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Dynamic Behaviour of an HMR Pre-Combustion Gas Power Cycle

Lei Zhao*, Finn A. Michelsen,**
Bjarne Foss*, Knut I. Aasen***

**NTNU, Department of Engineering Cybernetics,NO-7491 Trondheim, Norway*
(Tel: 0047 735 94497; e-mail: lei.zhao@itk.ntnu.no).
*** SINTEF ICT, Applied Cybernetics, NO-7491 Trondheim, Norway (e-mail: Finn.A.Michelsen@sintef.no)*
**** Statoil, Forskningsparken, NO-3908 Porsgrunn, Norway (e-mail: knas@statoil.com)*

Abstract: This paper explores dynamics for control design of a Hydrogen Membrane Reformer (HMR) pre-combustion gas power cycle. For this type of reforming to be competitive to power generation with carbon capture, low costs and emission of CO_2 and NO_x is required. Further, high operability and robustness is also required. This is achieved through an understanding of the system dynamics and robust control structure design. The paper presents a new dynamic model of the system which is validated against a static model and is the first analysis of dynamic behaviour of the HMR pre-combustion gas power cycle. The paper identifies important dynamic features of the reformer unit and focuses on the responses in outlet temperature and hydrogen concentration of the HMR unit to changes in important candidate inputs. An initial control study explores a simple control scheme for handling important disturbances like feed changes and load changes.

Keywords: Dynamic behaviour, gas power cycle, conversion, hydrogen membrane reformer, reforming.

1. INTRODUCTION

CO_2 capture and storage is becoming an increasingly important part of any discussion on clean coal and gas based power production. In this paper, the dynamic behaviour of a Hydrogen Membrane Reformer (HMR) pre-combustion gas power cycle has been studied. This power cycle was described by Smith et al. (2009). The HMR gas power cycle is a pre-combustion Carbon Capture and Storage (CCS) technology under development in Statoil. This technology is based on natural gas as power fuel. The core of the HMR plant is a syngas reactor based on a high temperature (1000-1100 °C) hydrogen selective membrane. Membrane reactors can potentially reduce the cost of CO_2 capture for such processes, and significantly reduce the NO_x emission (Metz 2005).

Since the start up in 2001 and through 2008 the development of the HMR gas power cycle has been financed by the Carbon Capture Project (CCP), with co-funding from the Research Council of Norway. The reactor system was developed through several stages and different process configurations were evaluated. One of the most cost effective HMR concepts is being studied in this work. It includes one single membrane reformer unit combined with traditional water gas shift (WGS) and syngas CO_2 removal processes.

For this type of reforming to be competitive for power generation, high operability and robustness is required. Important for this is a thorough understanding of the system dynamics and a robust control structure design. Metz (2005) identifies important dynamic features of the HMR reformer unit. Similar work on other pre-combustion CCS technologies include Imsland et al. (2005) where a semi-closed O_2/CO_2 gas turbine model is investigated and Kandepua et al. (2007) where a SOFC-GT-based autonomous power system is studied.

The main contribution of this study is to present a new dynamic model for a promising CCS process. The purpose of this model is to study dynamics, control and ultimately develop an overall robust operational strategy. In this paper we present steady state and dynamic analyses and a simple control scheme for handling important disturbances like feed changes and load changes. The model has been validated against a static model and test results of HMR reactor from experimental studies at Statoil.

The paper is organized as follows. Section 2 describes the HMR pre-combustion gas power cycle plant, relevant control issues and the simulation model. Section 3 shows steady state and dynamic responses to perturbations of inputs. Section 4 contains a discussion before some conclusions end the paper.

2. SYSTEM DESCRIPTION

2.1 Production plant

The HMR pre-combustion gas power cycle plant consists of reformers and separation units, compressors, gas and steam turbines and a heat recovery system. Fig. 1 shows a scheme of the part of the process that is focused here. CW is cold water, BFW boiled feed water, CC combustion chamber, LWGS low temperature WGS, HWGS high temperature WGS, HE heat exchangers and N_{rad} compressor speed. The air compressor, the expander and the CC constitute the gas turbine (GT). A

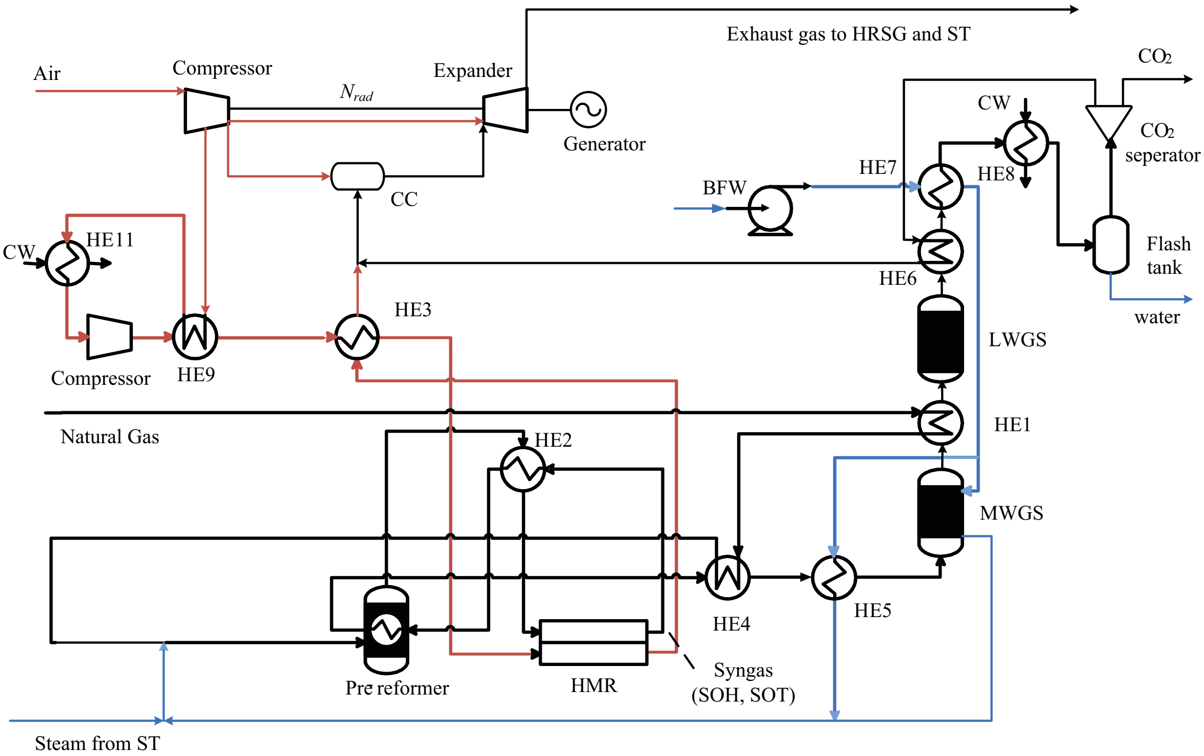

Fig 1. Sketch of the HMR process with HMR syngas reactor, CO_2 removal unit and gas turbine (Smith et al., 2009).

heat recovery system (HRSG) and a steam turbine (ST) are normally included in such processes but are not included in the proposed model since they are not important for the closed loop system analysis. A desulphurization unit for the natural gas is neither included in this model.

In the process to produce synthesis gas, natural gas is first saturated with steam and pre-reformed at about 500 °C in order to convert higher order (heavier) hydrocarbons to methane. The gas is then further heated and reformed to convert as much methane to hydrogen as possible in the HMR unit. This is done on the retentate side of the hydrogen conducting membranes by steam methane reforming (SMR) at about 1000 °C. The SMR reactions are rate limiting. Compressed air drawn from the gas turbine compressor is supplied to the permeate side of the HMR reactor. Permeated hydrogen is combusted, consuming approximately all oxygen in the air stream. This gives "CO_2 free" heat for the endothermic SMR reactions.

Syngas is generated with high concentrations of H_2, CO_2 and CO. Efficient utilization of this syngas is important to achieve an efficient pre-combustion process (Smith et al. 2009). Further, the syngas is fed via several heat exchangers to a medium and a low temperature water gas shift stage converting CO to CO_2. The purpose of the heat exchangers is to cool the gas from about 1000 °C down to the preferable WGS operating window between about 200 – 400 °C. The main reactions are given by:

$$
\begin{array}{lllll}
CH_4 & + H_2O & = CO & + 3H_2 & \text{(SMR)} \\
CO & + H_2O & = CO_2 & + H_2 & \text{(WGS)} \\
CH_4 & + 2H_2O & = CO_2 & + 4H_2 & \\
2H_2 & + O_2 & = 2H_2O & \text{(}H_2\text{ combustion)} &
\end{array}
$$

The outlet gas from the permeate side contains mainly H_2O and N_2 and is used to dilute the hydrogen fuel recovered in the CO_2 removal process. CO_2 removal may be performed by using a conventional absorption unit, a CO_2 membrane or a hydrogen membrane.

Since syngas and air is processed separately, and the high temperature air steam from HMR permeate side is fed directly to CC, the heat recovery will be very efficient. In addition, the higher CO_2 concentration will allow a more efficient CO_2 separation. This gives an overall efficiency (defined as electric power output/ fuel low heating value) including compression of CO_2 to 150 bar close to 50%.

The main focus of this study is the dynamic responses in the syngas outlet temperature (SOT) and the syngas outlet hydrogen concentration (SOH) from the HMR to changes in important manipulated variables (MVs). These outlet variables are closely related to the power load, CO_2 captured, and the efficiency of the whole plant. The MVs include feed flow rates of natural gas (NG), steam and air. This type of analysis, performed at an early stage, gives valuable information to control structure design as well as to further process design. The basis for the presented analysis is a new mathematical model based on first principles developed in MATLAB/SIMULINK.

2.2 Simulation model

SMR is among the most common technologies for converting methane to carbon monoxide and hydrogen. A number of 1-D first principles based dynamic models of large scale SMR processes for refineries etc. have been developed during the past decades, see Alatiqi et al. (1989), Alatiqi & Meziou (1991). A much referred kinetic model was developed by Xu & Froment (1989). Simulation of the SMR process using generic software packages for chemical engineering applications have also been performed, see e.g. Kolios et al. (2004). All these were distributed models.

In the analysis of dynamic behaviour for control purposes low order models are often sufficient. Hence, for simulation of the overall dynamics of the presented process we have developed a new lumped low order dynamic first principles model based on mass and energy conservation. The model has been developed in a standard way as described by e.g. Thomas (1999) and includes the units shown in Fig. 1. The following assumptions were made:

- 12 species are considered in each stream and reactor. The species are H_2O, CO, CO_2, H_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, O_2, N_2, Ar, and H_2S.
- Hyperbolic functions are used to approximate heat capacity at constant pressure (Rowley et al. 2007).
- The heavier hydrocarbons C_2 - C_4 reactions and the oxidation reaction are totally converted and always in equilibrium. A steady state reaction rate is used.
- All gases are ideal gases.
- Pressure drops are neglected.
- The outflow from each reactor is based on steady state overall mass balances.
- The reaction rate of SMR is from Xu et al. (1989); and the WGS reaction rate is from Rase et al. (1977).

For the reactors the molar balance and energy balance are:

$$\frac{dn_{1,i}}{dt} = \dot{n}_{1,i,in} + \dot{n}_{1,i,r} - \dot{n}_{1,i,out} - \dot{n}_{H_2,per} \tag{1}$$

$$\frac{dn_{2,i}}{dt} = \dot{n}_{2,i,in} + \dot{n}_{2,i,r} - \dot{n}_{2,i,out} + \dot{n}_{H_2,per} \tag{2}$$

$$\dot{n}_{i,o} = \frac{\lambda_i}{\sum_i \lambda_i w_i}\left(\dot{n}_{i,in} + \dot{n}_{i,r} + \dot{n}_{H_2,perm}\right) w_i \tag{3}$$

$$\left(\sum_i n_{1,i} c_{p1,i} + c_{p1,s} m_{1,s}\right)\frac{dT_1}{dt} = \sum_i n_{1,i,in} c_{p1,i,in} T_{1,in} \tag{4}$$

$$-\sum_i n_{1,i,in} c_{p1,i} T_1 - \sum_{j=1}^{m} \dot{n}_{2,j,r} \Delta H_j + UA_1(T_1 - T_2) - \dot{n}_{1,i,r} \Delta H_{H_2}$$

$$\left(\sum_i n_{2,i} c_{p2,i} + c_{p2,s} m_{2,s}\right)\frac{dT_2}{dt} = \sum_i n_{2,i,in} c_{p2,in} T_{2,in} \tag{5}$$

$$-\sum_i n_{2,i,in} c_{p2,i} T_2 - \sum_{j=1}^{m} \dot{n}_{2,j,r} \Delta H_j + UA_2(T_1 - T_1) + \dot{n}_{2,i,r} \Delta H_{H_2}$$

where n_i is the number of moles of component i, $\dot{n}_{i,o}$ the mole rate of component i, T temperature, c_p heat capacity at constant pressure, U the overall heat transfer coefficient between the two sides of the reactor, A the contact area between the two sides of the reactor, λ_i the mole fraction in the reactor; w_i the mole weight m mass and ΔH heat of reaction. Subscripts 1,2 denote each of the two sides of the reactor, *in* inlet flow, *o* outlet flow, *r* reaction, *s* the catalyst and wall, and $j = 1...m$ is the reaction number including m reactions.

Some additional assumptions for the other components are:

- The HEs are one-dimensional distributed models, discretised along the flow direction.
- An off-line design model is used for the GT. The compressor and turbine maps are from Lazzaretto. et al. (2001).
- The flash tank is described by a steady state model.
- The CO_2 separation unit is modelled as a steady state model.
- The stream separation and mixing units are described by steady state overall mass and energy balances.

2.3 Control issues

Candidate MVs in this process are:

- Feed flow rate of air, steam and natural gas (NG).
- Feed temperatures of steam.
- Inlet pressures of air, steam and NG.
- Cold water flow rates to coolers for air feed (one valve) and syngas (two valves).
- Bypass stream flow rates of heat exchangers.
- Split valve for air to the fuel gas.

The main control objective is to deliver electric power safely and reliably on some grid according to a demand. Transients occur due to load changes as well as disturbances. One disturbance is composition variations in the natural gas, e.g. a change in the methane content and a corresponding change in the ethane and propane content.

The energy demand determines the required NG flow rate and the SOH. If the compositions of the NG and air feed are constant, the oxygen-to-carbon ratio (O/C) can be controlled by the air-to-gas flow ratio (A/G). Likewise, under the same conditions the steam-to-carbon ratio (S/C) can be controlled by the steam-to-gas flow ratio (S/G). Otherwise O/C and S/C have to be controlled. These are, however, more costly implementations in terms of sensor investments.

The reaction temperature can be measured at the reactor outlet. According to Alatiqi et al. (1989) and Alatiqi (1990), control of SOT is adequate for control of the hydrogen concentration under feed composition variations only when S/C is controlled. In that case, there is a close relationship between the SOT and the hydrogen concentration.

Industrial heavy duty gas turbines are specially designed gas turbines for power generation. Most such GTs use single shaft between compressor, expander and generator (Cohen et al. 1996). For such a single shaft GT, the rotational speed N_{rad} is controlled at a constant setpoint, as the generator is required to produce electricity with constant frequency at 50 or 60 Hz. The speed is controlled by using the flow rate of NG as manipulated variable. Further, from the steady state and open loop dynamic simulations as shown in section 3.2 and 3.3, the response of SOT is more sensitive to the O/C ratio than to the S/C ratio. Hence, it is reasonable to use the steam flow rate as MV to control S/C and control the SOT by using the air flow rate as MV. This control structure has been suggested through discussions with the process designers and is shown in Fig. 2. Reformer includes pre-reformer, HMR, two WGS reactors, and associate heat exchangers.

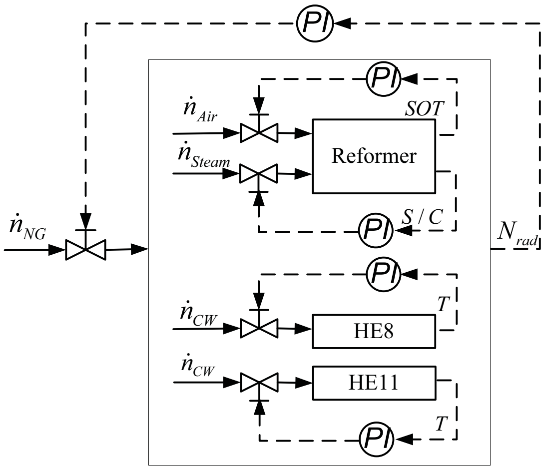

Fig. 2. Control structure for HMR power cycle.

The controller set points have to be adjusted according to the turbine load and within the constraints as defined below.

- The HMR temperature should be constrained by an upper limit of about 1100 °C to avoid damage of the reactor and catalyst materials.
- Less than 50% hydrogen in the fuel to the combustor. This secures low NO_x emissions.
- Low differential pressure across the HMR membrane in order to minimize any leakage through the membrane or sealing.
- S/C should be higher than 1.5 to avoid coke formation. There is also an upper bound to prevent catalyst activity deterioration.
- The inflow temperature of compressor and flash tank should keep in a low value to avoid damage and increase efficiency.

Normally, S/C of about 2.0 and O/C of about 1.0 are appropriate values.

3. SIMULATION RESULTS

In order for the control system to handle variations in the input disturbances at various operating points, knowledge of the response of the hydrogen production to changes in input variables is crucial.

The dynamic simulation model has been used to study how changes in the MVs affect SOT and SOH. The MVs have been varied over a range, which is, based on process knowledge, considered to be a normal operating range. The model has been simulated to steady state for a set of operating points within this region. The open loop dynamic responses of SOT and SOH to variations in the MVs are of special interest for control structure design. SOH is calculated as H_2 fraction in the syngas from the HMR. The control structure as suggested in section 2.3 is used for the closed loop control scenario.

3.1 Model adaptation

An Aspen Plus model was developed in the plant design phase for steady state process simulations. Our model was validated using available open literature data as well as data from in-house experiments. Parameters for reactions and heat exchange in the dynamic model were tuned for different operation points to obtain similar steady state values for compositions, flows, temperatures, pressures as obtained from the steady state data. The model errors are below 5%, which are satisfactory for the current study.

3.2 Steady state analysis

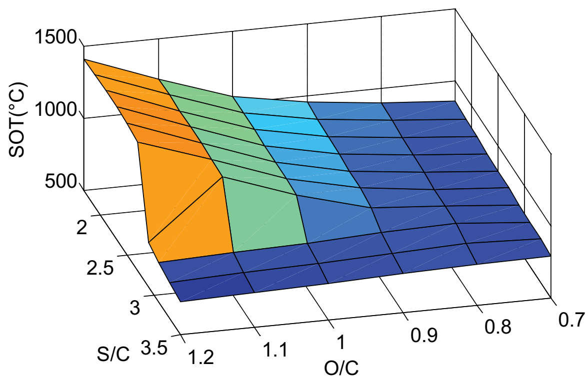

Fig. 3. SOT as a function of O/C ratio and S/C ratio.

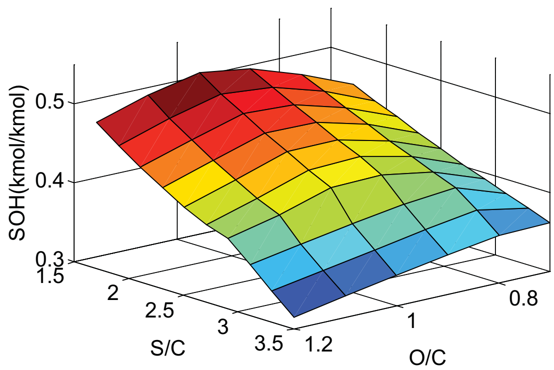

Fig. 4. SOH as a function of O/C ratio and S/C ratio.

Fig. 3 and Fig. 4 show the steady state SOT and SOH as functions of the O/C ratio and S/C ratio. For S/C ratios in the range 2.7 to 3.1, and O/C ratio above 0.9, the gain from the S/C ratio to SOT is large and negative. Otherwise, it is very small. The gain from the O/C ratio to SOT is low at low O/C ratios and increases at higher O/C ratios for S/C below 3.1. The gain from the O/C ratio to SOH changes sign at O/C ratio about 0.96 for lower S/C ratios. For higher S/C ratios, the gain changes sign at a lower O/C ratio. With increasing S/C, SOH is decreasing, and the gain from the S/C ratio to SOH varies slightly with O/C.

3.3 Analysis of open loop dynamic behaviour

Fig. 5 shows responses to a step in the air flow rate and steam flow rate at the steady state operating point O/C=0.96, S/C=2.2. The figures show fairly linear responses from the steam flow rate and considerable nonlinear responses from the air flow rate in this operating range. This is consistent with Fig. 3 and Fig. 4.

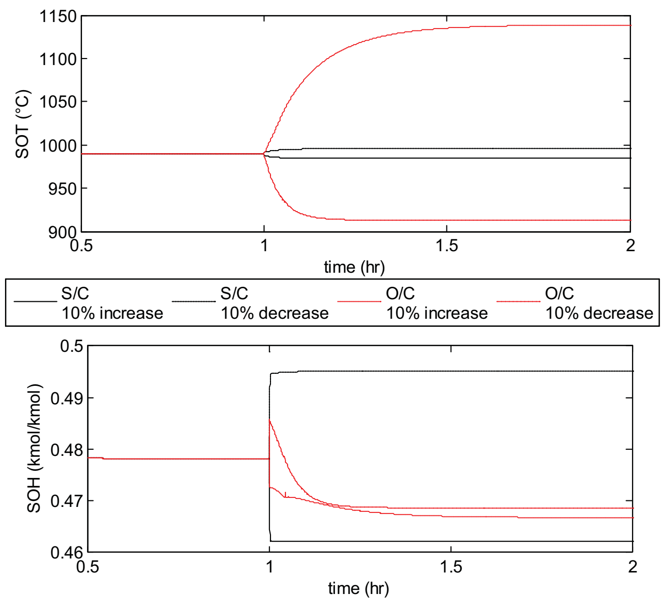

Fig. 5. Net step responses in SOT and SOH to a positive and a negative step change in air flow rate and steam flow rate.

3.4 Closed loop control

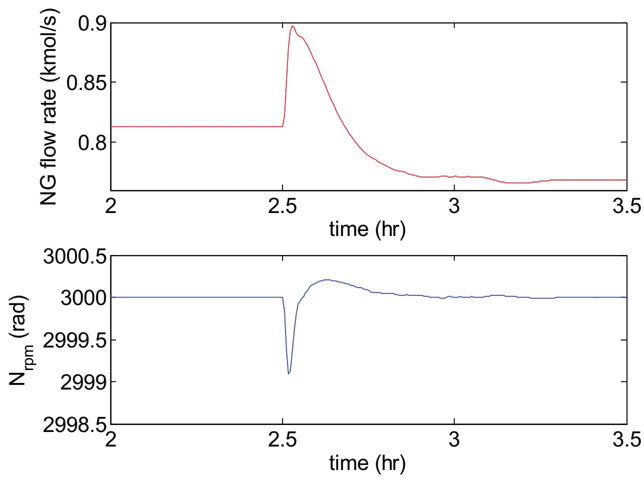

Fig. 6. NG flow rate control loop variables at NG composition change.

Fig. 6 and 7 show the responses to a 10% decrease in the methane and 5% increase in ethane and propane content of the feed NG at time 2.5 hours. The flow rate of NG is decreased and the flow rates of steam and air are decreased to keep N_{rad}, S/C and SOT at their respective setpoints. The setpoints are reached after approximately half an hour.

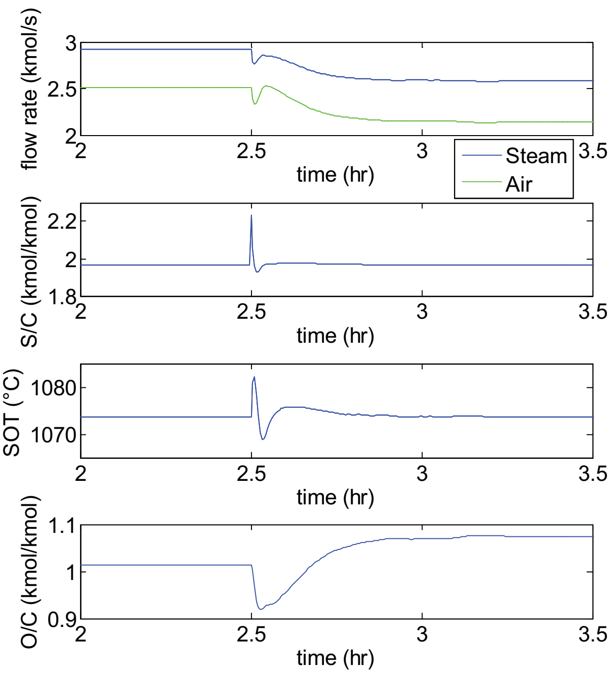

Fig. 7. S/C and SOT control loop variables at NG composition change.

4 DISCUSSIONS

The simulations are focused on how different process inputs affect the hydrogen production. They show that both the steady-state and dynamic behaviour of the plant depend strongly on the flow rates of feed streams. Further, they confirm that S/C of about 2.0 and O/C of about 1.0 are appropriate operating values, which provide high production of hydrogen. The responses are more sensitive to the O/C ratio than to the S/C ratio in this range. At higher S/C ratios, the sign of the gain from the O/C ratio to SOT changes and for S/C in the range 2.7 to 3.1 the gain from the S/C increases considerably. These results favour the O/C ratio as manipulated variable for control of the SOT. The inverse responses of SOH pose challenges to the control system design.

Closed loop simulations focused on variations in the NG composition as process disturbance. The result shows that the process can be controlled in a simple way achieving fairly good rejection of this disturbance, c.f. Alatiqi (1990).. The response time of the rotation speed control loop is large compared to the dynamics of the GT which is in the range of seconds. This loop may not be suitable for rapid load change. A duct burner, which uses NG as fuel, can be added upstream of the GT to reduce the response time.

There are several options for control structure design depending on the disturbances which have to be rejected. In this study, we have looked at one option. Alternatively, as suggested by Alatiqi (1990), the SOH may be controlled by manipulating the air flow rate. However, by this, the SOT will be very high for heavy gases. Hence, a continuous feedback loop from SOT to the O/C controller setpoint was suggested. By this, an improved strategy can be obtained where both SOT and SOH are controlled in a multivariable structure.

5. CONCLUSIONS AND FURTHER WORK

This paper has analysed one important part of the dynamic behaviour of a HMR pre-combustion gas power process. The paper has demonstrated that the design exhibits complex dynamic behaviour, which may pose challenges when designing a robust control structure with good performance for the process with all the constraints and operating objectives. A single loop control structure, designed for an initial control study, showed however that the process can be controlled fairly well by rejection of NG composition variations. The presented work is the first analysis of dynamic behaviour of the HMR pre-combustion gas power cycle.

Further work will include an analysis of other candidate controlled and manipulated variables, as well as the impact of other disturbances, to provide a more complete basis for control structure development. Constraint handling will be an important issue, which may be necessaries when using MPC type controllers. Another disturbance is leakage through the membrane in the HMR. A typical scenario is operation with too large pressure difference between the retentate side and the permeate side such that gas leaks into the permeate side. Such a leakage will typically occur instantly due to a cracked membrane module. A leakage of the reactor will cause more hydrogen on the permeate side than requested. Thereby, the increased combustion at the location near the leakage may increase the temperature locally to values that may destroy the membrane and/or the catalyst.

Load changes are also important process upsets. These changes will probably lead to pressure fluctuations, which might cause large differential pressure across the HMR membrane leading to leakage through the membrane. In the further work, the relations between flow rates and pressures will be included model such that the impact and proper handling of this upset can be treated.

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