH_4) is not only one of the primary sources of hydrogen in state-of-the-art hydrogen production processes, but it is also widely available with the supply of natural gas. Liquid petroleum gases (LGPs) are an interesting option for on-site hydrogen production because they are widely available, and they can be easily transported in low-pressure vessels. LPGs are even considered as direct fuel option for passenger vehicles operated in fleet operation. Synergies between filling stations providing LPG as fuel for direct propulsion and as source for hydrogen production thus suggest themselves. Propane (C_3H_8) and butane (C_4H_{10}) are considered with the analysis presented in the following. The third category of hydrocarbon fuel options investigated with this analysis is liquid hydrocarbons. Heptane (C_7H_{16}) and octane (C_8H_{18}) are considered. Both have a strong relevance in transportation applications, heptane has also been applied in investigations performed with the laboratory-scale RESC system operated in the Christian-Doppler Laboratory for Fuel Cell Systems.

3.3.5. Example calculation performed with the RESC model

An example calculation of the full RESC simulation is described in the following sub-section. Typical operation of two reference cases is presented, comparing characteristic performance data for RESC operation with methane (CH_4) and heptane (C_7H_{16}) fuel. Governing simulation parameters are assigned according to the values presented in Table 2.

Variation of the molar flux of species is presented in Table 3, with five different positions in the reduction mode of the RESC. In this, the five positions refer to points 1–5 in Fig. 5. 'Feed' refers to the hydrocarbon species that is supplied as fuel. 'After mixing' refers to the condition after mixing the fresh hydrocarbon fuel and the recycle gas stream. 'Reformer output' refers to the gas that is coming out of the reformer unit. 'SIR output' refers to the SIR offgas, and 'Offgas' refers to the lean gas leaving the RESC after being combusted in the burner unit and cooled down in the heat exchangers. The values given are dimensionless and present the number of moles of species per mole of methane fuel supplied to the system. The characteristic reduction in the flux of hydrogen and carbon monoxide between reformer output and SIR output corresponds to the reduction of iron oxides by oxidation of gaseous species. The offgas composition resembles the hydrocarbon fuel plus the air (i.e. oxygen and nitrogen) added to the flow of species in the lean gas burner. The flux of nitrogen leaving the RESC is not shown for the sake of simplicity.

Table 4 gives an overview of the variation of molar fluxes with heptane fuel. Significantly larger molar fluxes are derived per mole of heptane fuel supplied to the system due to the fact that 1 mole of heptane is converted into 15 moles of synthesis gas, rather than just in 3 moles as it is the case with methane. The fraction of hydrogen and carbon monoxide utilised for reducing the pellets is similar to the respective values derived for the methane-fuelled RESC (57.0% of hydrogen and carbon monoxide supplied to the RESC are utilised with the heptane-fuelled RESC compared to 53.4% with the methane-fuelled RESC). A detailed analysis of the variation of the utilisation of hydrogen and carbon monoxide with process parameters is given in Section 4.2.4.

Deriving the thermal energy balance for the RESC is of special importance with respect to the conversion efficiency of hydrocarbon fuel into hydrogen. The thermal energy balance for methane and heptane fuel is presented in Table 5 for the reduction cycle of the RESC. The values are again calculated per mole of hydrocarbon fuel supplied. According to the values

Table 2
RESC simulation parameters, reference case

Reformer temperature	800 °C
SIR temperature	800 °C
Hydrocarbon fuel temperature	25 °C
Liquid water input temperature	25 °C
RESC offgas temperature	150 °C
HC burner offgas temperature[a]	150 °C
Evaporator temperature[b]	150 °C
System pressure	1 bar
Recycle rate	50%

[a] Hydrocarbon burner unit for oxidation mode.

[b] For liquid hydrocarbon evaporator (reduction mode) and liquid water evaporator (oxidation mode).

Table 3
Overview of the molar flux of species within the reduction cycle of the RESC per mole of methane fuel supplied (recycle rate is 50%, process temperature is 800 °C)

	Feed	After mixing	Reformer output	SIR output	Offgas
H_2	0.00	0.81	3.45	1.62	0.00
H_2O	0.00	1.17	0.51	2.34	2.00
CO	0.00	0.39	1.71	0.79	0.00
CO_2	0.00	0.60	0.27	1.19	1.00
CH_4	1.00	1.01	0.02	0.02	0.00

Table 4
Overview of the molar flux of species within the reduction cycle of the RESC per mole of heptane fuel supplied (recycle rate is 50%, process temperature is 800 °C)

	Feed	After mixing	Reformer output	SIR output	Offgas
H_2	0.00	3.15	14.48	6.31	0.00
H_2O	0.00	4.56	0.95	9.13	8.00
CO	0.00	2.72	12.82	5.45	0.00
CO_2	0.00	4.13	0.89	8.27	7.00
C_7H_{16}	1.00	1.00	0.00	0.00	0.00

Table 5
Overview of temperatures and thermal energy balance for the reduction cycle of the RESC

	Methane fuel		Heptane fuel	
	Temperature (°C)	Heat balance (kJ)	Temperature (°C)	Heat balance (kJ)
Hydrocarbon feed	25	0	25	0
Evaporator	–	0	150	61
Gas mixing	568	0	587	0
Heat exchanger	800	44	800	209
Reformer	800	235	800	1261
SIR	800	36	800	129
Offgas heat extraction	150	−378	150	−1966
Energy balance reduction	–	−63	–	−306

calculated, the reduction cycle is mildly exothermic with both fuels. The heat, that can be drawn out of the hot lean gas after combusting it in the burner unit with air, is slightly larger than the heat that is required to heat the gases to process temperature and to run the SIR in reduction mode.

The thermal energy balance of the RESC operated in oxidation mode is outlined in Table 6. The five positions presented in the table refer to points 6–10 in Fig. 6. ‘Water feed’ refers to the liquid water that is supplied to the RESC, ‘Evaporator’ refers to the energy balance of the water evaporator unit, ‘Heat exchanger’ represents the gas condition after the heat exchangers, which corresponds to the SIR input conditions. ‘SIR’ refers to the reactor outlet conditions, and ‘Offgas heat extraction’ refers to the RESC process offgas conditions. A considerable amount of energy is thus required for evaporating the water, and for heating the steam to process temperature. Offgas heat extraction can only provide a fraction of the total amount of thermal energy required. Operating the RESC in oxidation mode is therefore endothermic, consuming more thermal energy that the exothermic reduction cycle can provide. This explains why the additional hydrocarbon burner unit shown in Fig. 6 has to be installed.

The overall RESC thermal energy balance is positive in case of methane as well as in case of heptane fuel. In both cases, a net input of heat is thus required to maintain the temperature level of 800 °C. This additional energy could be supplied by electric heaters – as it is done with the small laboratory-scale RESC device operated at Graz University of Technology – or by burning additional quantities of hydrocarbon fuel. Considering a stand-alone RESC unit for on-site hydrogen production, this required heat could be generated by burning additional quantities of the same hydrocarbon fuel already utilised with the hydrogen production process. This additional fuel consumption has to be considered in an overall energy balance of the RESC system, and results in a significant reduction of the overall hydrocarbon to hydrogen conversion efficiency.

4. Results

4.1. RESC process conversion efficiency

The overall conversion efficiency η (%) of the RESC process is defined according to Eq. (12). This definition considers the dimensionless number of moles of hydrogen (n) produced out of each mole of hydrocarbon fuel supplied, including the fraction of input fuel supplied to the hydrocarbon burner for heating purposes in oxidation mode. The values of efficiency presented in the following can therefore be referred to as the energetic efficiency of the complete RESC system, comparing the energy available with the product hydrogen gas with the total energy supplied with the hydrocarbon fuel. Energy content of hydrogen and hydrocarbon fuels is compared with respect to the lower heating value (LHV)

$$\eta = 100 \times \frac{n\,\mathrm{LHV}\,(\mathrm{H_2})}{\mathrm{LHV}\,(\mathrm{Fuel})} \qquad (12)$$

4.1.1. Conversion efficiency as a function of recycle rate and process temperature

Fig. 7 shows the variation of RESC process efficiency in case of an operation with methane fuel as a function of recycle rate and process temperature. Applying very small recycle

Table 6
Overview of temperatures and thermal energy balance for the oxidation cycle of the RESC

	Methane fuel		Heptane fuel	
	Temperature (°C)	Heat balance (kJ)	Temperature (°C)	Heat balance (kJ)
Water feed	25	–	25	0
Evaporator	150	200	150	1131
Heat exchanger	800	103	800	581
SIR	800	−67	800	−380
Offgas heat extraction	150	−88	150	−495
Energy balance oxidation	–	148	–	837

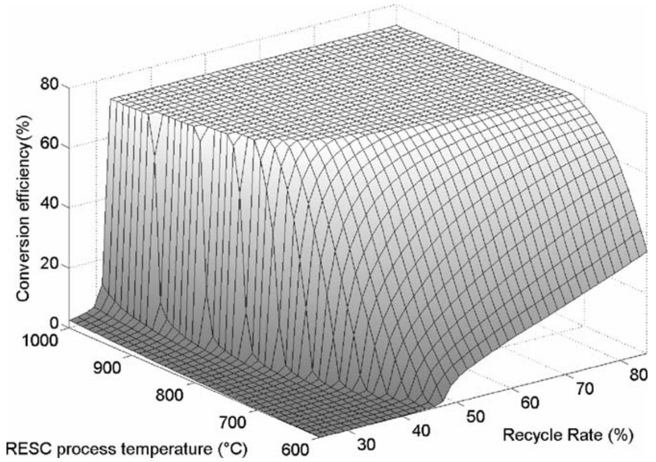

Fig. 7. Overall RESC conversion efficiency with methane fuel as a function of RESC process temperature and recycle rate (%).

rates leads to low conversion efficiencies primarily due to the low concentrations of steam and carbon dioxide in the reformer input gas stream. Thus, only a fraction of the hydrocarbon fuel can actually be converted into hydrogen and carbon monoxide within the reformer, and only this small fraction can reduce iron oxides within the SIR. A limiting recycle rate is primarily derived with higher process temperatures. If a recycle rate is applied, that is smaller than the limiting rate, the RESC process efficiency is drastically reduced down to almost zero. The recycle gas stream thus contains large fractions of methane fuel and only small quantities of carbon dioxide and steam, that would be required with the reforming reaction. The process can thus not be operated appropriately, and large quantities of methane are fed through the system without getting reformed, and thus also without reducing iron oxides. An external supply with steam and/or carbon dioxide would therefore be required if the process was to be operated with very small recycle rates or without any recycling, respectively. Maximum efficiencies derived for the RESC process with methane fuel are in the order of 75%. Applying very large recycle rates is neither beneficial with respect to the overall conversion efficiency, nor with respect to the large volumes that have to be circulated within the system. A process temperature level in the range of 800 °C is sufficient to achieve good overall conversion efficiencies. Applying higher temperatures does not lead to an increase in overall conversion efficiency due to the energy requirements of heating the gases to process temperature. A reduction in temperature is particularly limiting with respect to the SIR performance.

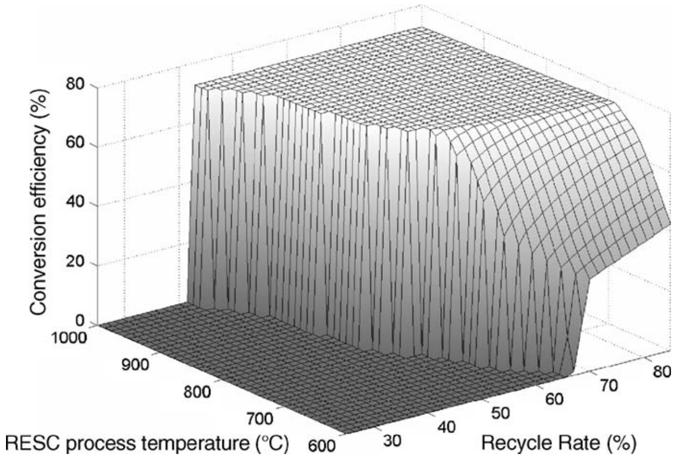

Fig. 8. Overall RESC conversion efficiency with heptane fuel as a function of RESC process temperature and recycle rate (%).

Table 7
Maximum conversion efficiencies computed for the RESC with different hydrocarbon fuels

Fuel	Chemical formula	Moles of hydrogen per mole of fuel	Maximum efficiency vs. LHV (%)
Methane	CH_4	2.78	74.77
Propane	C_3H_8	7.17	79.53
Butane	C_4H_{10}	9.36	79.43
Heptane	C_7H_{16}	15.94	74.44
Octane	C_8H_{18}	18.13	74.25

Fig. 8 shows the RESC process efficiency in case of an operation with heptane fuel. Maximum conversion efficiencies achieved with methane and heptane fuel are in a similar range. Operating the RESC with heptane fuel requires significantly larger recycle rates in order to achieve these good conversion efficiency, though. A strong reduction in efficiencies is again derived if the recycle rate is smaller than the limiting recycle rate for the investigated process temperature of 800 °C.

4.1.2. *RESC conversion efficiency for different hydrocarbon fuels*

Peak hydrocarbon to hydrogen conversion efficiencies achieved with different fuels are presented in Table 7. The efficiencies for methane, heptane and octane versus LHV are almost identical. Significantly higher efficiencies are only derived for propane and butane fuel. LPG is therefore an interesting hydrocarbon source for hydrogen production with the RESC process.

4.2. *Mass and energy balances of the complete RESC*

Key parameters in RESC operation with methane and heptane fuel are compared in the following section. In order to provide a compressed overview of the performance, the plots are limited to a reduced range of operating parameters. The investigated range of operating temperature is 750–1000 °C with both fuels, and a recycle rate between 40% and 80% is applied with methane fuel and 55–80% with heptane fuel. Lower temperatures and smaller recycle rates are not considered due to the low conversion efficiencies achieved with these operating conditions. Higher temperatures and larger recycle rates are not investigated due to limitations in plant size and material properties.

4.2.1. *RESC hydrogen production capability*

One of the key figures applied in describing the RESC hydrogen production capability is the ratio of the number of moles of hydrogen produced per mole of hydrocarbon fuel supplied to the system. Figs. 9 and 10 provide an overview of the hydrogen production capability for the RESC operated with

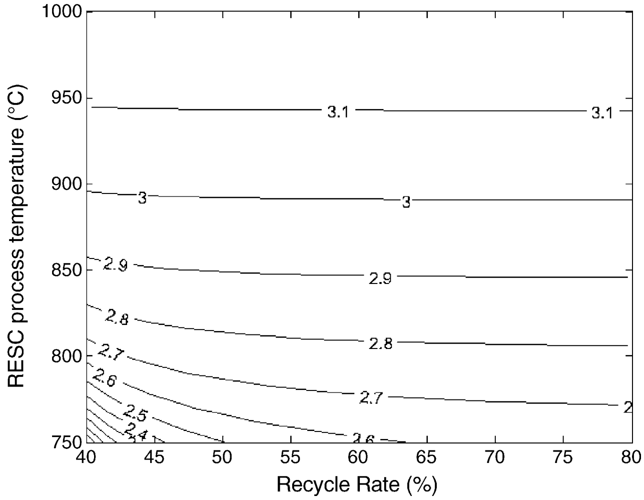

Fig. 9. Moles of hydrogen produced per mole of methane fuel supplied.

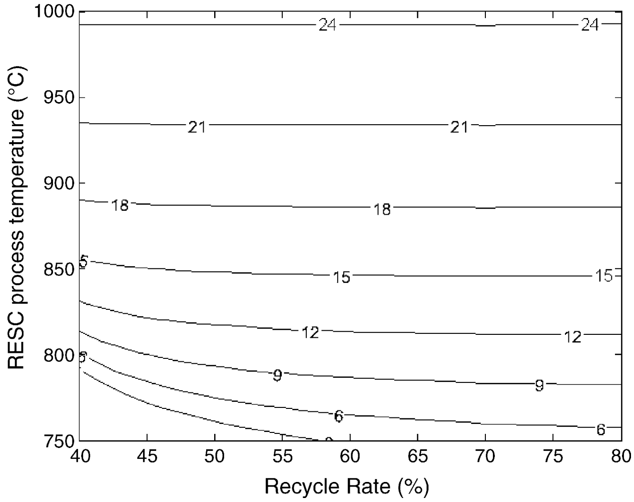

Fig. 11. Fraction of total methane fuel consumption required for heating purposes (%).

methane and heptane fuel. In this, the amount of fuel consumed for additional heating purposes is neglected. Considering only the amount of fuel that is actually supplied to the RESC reformer is particularly interesting with respect to the fact, that the additional heat required to run the process could also be supplied by utilising waste heat of a different process (e.g. in a refinery). Higher process temperatures and higher recycle rates generally lead to an increase in the hydrogen production capability.

4.2.2. Additional hydrocarbon fuel required for heating purposes

The fraction of fuel, that is required for heating purposes in the hydrocarbon burner units, is presented in Figs. 11 and 12. This assumes, that the additional heat required for the endothermic RESC process is generated by combusting some of the methane or heptane fuel outside of the system. Operation at elevated temperatures requires a significant amount of energy primarily to heat the input gases to process temperature. Roughly a quarter of the RESC fuel is thus required for heating purposes with methane as well as with heptane fuel with the maximum process temperature of 1000 °C investigated.

4.2.3. Overall molflux supplied to the SIR

Large recycle rates result in large volumes that have to be moved through the different components of the RESC system. A careful evaluation between an increase in process efficiency and a reduction in plant size therefore has to be made in order to derive a compact setup that can be operated efficiently. Fig. 13 shows the variation of SIR input molflux per mole of hydrocarbon fuel supplied. Increasing the recycle rate from 50% to 75% doubles the molflux, implying that reactor and tubing have to be designed correspondingly larger. Similar values are also derived for the heptane-fuelled RESC plant as shown in Fig. 14.

4.2.4. Fuel utilisation of the SIR as a function of operating condition

A key aspect in SIR operation is investigated in Figs. 15 and 16. The plots show the fraction of hydrogen and

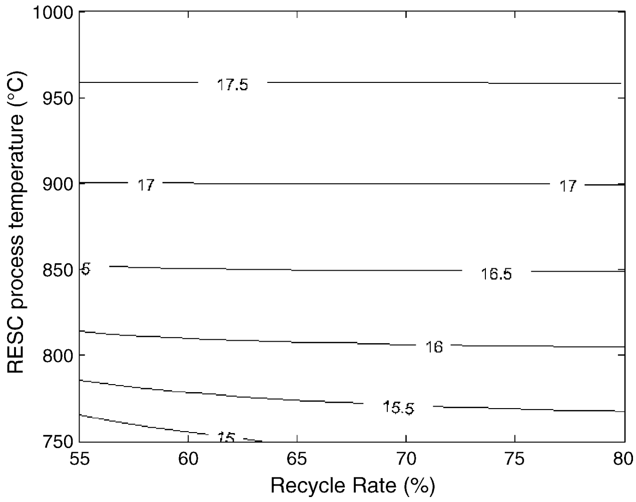

Fig. 10. Moles of hydrogen produced per mole of heptane fuel supplied.

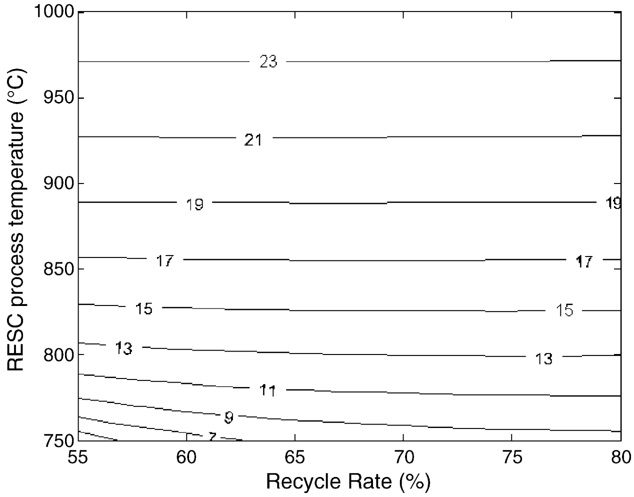

Fig. 12. Fraction of total heptane fuel consumption required for heating purposes (%).

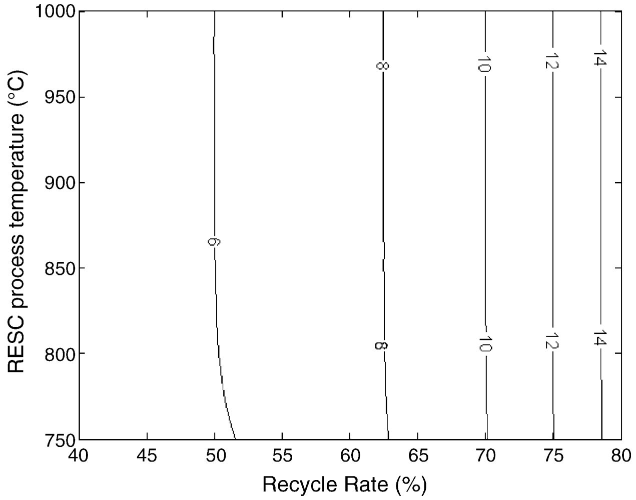

Fig. 13. Input molflux of the SIR in case of methane fuel (in moles per mole of methane fuel supplied).

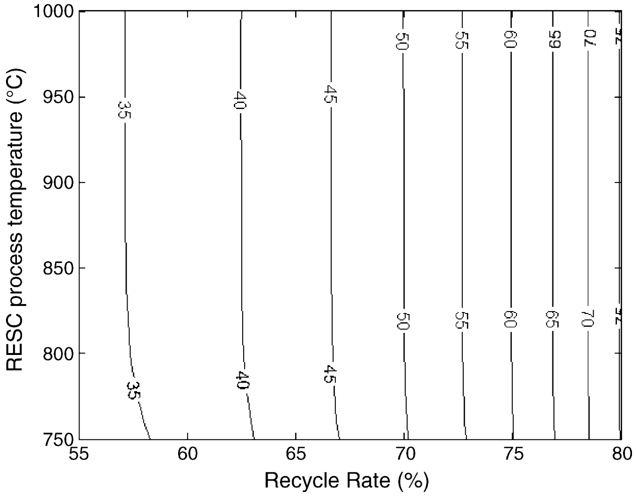

Fig. 14. Input molflux of the SIR in case of heptane fuel (in moles per mole of heptane fuel supplied).

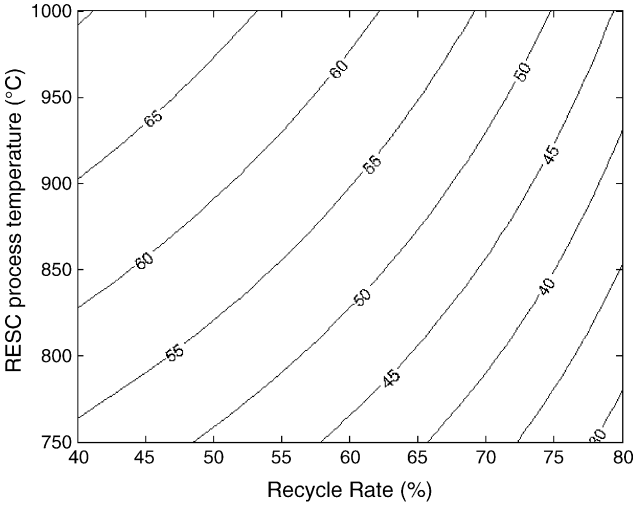

Fig. 15. Fraction of carbon monoxide and hydrogen supplied to the SIR that is utilised for iron oxide reduction in case of methane fuel (%).

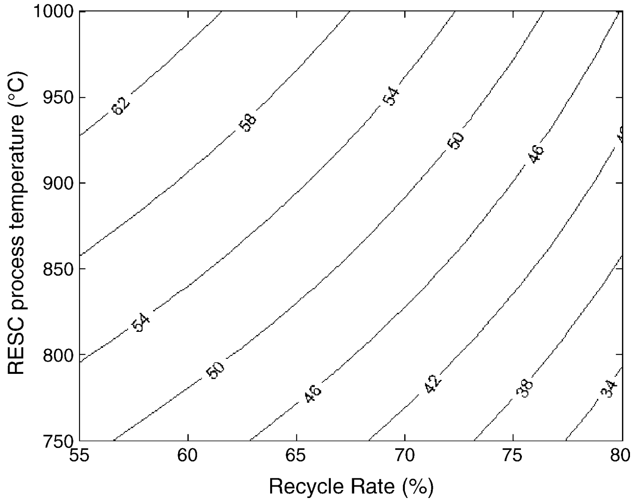

Fig. 16. Fraction of carbon monoxide and hydrogen supplied to the SIR that is utilised for iron oxide reduction in case of heptane fuel (%).

carbon monoxide supplied to the SIR that is actually utilised for reducing iron oxides. This fraction is generally quite low, being in the order of 30–70% for the range of operating conditions considered. High recycle rates lead to particularly low rates of utilisation due to the thinning of the reducing gases with steam and carbon dioxide. The low rates of utilisation show the strong importance of utilising SIR output gases as heat source for the reforming reaction. Thus, the energy of hydrogen and carbon monoxide, that is not utilised in the SIR, is not lost for the process, but is added to produce additional quantities of hydrogen and carbon monoxide in the reformer unit.

5. Conclusions

A complete thermodynamic analysis of the reformer sponge iron cycle (RESC) is presented. The process simulation comprises of individual component models of the hydrocarbon reformer, the sponge iron reactor (SIR), as well as of the auxiliary devices required to operate the system. A number of different hydrocarbons are investigated as RESC input species. A full analysis of hydrocarbon to hydrogen conversion efficiencies is presented.

The primary conclusion derived from the thermodynamic analysis of the idealised RESC system is, that the process offers hydrocarbon to hydrogen conversion efficiencies in the order of 75% versus LHV for methane, heptane and octane. Slightly better conversion efficiencies are derived for RESC operation with propane and butane. Simulations also revealed, that the process efficiency can be considered as being almost constant as long as the recycle rate is larger than a certain limiting rate. This limiting recycle rate is a function of temperature and RESC input fuel. Variation of conversion efficiencies with process temperatures is only significant with temperatures below 800 °C. An application of higher operating temperatures does not result in an increase in conversion efficiencies.

The thermodynamic calculations also revealed, that an additional heat source is required to operate the process in the realistic temperature range of 750 °C and above. This heat has to be supplied to the SIR operated in the endothermic oxidation cycle, whereas the reduction cycle is slightly exothermic. A significant fraction of fuel thus has to be supplied for heating purposes with elevated operating temperatures. This does, however, not cause a significant drop in the overall conversion efficiency of the process, because the thermal energy is directly stored in the stream of gases during the heating process as well as during the reforming reaction. This thermal energy can be fully recovered with the system of heat exchangers, assuming that the offgas leaving the RESC system has a defined temperature, and the heat flux to ambient is neglected.

The next step will be to apply the thermodynamic RESC model in designing a small on-site hydrogen production facility for a hydrogen vehicle filling station. These analyses will provide estimates of the system dimensions as well as the iron pellet mass.

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