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REFORMING OF BIOETHANOL TO HYDROGEN FOR USE IN FUEL CELL COGENERATION PLANTS

BIOETANOLA PĀRVEIDOŠANA ŪDEŅRADĪ IZMANTOŠANAI KURINĀMĀ ELEMENTA KOĢENERĀCIJAS IEKĀRTĀS

Darja Markova, *researcher, Mg.sc.ing. (PhD student)*
Riga Technical University
Faculty of Energy and Electrical Engineering
Institute of Energy Systems and Environment
Kronvalda boulv. 1, Riga, LV-1010
e-mail: darja_markova@inbox.lv

Kārlis Valters, *assistant professor, Dr.chem.*
Riga Technical University
Faculty of Energy and Electrical Engineering
Institute of Energy Systems and Environment
Kronvalda boulv. 1, Riga, LV-1010
e-mail: karlis@norden.lv

Gatis Bažbauers, *associate professor, Dr.sc.ing.*
Riga Technical University
Department of Energy and Electrical Engineering
Faculty of Energy and Electrical Engineering
Institute of Energy Systems and Environment
Kronvalda boulv. 1, Riga, LV-1010
e-mail: bazbauer@latnet.lv

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Introduction

It is important for Latvian electricity supply system to develop domestic power production capacity and use local renewable energy sources at the largest extent for the electricity production. Well developed district heating systems of various sizes allow to utilise advantages of cogeneration of electricity and heat. The use of bioethanol fuel cell cogeneration systems could help to reduce reliance on imported electricity and fuel and increase the share of electricity produced from renewable energy sources since fuel cell cogeneration plants can achieve high energy efficiencies, and bioethanol can be produced from various sources such as cellulose, waste etc. Maximisation of hydrogen production from bioethanol via reforming process is one of the main tasks for advancing techno-economic feasibility of fuel cell cogeneration systems. The main goal of the work was to obtain regression relations between most critical dependent variables such as hydrogen and carbon monoxide content of reformate gas and independent factors such as air-to-fuel ratio (λ) which is calculated as actual air-to-fuel ratio divided by stochiometric air-to-fuel ratio, steam-to-carbon ratio (*S/C*), inlet temperature of reactants into reforming process, etc. by using the data from experimental investigations of the bioethanol reforming process. The obtained regression equations allow to optimise the reforming process for obtaining the highest yield of hydrogen and minimising carbon monoxide concentration in the reformate gas.
The work is based on experiments done in Fraunhofer Institute for Solar Energy Systems on the experimental autothermal reforming (ATR) system where bioethanol is used as a fuel. The ATR system consists mainly of evaporator, ATR reactor and low-temperature water-gas shift reactor. All parts of the system were tested at various operational conditions by varying *S/C* ratio, λ value, inlet temperature of reactants flowing into ATR, temperatures of water-gas-shift reactors etc. with the aim to achieve the best operational point for the system, i.e. maximum hydrogen content and minimum carbon monoxide content in the reformate gas. The experimentally obtained results of hydrogen and carbon monoxide concentrations downstream of ATR reactor are compared with equilibrium calculations done with the simulation program of chemical processes „ChemCAD".
The results of the work show the empirical relations between hydrogen and carbon monoxide content and the controlling parameters downstream of ATR reactor. The obtained regression relations allow to maximise hydrogen content and minimise carbon monoxide content in the final reformate gas composition which is fed into the fuel cell.

Experimental investigation of autothermal reforming process of bioethanol

The autothermal reforming is a combination of steam and partial oxidation reforming pathways – where preheated fuel (bioethanol), water and air are fed into ATR reactor (figure 1).

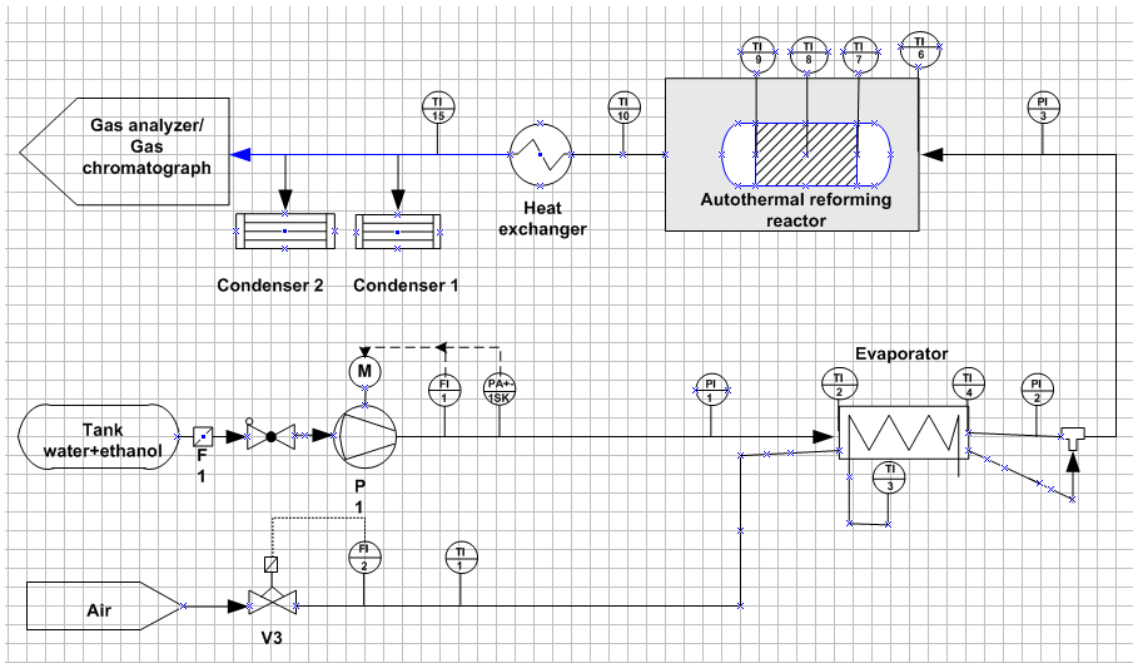

Figure 1. Process flow diagram

The system was operated at several conditions, were parameters were varied in the following ranges: *S/C* – 0,5…2,5; λ – 0,19…0,36; pressure in the reactor (p) – 0,12…0,47 bar; inlet temperature of reactants into ATR (T_{in}) – 230…360 ºC; mass flow of reactants (M) – 0,56…1,07 kg/h (mass flow of mixture of bioethanol, water and air). Concentrations of the following reaction products: hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen and water were measured with gas chromatography.
The central aim of the investigation of the reforming process was to achieve high hydrogen concentration and low carbon monoxide concentration since the reformate gas was fed into proton exchange membrane fuel cell, which is highly sensitive to *CO*.

Results of experiments

The regression equations are based on measurements of reformate gas composition downstream of ATR reactor. *S/C*, λ, T_{in}, p and mass flow of reactants divided by volume of the catalyst (M/V_{cat}) were chosen as the independent variables that are used in regression analysis. Factor *M/Vcat* was included in the list of explanatory variables because it was found during experiments that with increase of mass flow of reactants concentration of hydrogen in the reformate gas increases as well at constant size of catalyst. Inclusion of this factor considerably improved correlation between the experimental data and the regression values. This can be explained by the fact that increase of mass flow of reactants over surface of catalyst improves utilisation of the catalyst surface. Regression equation obtained for hydrogen concentration in the reformate gas downstream of ATR reactor is the following:

$$H_2 = -24{,}824 + 0{,}04 \cdot \left(M/V_{cat}\right) + 0{,}270 \cdot \left(S/C\right)^2 - 274{,}092 \cdot \lambda \cdot p - 601{,}194 \cdot \lambda^2 - \\ - 108{,}468 \cdot p^2 - 0{,}022 \cdot T_{in} + 371{,}833 \cdot \lambda + 141{,}73 \cdot p \qquad (1)$$

where

H_2 – hydrogen concentration (% vol. in dry gases);
V_{cat} – catalyst's volume (l).

Number of data points used in regression analysis is 146; value of R-squared of the model is 84,3 %. Achieved F-ratio is 91,75 which is much larger than the critical value F_{tab} = 2,64 at the significance level p = 0.01 which indicates that the regression equation can be used in the studied range of independent parameters. Independent parameters which are used in the regression equation are all statistically significant at the 99% confidence level since for all coefficients $|t| > t_{tab}$ (where t_{tab} – critical t-value at the significance level p = 0.01).

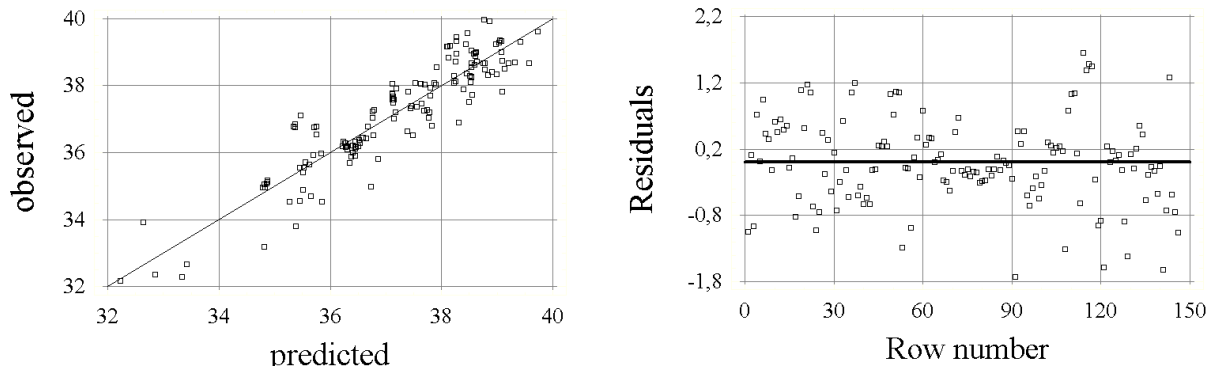

Figure 2. Visual representation of predicted versus observed values of hydrogen concentration and residuals versus row number

By using multiple linear regression analysis the model which describes dependence of concentration of carbon monoxide in the reformate gas downstream of ATR reactor as the function of the considered independent variables is the following:

$$CO = 24{,}15 - 30{,}644 \cdot p + 0{,}053 \cdot T_{in} + \\ + 134{,}468 \cdot \lambda \cdot p + 6{,}565 \cdot \left(S/C\right)^2 + 12{,}747 \cdot \ln\left(S/C\right) - 34{,}432 \cdot S/C \qquad (2)$$

Number of data points used in regression analysis is 138; value of R-squared of the model is 95,9 %. Achieved F-ratio is 515,94 which is much larger than the critical value F_{tab} = 2,94 at the significance level p = 0.01 which indicates that the regression equation can be used in the studied range of independent parameters. Independent parameters which are used in the regression equation are all statistically significant at the 99% confidence level since for all coefficients $|t| > t_{tab}$. Plot of the residuals versus row order (Fig.2, 3) do not indicate autocorrelation and heteroscedasticity problems of the residuals.

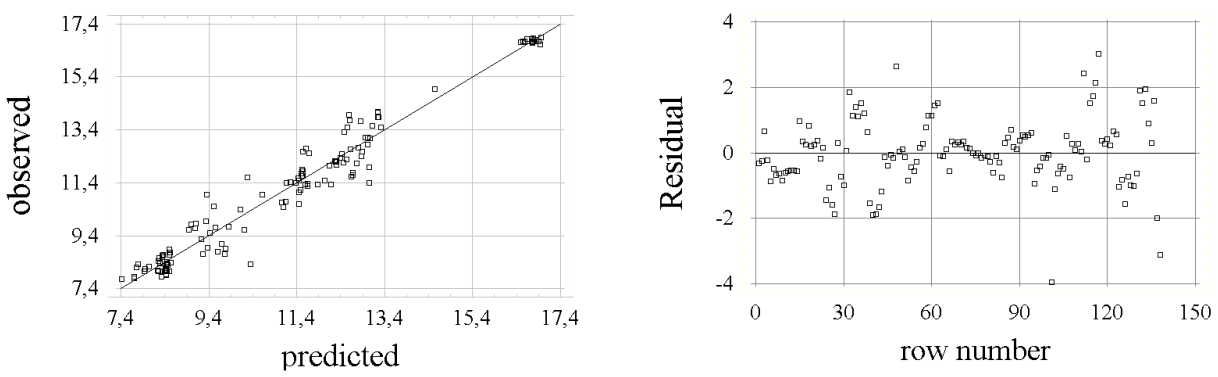

Figure 3. Visual representation of predicted versus observed values of hydrogen concentration and residuals versus row number

The regression equation for *CO* concentration (Eq. 2) does not contain *M*/*Vcat* factor since inclusion of it gave multicollinearity with *S/C*.
To check whether the obtained regression expressions give the same characteristics of change of the dependent variables as would be expected according to theoretical calculations, chemical equilibrium simulations with "ChemCAD" were done, where ATR reactor was chosen as adiabatic Gibbs reactor, which means that the enthalpy change is 0. In the first simulation, the λ value was changed from 0,24 to 0,34 corresponding to the range of experimental data used in the regression analysis (Fig. 4) and equilibrium concentrations of H_2 and *CO* were calculated at constant values of other independent variables, and the results were compared with the values given by the regression models.

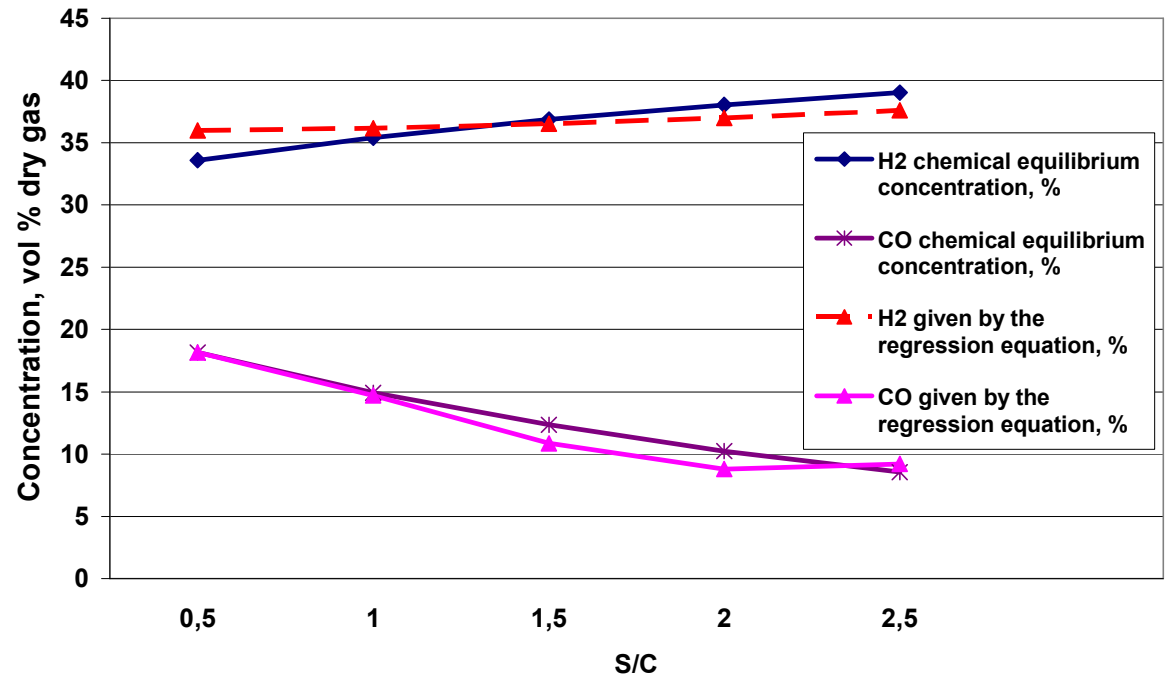

Figure 4. Comparison of dependence of H_2 and *CO* concentrations downstream of ATR reactor on λ value given by chemical equilibrium calculations and regression equations at *S/C*=1.5; *p*=0.26 bar; T_{in}=300^{0}C; M/V_{cat} = 43,83 l

In the second simulation, the *S/C* value was changed from 0,5 to 2.5 corresponding to the range of experimental data used in the regression analysis (Fig. 5) and equilibrium concentrations of H_2 and *CO* were calculated at constant values of other independent variables, and the results were compared with the values given by the regression models. As can be seen, the changes of response variables depending on explanatory variables given by regression equations and equilibrium calculations are in quite good agreement (Fig. 4, 5).

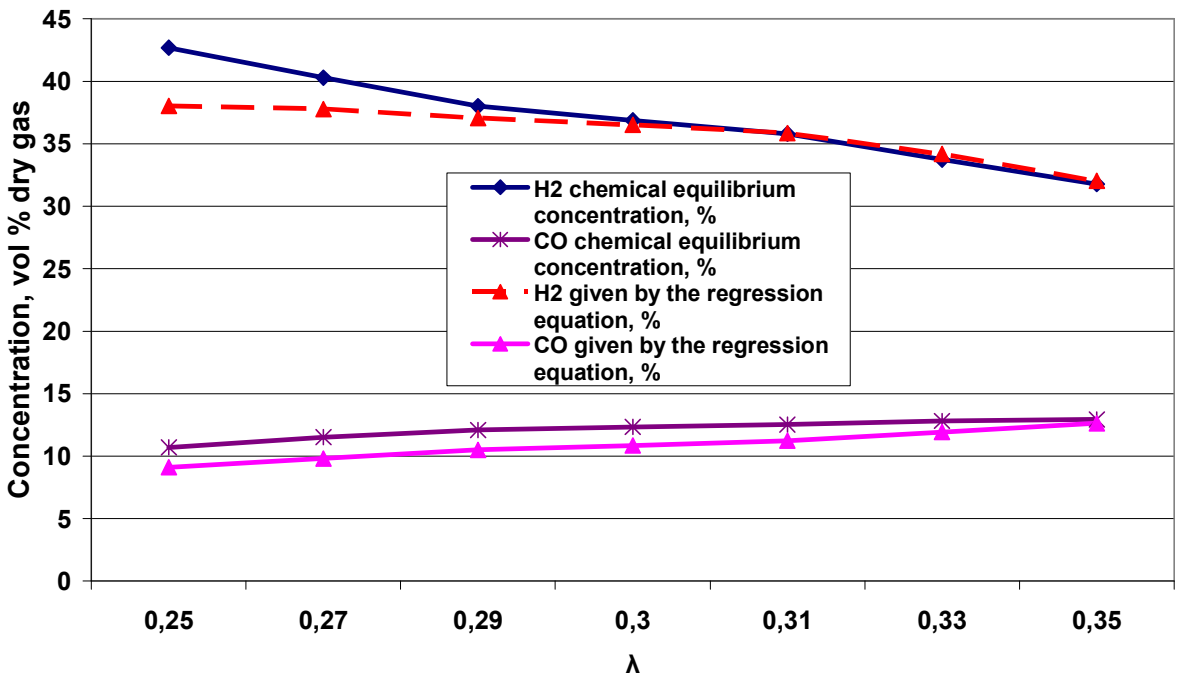

Figure 5. Comparison of dependence of H_2 and CO concentrations downstream of ATR reactor on S/C value given by chemical equilibrium calculations and regression equations at λ=0.3; p= 0,26 bar; T_{in}=300^{0}C; M/V_{cat} = 43,83 l

Conclusions

Multiple regression analysis of the data obtained by measurements of the reformate gas composition downstream of ATR reactor shows that the equations which can be used to evaluate H_2 and CO concentrations in the reformate gas depending on S/C, λ, p, T_{in} and mass flow of reactants can be obtained. Statistical analysis of the obtained regression models showed that the models can be used for calculation of the considered dependent variables. Comparison of the results obtained from the regression equations and chemical equilibrium calculations show that the regression model correctly reflects also physical nature of relation between response and explanatory variables. The obtained regression equations can be used further for optimisation of the reforming process within the range of influential parameters measured in this work.

Markova D., Valters K., Bažbauers G. Bioetanola pārveidošana ūdeņradī izmantošanai kurināmā elementa koģenerācijas iekārtās
Darbā ir veikta bioetanola autotermiskās pārveidošanas procesa eksperimentālā izpēte un iegūto mērījumu datu regresijas analīze. Darba galvenais mērķis bija, izmantojot eksperimentālos datus, iegūt regresijas sakarības starp būtiskākajiem atkarīgajiem mainīgajiem, tādiem kā ūdeņraža un oglekļa oksīda koncentrācija iegūtajā gāzē, un neatkarīgajiem mainīgajiem, tādiem kā gaisa patēriņa koeficients, ūdens-oglekļa molārā attiecība, reaģentu temperatūra pārveidošanas reaktora ieejā un spiediens reaktorā. Eksperimentālā autotermiskā pārveidotāja sistēma sastāv no iztvaicētāja, reaktora un vienpakāpes ūdens-gāzes apmaiņas reakciju reaktora. Darbā attēlotas empīriski iegūtas sakarības starp ūdeņraža un oglekļa oksīda koncentrācijām un tās ietekmējošiem faktoriem izejā no autotermiskās pārveidošanas reaktora. Ūdeņraža un oglekļa oksīdu koncentrāciju vērtības, kas aprēķinātas ar regresijas vienādojumiem, tiek salīdzinātas ar vērtībām, kuras tiek iegūtas no ķīmiskā līdzsvara aprēķiniem, kas veikti ar imitācijas datorprogrammu „ChemCAD". Iegūtos regresijas vienādojumus var lietot pārveidošanas procesu optimizēšanai, lai iegūtu maksimālas ūdeņraža un minimālas oglekļa oksīda koncentrācijas pārveidotajā gāzē.

Markova D., Valters K., Bazbauers G. Reforming of bioethanol to hydrogen for use in fuel cell cogeneration plants
Experimental investigation of the autothermal reforming (ATR) process of bioethanol and regression analysis of the data is performed in the work. The main goal of the work was to obtain regression relations between the most critical dependent variables such as hydrogen and carbon monoxide content of reformate gas and independent factors such as equivalent air-to-fuel ratio, steam-to-carbon ratio, inlet temperature of reactants into reforming process and pressure in the reforming reactor by using the data from experimental investigations of the bioethanol reforming process. The experimental ATR system consists of an evaporator, a ATR reactor and a one-stage water-gas shift reactor. The results of the work show the empirical relations between hydrogen and carbon monoxide content and the controlling parameters downstream from the ATR reactor. The values of hydrogen and carbon monoxide concentrations calculated from the regression models are compared with the results of the equilibrium calculations made with the simulation program of chemical processes „ChemCAD". The obtained regression equations permit to optimise the reforming process for obtaining the highest yield of hydrogen and minimising carbon monoxide concentration in the reformate gas.

Маркова Д., Валтерс К., Бажбауэрс Г. Реформинг биоэтанола для получения водорода для использования в когенерационных установках топливных элементов
В работе произведены экспериментальные исследования процесса автотермического реформинга этанола и регрессионный анализ полученных данных. Главная цель работы, используя экспериментальные данные, получить регрессионные уравнения, используя существенные зависимые переменные, такие как коэффициент потребляемого воздуха, молярное отношение воды и углерода, температура реагентов на входе в реактор и давление в реакторе. экспериментальная схема автотермического реактора состоит из испарителя, реактора и одноступенчатого реактора, на основе реакции замещения. В работе представлены эмпирические зависимости между концентрациями водорода и окиси углерода и влияющими факторами на выходе из автотермического реактора. Значения концентраций водорода и окиси углерода, которые рассчитаны используя регрессионные уравнение, сравнены со значениями, полученными из расчётов химического равновесия, используя имитационную программу „ChemCAD". Полученные регрессионные уравнения могут быть использованы, чтобы оптимизировать процесс реформинга с целью получения максимальной концентрации водорода и минимальной концентрации окиси углерода в полученном газе.