

COMPARISON OF ETHANOL STEAM AND AUTOTHERMAL REFORMING PROCESSES

ETANOLA TVAIKA UN AUTOTERMISKĀS PĀRVEIDOŠANAS PROCESU SALĪDZINĀJUMS

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Introduction

There has been an increased interest in fuel cell technology as a means of producing effective non-pollution or low pollution energy during the past years. Since the hydrogen, which is the fuel for most types of fuel cells, cannot be found on Earth in pure form, the ways of producing hydrogen from other energy sources are widely discussed. Ethanol, produced from renewable feedstock is one of the most promising sources of hydrogen production. Ethanol is non-toxic and can be easily produced in great quantities by the biomass fermentation process, and the ethanol's theoretical mass energy density is about 8 kWh/kg.

The generation of hydrogen rich gas for fuel cells from alcohols can be done in three different ways: steam reforming (STR), partial oxidation and autothermal reforming (ATR). STR process, which is endothermic, and ATR process, which is exothermic are discussed in the present work. The STR process requires an external heat source but can achieve higher hydrogen concentration in reformat gas in comparison with ATR. Although the hydrogen amount in the ATR process is smaller than obtained by the STR process, the ATR does not require an external heat source and therefore results in a simpler design. The next steps of fuel reforming – water gas shift reactor (WGS) and CO removal by methanation or oxidation are selected for each technology separately.

It is assumed that the reformat gas is fed into the proton exchange membrane (PEM) fuel cell after all cleaning steps, which means, that the CO concentration at the exit of reformer-system should do not exceed 20 ppm.

The start-up energy and time, possibilities of minimisation of carbon formation, influence of steam to carbon ratio on amount of produced hydrogen are investigated in the work. The influences of all above parameters on the total system efficiency are shown, and the results demonstrate the advantages and disadvantages of each reforming process. As a result of this analysis, the most favourable process for application in stationary PEM fuel cell systems is determined.

The work is based on the results of experimental research and simulations.

The differences between ethanol steam and ethanol autothermal reforming processes

The following three thermochemical reforming processes could be applied to produce hydrogen from ethanol: steam reforming, partial oxidation reforming and autothermal reforming. From a thermodynamic point of view, these processes can be categorised in two basically different types of processes. One is steam reforming, where ethanol reacts with steam, and the reaction is endothermic. The required heat could be supplied from external sources by combustion of part of the feed, by burning combustible off gases or by a combination of both. The other reforming process – partial oxidation is exothermic, where the feed reacts directly with air or pure oxygen (in large plants). The autothermal process combines these two processes. The process require less water compared with steam reforming however it also results in less hydrogen content in reformat [3, 1].

Reforming ethanol by reacting it with steam requires three water molecules for each molecule of ethanol as shown by the overall reaction (1) [2]:



The overall reaction that characterises autothermal process is [6]:



The reaction (2) shows that from 1 mole of ethanol 5 moles of hydrogen can be produced in autothermal process. However, although these both processes are different, many system components are quite similar (air is fed only in autothermal process, and the burner, which uses anode off-gasses, provides external heat for steam reforming process) (Fig. 1):

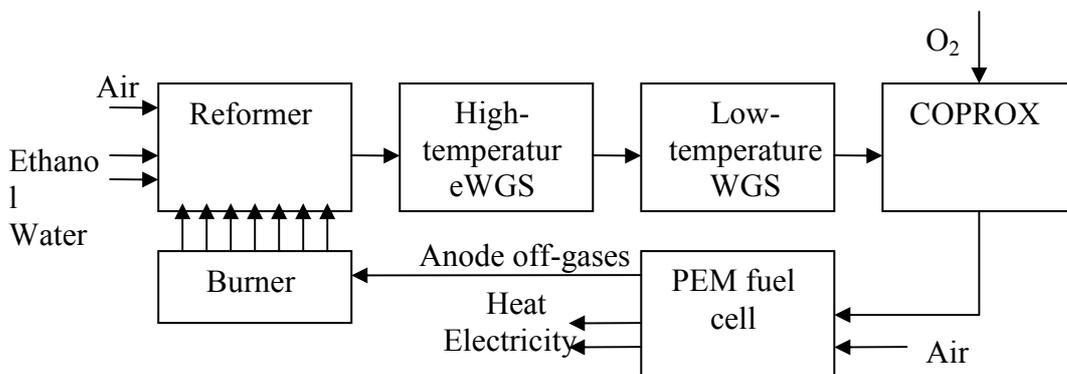
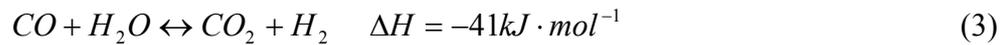


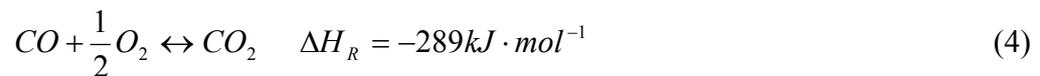
Figure 1. Fuel cell-reformer system

The reformer-fuel cell system for autothermal or steam reforming of ethanol may consist of high-temperature water-gas-shift reactor (WGS), which operates at temperatures of about 350°C, low-temperature water-gas-shift reactor, which operates at temperatures of about 200°C, catalytic partial oxidation reactor (COPROX), which operates at temperatures of about 100°C. The reactions (3, 4) which take place in above mentioned reactors are:

Water-gas shift reaction:



Partial oxidation reaction:



Theoretically, also hydrogen oxidation reaction can take place, but catalysts used can prevent it. As the Figure 1 shows, the differences in systems are mainly at the reforming part and probably at the pre-heating part, where air should be fed and pre-heated for autothermal reforming, and external heat from burner provided for steam reforming.

Experiments and results

The ChemCAD program was used for simulation, and with the help of it simulation of the whole processes could be done at equilibrium conditions (Fig. 2).

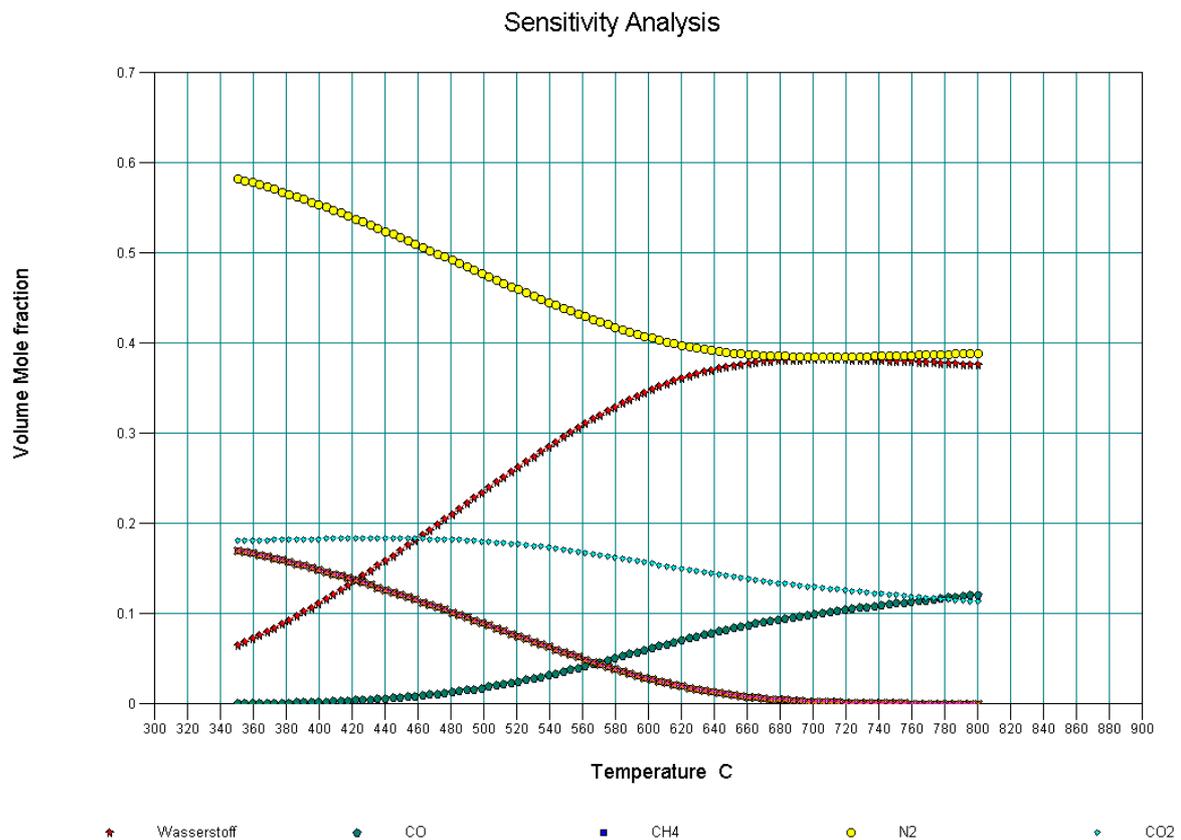


Figure 2. Sensitivity analysis of ethanol autothermal reforming process for steam/carbon ration (S/C) -1,5

The optimal operation temperature for the autothermal reforming process is approximately 700°C (Fig.2), whereas by steam reforming it should be in a range of 600-850°C (Fig. 3) [6]. As shown in Figure 4, the ignition starts in about 1 min after pre-heated ethanol is fed into the reformer, and temperatures of ATR and respectively the gas mixture also stabilise after some minutes. But the reformer must be heated with water vapour and therefore the reforming can start only approximately after 54 min. from the beginning of the heating. The ignition-phase starts at 180°C – 230°C in comparison to steam reforming where the ignition-temperature of ethanol-air mixture is approximately 120°C [1].

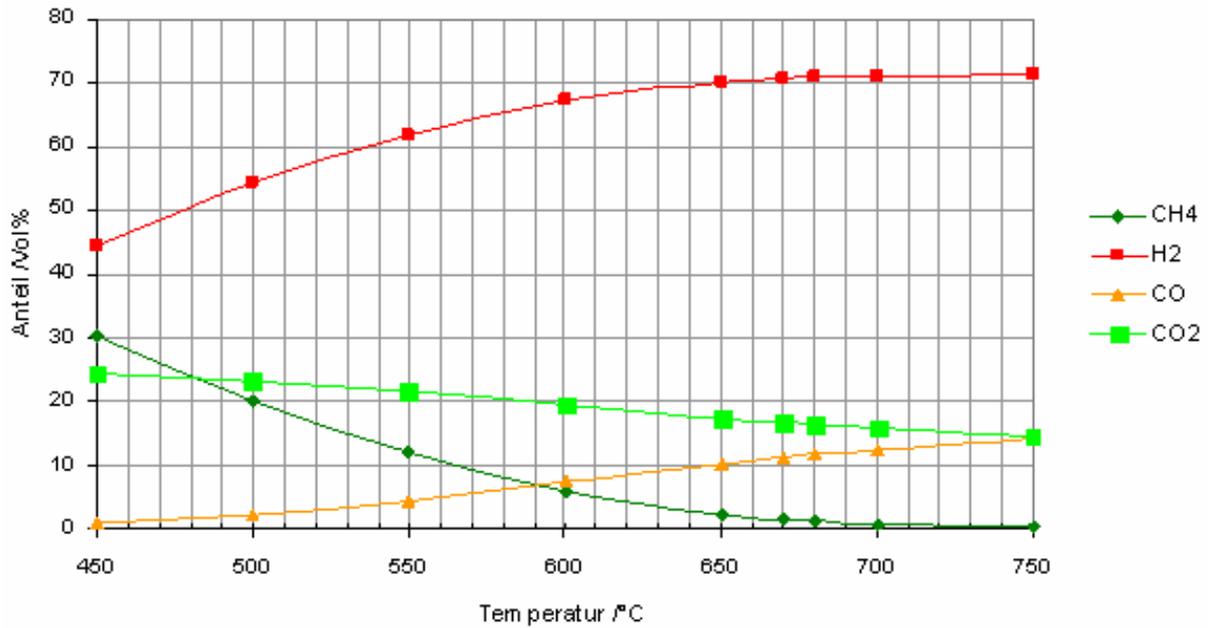


Figure 3. Ethanol steam reforming sensitivity analysis for S/C-3 [6]

However, the experiments show that it takes 53.5 minutes to become hydrogen-rich gas. Therefore, it should be taken into account that the system's components were not optimized and the thermal integration was not done, and that surely influenced required pre-warming period.

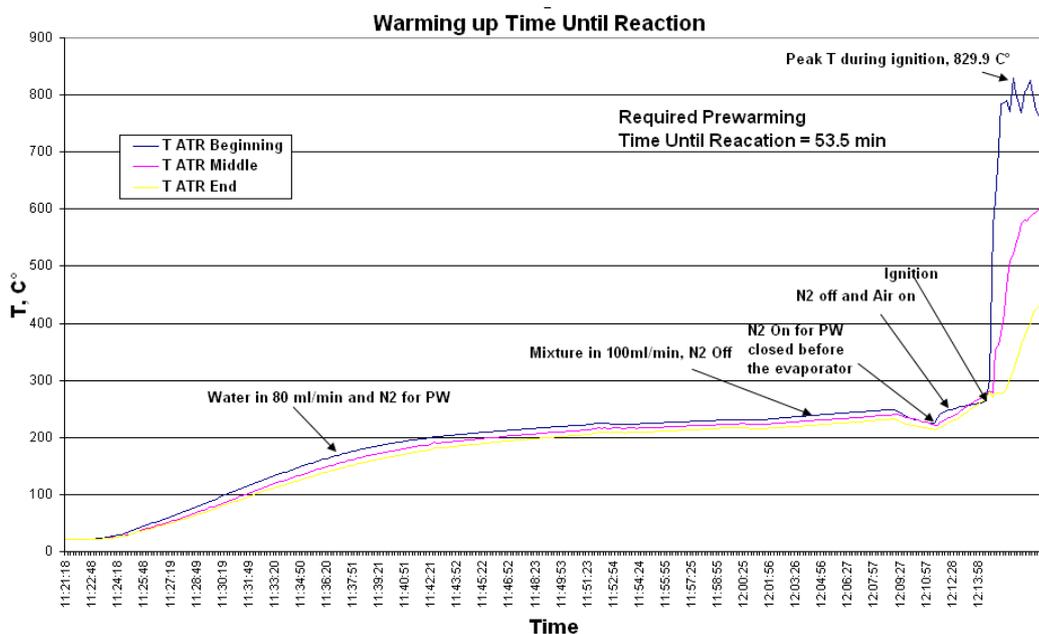


Figure 4. Warm up and ignition phases of ethanol

Previous estimations, the simulations and experiments [4] have shown that although the autothermal reforming is mostly used for automotive purposes, and requires less energy for start-up, it is able to produce less hydrogen than the steam reforming process. It should be noted that the steam reforming is more sensitive to carbon formation than autothermal reforming, but carbon formation should be also taken into account for autothermal reforming.

Results of research show that possible efficiency of the system or reformer could be 70% for autothermal reforming and a maximum 81,2% for steam reforming of ethanol with burning anode off-gasses [2,6]. It was estimated that the fuel choice is also very important for start-up energy as well as for the overall efficiencies [5].

Conclusions

Although the simulation, experiments and previous estimations for the most part show that steam reforming is more effective, other scientists conclude autothermal reforming as the most effective way to produce hydrogen. Autothermal reforming is also widely used for automotive applications because of faster start-ups. However, the experimental results of this work show the fastest start-up time is approximately 50 min. The estimated system efficiency was 70 %, where the steam reformer showed higher efficiency as well as faster start-up. This was a result of better system's components optimization and heat recovery.

Main differences between autothermal and steam reforming processes were shown in this work. Potentially, autothermal reforming, with optimised parts of fuel cell-reforming system, especially with focus on pre-heating of feed streams and possible heat recovery, could show better results as steam reforming process of ethanol.

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Markova D., Bažbauers G. Etanola tvaika un autotermiskās pārveidošanas procesu salīdzinājums.

Darbā tika apskatīti un salīdzināti divi termokīmiskās pārveidošanas procesi: autotermiskā etanola pārveidošana un etanola tvaika pārveidošana. Darbā parādīta iespējamā sistēmas shēma, kurā izmantoti abi procesi ūdeņraža iegūšanai protonu apmaiņas kurināmā elementa vajadzībām. Norādītas arī sistēmas atšķirības atkarībā no izmantotā pārveidošanas veida. Noteikts, ka vairāk uzmanības jāpievērš papildu enerģijas pievadīšanai tvaika

pārveidošanā un papildu gaisa uzsildīšanai autotermiskajā procesā. Tika konstatēts, ka liela nozīme ir arī izmantotā kurināmā īpašībām, it īpaši attiecībā uz darba uzsākšanai nepieciešamo enerģijas apjomu. Ar datormodelēšanas palīdzību tika iegūtas pārveidošanas procesa sakarības, konkrēti, gāzes sastāva atkarība no pārveidošanas temperatūras. Izmantojot veiktos eksperimentus, tika parādīts iespējamais ieejas produktu, reaktora un katalizatora uzsildīšanai nepieciešamais laiks, kas eksperimentālajai etanola autotermiskās pārveidošanas sistēmas iekārtai ir aptuveni 50 minūtes. Tas ir samērā ilgs laika periods, salīdzinot ar iepriekš veiktajiem pētījumiem. Autotermiskās etanola pārveidošanas sistēmas lietderības koeficients ir aptuveni 70%. Etanola tvaika pārveidošanas sistēmai tas ir lielāks – aptuveni 80%. Darbā tika definētas darba uzsākšanas laika apjoma samazināšanas un kopējās sistēmas efektivitātes paaugstināšanas pamatiespējas, ko var nodrošināt, optimizējot sistēmas komponentes un izmantojot siltummaiņus.

Markova D., Bazbauers G., Comparison of ethanol steam and autothermal reforming processes.

Two thermochemical fuel reforming processes were analysed and compared in the present work: autothermal and steam reforming of ethanol. Possible layout of the reforming process system is shown which combines both hydrogen production processes for needs of proton exchange membrane fuel cell. Differences of the system depending on used reforming process were also shown. It was determined, that more care has to be addressed to extra energy use in steam reforming process and air pre-heating in autothermal process. It is concluded that properties of fuel play a large role, especially in the determination of amount of energy required during start-up. Dependence of composition of reformat gas on reforming temperature is obtained with help of computer simulations. By using experimental results, it was shown that time period required for heating up inlet products, reactor and catalyst is approximately 50 minutes for experimental autothermal reformer. This is a relatively large period of time comparing to results of previously made investigations. Efficiency of autothermal ethanol reforming system is approximately 70%. Ethanol steam reforming system has higher efficiency – about 80%. Possibilities for reduction of start-up time period and improvement of overall system efficiency which could be achieved by optimisation of system components and by using heat exchangers.

Маркова Д., Бажбауэр Г., Сравнение парового и автотермического процессов реформинга этанола.

В работе рассмотрены и сравнены два процесса термохимического преобразования: автотермический реформинг этанола и парового реформинг этанола. Показана возможная схема системы для объединения с топливным элементом обмена протонов, описаны различия систем в зависимости от используемого процесса. Определено, что необходимо уделить больше внимания способу использования дополнительной энергии при паровом реформинге и нагреванию воздуха при автотермическом реформинге. Указано так же, что немаловажную роль в объемах стартовой энергии играет вид используемого топлива. С помощью симуляции показаны зависимости в процессе реформинга, а именно, зависимость состава газа от температуры. Используя проделанные эксперименты, определено возможное время нагревания входящих продуктов, реактора и особенно катализатора; которое составляет 50 минут для системы автотермического реформинга этанола, что, в сравнении с предыдущими исследованиями, довольно таки долго. Коэффициент полезного действия системы - около 70 %, в то время как для системы парового реформинга - около 80 %. В работе определены основные возможности уменьшения необходимой стартовой энергии и повышения эффективности всей системы, что возможно проделать, оптимизируя компоненты системы и анализируя возможности использования теплообменников.