

Modeling Methanol Steam Reforming for Internal Combustion Engine

Leonid Tartakovsky*, Vladimir Baibikov, Mark Veinblat

Faculty of Mechanical Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

Abstract Methanol steam reforming is studied using the thermodynamic equilibrium assumption and the Gibbs free energy minimization method. Different reaction paths of methanol steam reforming are simulated and analysed. An empiric correlation derived on the base of previous experimental studies is suggested to bring the simulation results closer to the actual findings. Composition of the methanol steam reforming products is analysed for different temperatures and water to methanol ratios. Energy analysis is carried out to determine the optimal conditions of the methanol steam reforming for powering an internal combustion engine.

Keywords Thermo-chemical recuperation, Methanol, Steam reforming, Energy analysis, Hybrid propulsion system

1. Introduction

Energy efficiency improvement is one of society's most important instruments for mitigating climate change. Transportation is responsible for a large part of the energy consumption worldwide. According to International Energy Agency (IEA) data, about 26% of all energy-related CO₂ emissions were caused by transportation[1]. It is likely to account for a higher share in the future, unless special measures are taken. To limit the long-term global heating down to acceptable levels, United Nations Intergovernmental Panel on Climate Change (IPCC) recommended that annual global greenhouse gas (GHG) emissions must be reduced by 50 - 85% by year 2050 in comparison with the emissions level in 2000[2]. According to the IEA's BLUE map scenario[1], above 80% of the projected GHG emission mitigation may be achieved by improvement of vehicle efficiency, introduction of alternative fuels and electricity decarbonization.

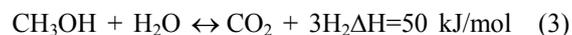
Results of recent studies suggest that there is a big potential for improvement of internal combustion engine (ICE) technologies[3-6]. It is well known that about 30% of fuel energy introduced to ICE is wasted with engine exhaust gases[3]. Even its partial utilization could lead to a significant improvement of ICE energy efficiency.

One of the ways to recover an engine's waste heat is by using the energy of the exhaust gases to promote endothermic reactions of alcohol steam reforming – ASR[7, 8]. In principle, any renewable fuel may be used, not only

alcohol. ICE is fed by the gaseous products of ASR, mainly mixture of hydrogen and carbon monoxide, frequently called syngas. The latter has, as a rule, greater heating value than the primary liquid fuel and may be more efficiently burned in the engine compared with the original fuel. This approach, called thermo-chemical recuperation (TCR), is considered nowadays as one of the possible methods of powertrain efficiency improvement and emissions reduction[7].

Many studies published on TCR are focused on gas turbine applications[9-11]. Ivanic et al.[12] studied a partial fuel reforming for ICE. Computational analysis of a spark ignition (SI) engine performance was carried out by Galloni and Minutillo[13] for partial gasoline replacement by a reformat gas. In their work the reformat gas was produced by exothermic partial oxidation of gasoline rather than bio-fuel.

Alcohol reforming to a syngas is widely investigated today as a promising hydrogen source for propulsion systems based on fuel cells[14-16]. The thermodynamics of methanol reforming has been extensively discussed in the literature[17-19]. The methanol steam reforming process may be described by three main reactions, namely, methanol decomposition (1), water gas shift -WGS (2) and direct methanol steam reforming (3):



Reactions (1) and (3) are endothermic, whereas WGS is exothermic. In overall, the process is endothermic; therefore, heat has to be supplied from an external source. Methanol steam reforming may be effectively performed over the commercially available methanol synthesis catalyst, alumina-supported Cu/ZnO, the kinetics of which is already

* Corresponding author:

tartak@technion.ac.il (Leonid Tartakovsky)

Published online at <http://journal.sapub.org/ep>

Copyright © 2014 Scientific & Academic Publishing. All Rights Reserved

well-studied. The Cu/ZnO catalyst has a good activity at moderate temperatures of 250-300 °C. More important, the Cu catalyst is not active for the methanation reaction (reverse reforming reaction) and a methane-free gas can be produced at low temperatures and at high pressures to yield full conversion to CO₂, CO and hydrogen. The optimum choice of operating conditions of Cu/Zn/Al catalysts[20], mainly employed in small hydrogen plants, is close to water-to-methanol ratio of 1.5 and temperature range of the 250- 300°C. The equilibrium conversion is above 99%. Other catalysts may be also considered. As copper catalysts are sensitive to air exposure during start-up of on-board reformers, there had been an interest in noble metal catalysts for the methanol reforming process. Noble metal catalysts also show better thermal stability and lower deactivation rates[21]. Research & development of reformers for methanol steam reforming benefit from the interest in fuel cells for automotive applications[22, 23]. Ethanol steam reforming is not as simple as the conversion of methanol, because ethanol is easily dehydrates to ethylene, which is a coke precursor. In addition, optimal conditions for ethanol steam reforming appear at high temperatures – around 1000-1100K[24], thus making problematic utilization of the engine's exhaust gases heat. On the other hand, ethanol is much less toxic compared with methanol.

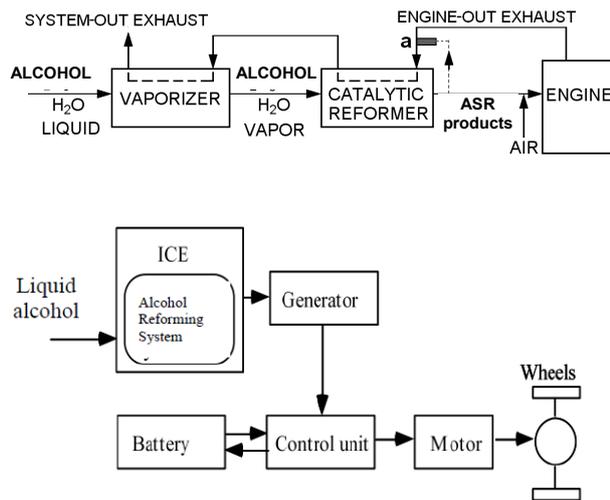


Figure 1. Hybrid propulsion system with a reformer-ICE

Some efforts have been made to feed ICE with methanol reforming products[25-26]. The obtained results exposed a number of serious problems, mainly caused by the multi-regime nature of the ICE operation in a motor vehicle (cold startability, need to address momentary change of load etc.). The catalytic reformer, if used in the motor vehicle, should operate efficiently in a wide range of fuel flow rates and exhaust gas temperatures because of engine load and speed changes. Low initial temperatures during the engine cold start and warm-up result in a non-efficient operation of the reformer. The requirement of addressing any momentary change in engine load leads to a serious complication of the

fuel supply and engine control systems. In order to enable satisfactory engine operation in the whole range of working regimes, different amounts of liquid methanol were added to the methanol reforming products in the work[25]. This brought up the problems typical for methanol fuel: higher aldehyde emissions, increased wear, poor cold startability etc. These problems remain unsolved, thus precluding further development of the reformer-ICE concept. We propose considering a hybrid propulsion system (Figure 1) that has an additional energy source and thus provides a basis for overcoming these drawbacks.

2. Methodology

In fuel cell applications dealing with alcohol steam reforming an effort is focused on achievement of maximal possible hydrogen outcome together with prevention of CO formation, which is a poison for the fuel cell catalyst. For these purposes, the overall reaction (3) is preferable, thus implying that the WGS reaction extent is very high. In contrast with the strict requirement of high-purity hydrogen typical for fuel cells application, ICE is much more flexible and can effectively burn different mixtures of hydrogen, carbon monoxide and other gases. This feature greatly reduces the cost of energy obtained from renewable fuels. In this case methanol reforming to CO₂ and H₂ is undesirable, because CO₂ is a diluent gas and does not carry energy. Therefore, for ICE fuelling, realization of the reaction (1) would be preferable with negligible WGS reaction extent. In ICE the exhaust heat is used to promote on-board reforming of methanol into a mixture of hydrogen and carbon monoxide with small amounts of diluents and contaminants (carbon dioxide, unreacted water, etc.). Because this gas has a greater heating value and may be more efficiently burned than the primary fuel, an improvement in engine fuel economy can be expected along with a sensible emissions reduction. CO formed in reaction (1) does not constitute an environmental hazard because it is further oxidized to CO₂ during the combustion in the engine. Therefore, for ICE application methanol reforming process has to be optimized for the maximal yield of hydrogen and CO together with prevention of contaminants formation.

One important parameter that should be used in reformer optimization is the energy efficiency of the reforming process[24] defined as a ratio of the added enthalpy of combustion ($H_{out} - H_{in}$) to the heat duty, H_d (the sum of the ASR reactions heat, latent heat of methanol vaporization and sensible heat):

$$\eta = (H_{out} - H_{in}) / H_d \quad (4)$$

where H_{out} and H_{in} are enthalpy of combustion of the reforming products and primary reactants, respectively. Calculations performed for the example of steam reforming of methanol (SRM) at H₂O/CH₃OH ratio = 1.3 and T=570K derives the following result: $H_{out} = 22.3$ MJ/kg, whereas $H_{in} = 19.9$ MJ/kg[34].

The lack of detailed kinetic data (reaction rates, residence time, known intermediate species, etc.) has determined a modelling of the steam reforming by using the equilibrium reactor and Gibbs reactor models of the CHEMCAD software package. We simulated a chemical reactor by solving the heat and mass balances and minimizing the free energy of the components that can be produced during a reforming process. The minimization of total Gibbs free energy is a suitable method to calculate the equilibrium compositions of any reacting system. The method of minimizing the Gibbs free energy is normally preferred in the fuel reforming analysis[27]. The total Gibbs free energy of a system is given by the sum of i species:

$$G_t = \sum_{i=1}^N n_i G_i^0 + RT \sum_{i=1}^N n_i \ln \frac{f_i}{f_i^0} \quad (5)$$

where: G_t is the total Gibbs free energy, the G_i^0 - standard

Gibbs free energy of species i , R - the molar gas constant, T - the temperature of the system, f_i - the fugacity in the system, f_i^0 - the standard-state fugacity, and n_i - the mole number of species i . For reaction equilibrium in gas phase $G_i^0 = \Delta G_{f_i}^0$ are assumed, where $\Delta G_{f_i}^0$ is the standard Gibbs free energy of formation of species i .

The reaction paths including reactions (1) – (3) as well as carbonation, dehydrogenation, olefine and formaldehyde synthesis, methanation and other reactions were considered. For the analysis simplification the following main assumptions have been made:

- Chemical equilibrium in the reactor;
- Ideal heat exchanger;
- All gases are ideal.

The products of the reforming were calculated for a reactor with minimum Gibbs free energy, when all the possible products were taken into account under the following working conditions of the reactor: atmospheric pressure, water-to-methanol molar ratio 0.6-3 and temperature range of 150-950°C.

3. Results and Discussion

3.1. Equilibrium Simulation Results

The examples of the calculation results obtained with the assumption of chemical equilibrium are shown in Figure 2.

The obtained results showed 100% methanol conversion efficiency at any reforming temperature and steam to methanol ratios. The reforming products obtained from the calculations in sensible yields are hydrogen, carbon monoxide, carbon dioxide, methane, carbon and unreacted water. The higher the reforming temperature – the less water is remained and more hydrogen is yielded. The carbon (coke) yield decreases with temperature rise or with increase of the water-to-methanol ratio.

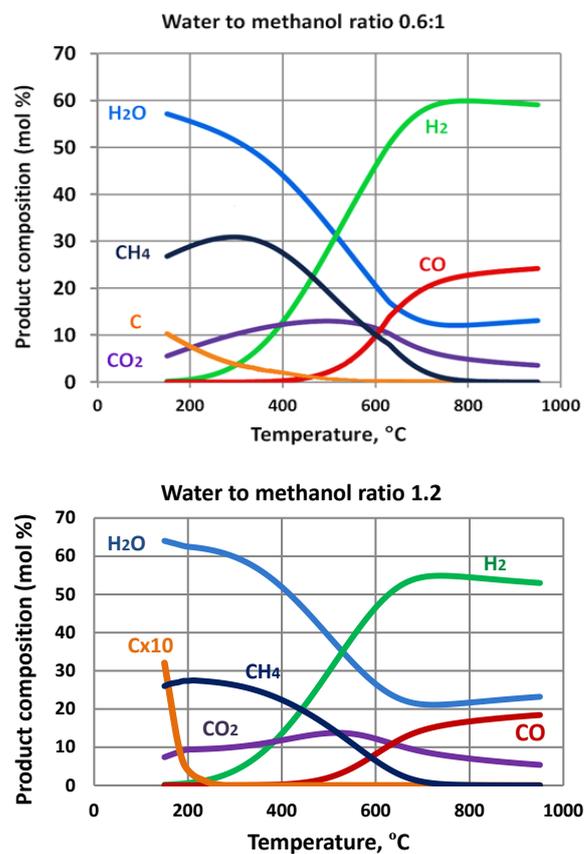


Figure 2. Methanol reforming products – equilibrium assumption

3.2. Comparison with Available Experimental Data

The available experimental results[28-31] show that the actually measured methanol reforming products are usually composed of: hydrogen, carbon monoxide, water and carbon dioxide (Figure 3). Methane normally does not present between the reforming products. The experimental results also show that the methanol conversion is less than 100% under the temperatures lower than 300 °C (Figure 3). The methanol conversion increases with the temperature rise until full conversion is reached. Full conversion of methanol is usually observed at temperatures of 300-320 °C.

The results obtained with the equilibrium model do not agree with the experimental data because this model considers an equilibrium state within an infinite reactor with full methanol conversion. The experimentally tested reformers are not infinite, and they usually do not reach equilibrium state. The measured data are normally obtained for catalytically supported reactions, whereas in the equilibrium theoretical calculations the presence of catalyst cannot be taken into account.

The theoretical analysis suggests that the methane appears in the reforming products at all steam-methanol ratios. Its yield decreases to zero with increasing the temperature. In the experiments, even at low temperatures,

the methane does not appear among the reforming products. One possible explanation of this phenomenon may be in the fact that the real reformer does not reach the steady state as assumed in the theoretical model. This hypothesis is supported by the results of Jones et al[32], who showed that in the methanol steam reforming the appearance of methane in the reforming products is a function of time. Its yield was found to be increasing with a time. The available experimental results show that there is an influence of the catalyst material on the appearance of methane in the final reforming products. With a catalyst based on Cu the formation of methane is normally suppressed, whereas with other catalytic materials, such as Pt, Rh, Ru and Pd, formation of methane is possible. It is important to note that also carbon was not found in the reforming products with most of the catalysts, which somewhat simplifies the methanol reforming analysis and reactors development.

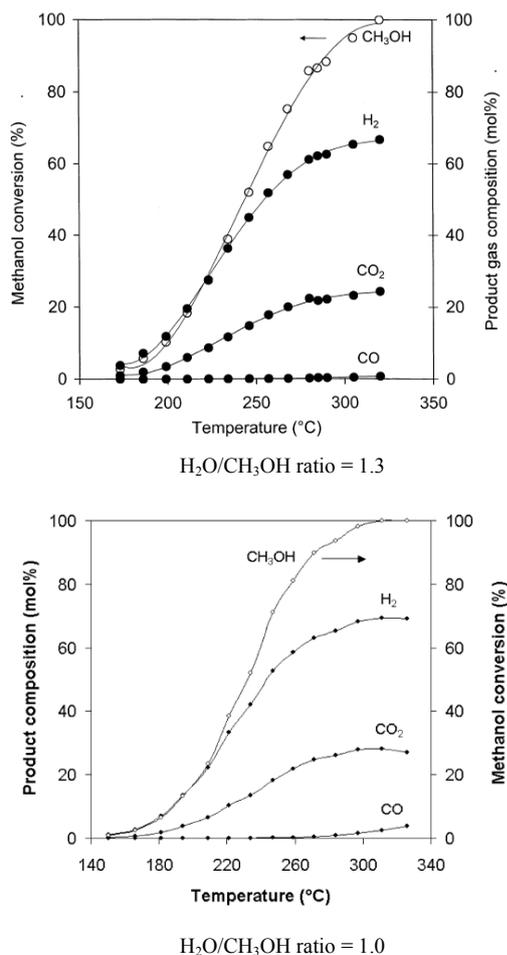


Figure 3. Methanol reforming products – experimental data. Reprinted from: Journal of Power Sources, Vol. 106, Agrell, J., Birgersson, H., Boutonnet, M., Steam reforming of methanol over a Cu/ZnO/Al₂O₃ catalyst: a kinetic analysis and strategies for suppression of CO formation, 249-257, Copyright (2002); Applied Catalysis A: General, Vol. 253, Agrell, J., Boutonnet, M., Fierro, J.L.G., Production of hydrogen from methanol over binary Cu/ZnO catalysts. Part II: catalytic activity and reaction pathways, 213–223, Copyright (2003) with permission from Elsevier

3.3. Empiric Correction of Equilibrium Predictions

To improve accuracy of the equilibrium predictions and account for the non-equilibrium reforming behaviour, empiric correction of the simulation results was applied. The empiric correction functions were developed using available experimental results for copper-based catalysts[28, 29]. These functions are suggested for the all products appearing in the experiments (CO, CO₂, H₂ and CH₃OH). Carbon and methane, which normally are not observed in the reforming products, were excluded from consideration. The proposed correction functions are shown in Table 1. Here indexes "cor" and "eq" relate to corrected and equilibrium molar fractions, respectively; CH₃OH^{conv} – methanol conversion ratio; T – reforming temperature, °C.

Table 1. Empiric Correction Functions

Species	Correction function
Carbon monoxide	$CO_{cor} = 1.4 \cdot 10^{-6} \cdot CO_{eq} \cdot T^{1.996}$
Carbon dioxide	$CO_{2cor} = 10^{-7} \cdot CO_{2eq} \cdot T^{2.827}$
Hydrogen	$H_{2cor} = 0.05 \cdot H_{2eq} \cdot e^{0.01T}$
Methanol conversion	$CH_3OH_{cor}^{conv} = 22.44 \cdot 10^{-3} \cdot CH_3OH_{eq}^{conv} \cdot e^{0.013T}$

The empiric correction should be applied, if methanol conversion is below 100%. When full methanol conversion is reached, the equilibrium model can be used without correction, because under these conditions it provides acceptable prediction accuracy.

To validate the suggested empiric correction functions, a comparison of the corrected simulation results with the experimental data[30, 33], which were not used in the correction functions development, was performed. An example of the comparison between the empirically corrected predictions and experimentally measured results is shown in Figure 4. As can be seen, reasonable agreement between the predictions and the experimental data was obtained. The developed correlations were not validated for catalyst types other than copper-based.

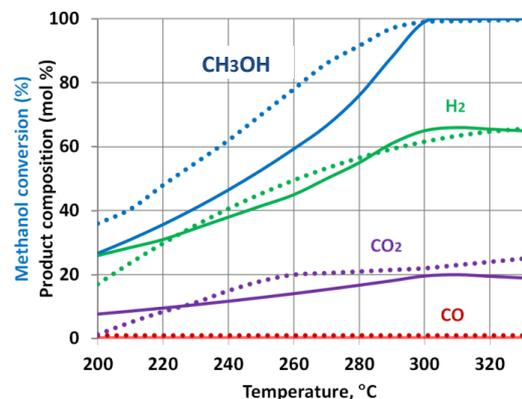


Figure 4. Comparison of the corrected prediction with experimental data from[30]. - theoretical prediction; experimental data H₂O/CH₃OH ratio = 1.3

Figures 5-8 show the prediction results after applying the empiric correction to the equilibrium simulation data. As can be seen, the predicted dependence of the methanol steam reforming products on steam-to-methanol ratio and reforming temperature is qualitatively similar to the available experimental data[30].

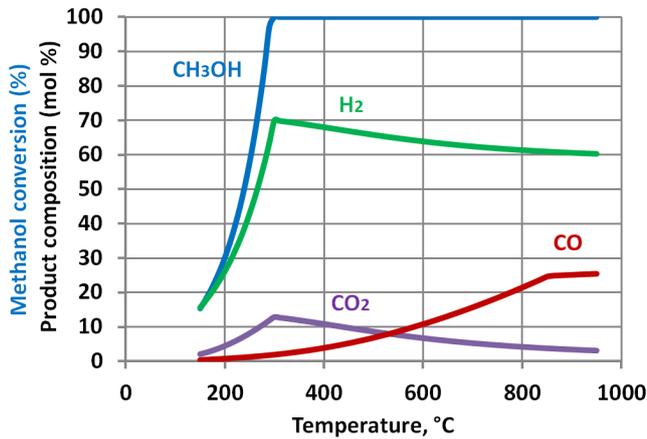


Figure 5. Methanol reforming products - corrected prediction. Water to methanol ratio – 0.5:1

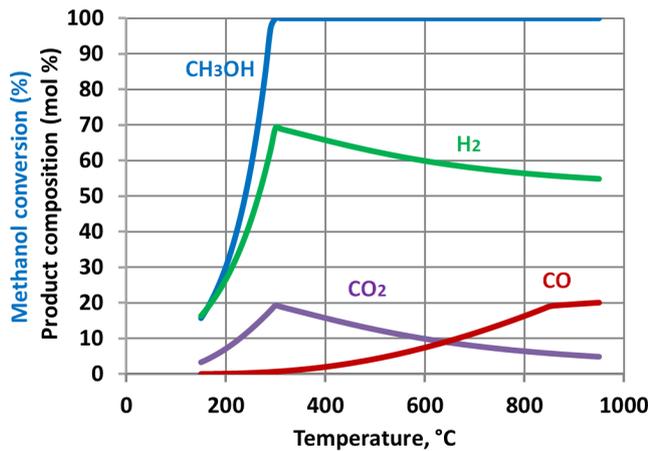


Figure 6. Methanol reforming products - corrected prediction. Water to methanol ratio – 1:1

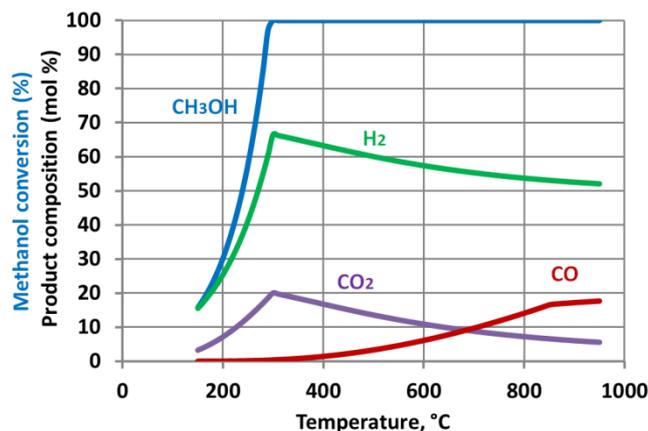


Figure 7. Methanol reforming products - corrected prediction. Water to methanol ratio – 1.3:1

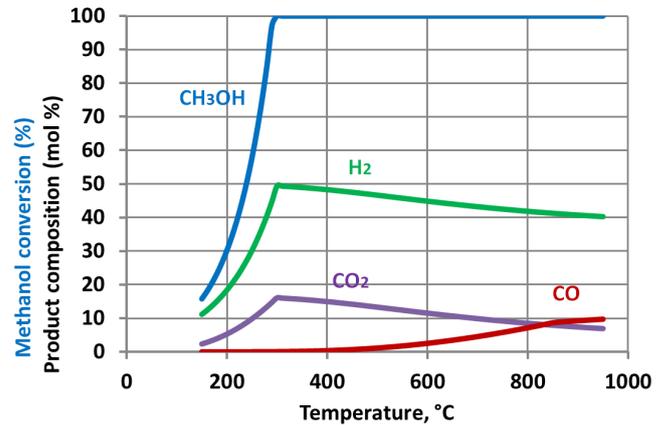


Figure 8. Methanol reforming products - corrected prediction. Water to methanol ratio – 3:1

3.4. Analysis of Simulation Results

Simulation results show that increase of the steam to methanol ratio leads to reduction of the H₂ and CO yields with an appropriate increase of CO₂ formation. Starting from a temperature of circa 300-350°C the methanol is totally converted. As the temperature further increases, the yields of H₂ and CO₂ reduced. This phenomenon is linked to the reverse water gas shift reaction. The reaction uses hydrogen to produce H₂O, and is thermodynamically dominant above 300-350 °C.

The prediction results show that maximum hydrogen production can be achieved at a relatively low temperature of approximately 300°C. At the same temperatures full methanol conversion is taking place, as well. The moderate temperature of methanol reforming makes possible utilization of the ICE exhaust gases heat to sustain the endothermic reactions in the reformer.

Figure 9 shows the maximal energy efficiency values of methanol steam reforming as a function of the water/alcohol ratio. The required values of the reforming process temperature are shown near corresponding points of the plot. Simulation results showed that the energy efficiency of methanol steam reforming approached maximal value of 0.66 at water to methanol ratio of 1.3 and the reaction temperature of approximately 300°C. For the all considered water to methanol ratios (0.5 – 3.0) maximal energy efficiency of the reforming process was observed in the narrow range of temperatures 297-307°C.

Comparison of energy efficiency values achievable for methanol steam reforming with those of ethanol[34] show that the difference between the maximal values of energy efficiency for these two fuels is not significant. However, for methanol it can be achieved under much lower temperature: 570K compared with 1100K for ethanol. This is a significant benefit of methanol over ethanol in the view of the TCR concept realization. A potential of ICE efficiency improvement and emissions reduction by application of the TCR concept is analysed in[34].

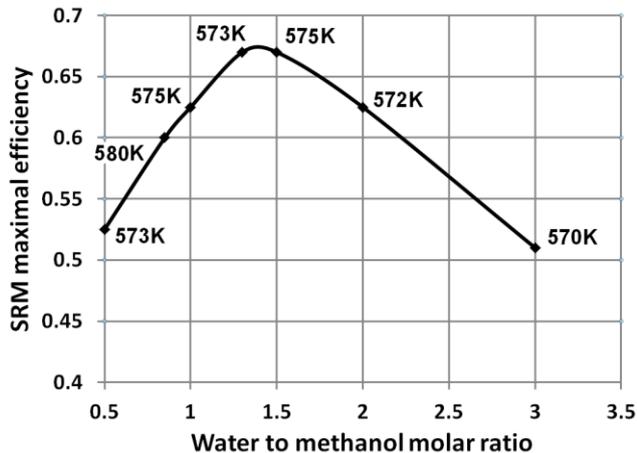


Figure 9. Energy efficiency of methanol reforming calculated by eq.(4)

4. Conclusions

Modelling and analysis of the methanol steam reforming for the purpose of ICE feeding was performed. The results obtained with the equilibrium simulation model do not agree with the experimental data because this model considers an equilibrium state within an infinite reactor with full methanol conversion. An empiric correlation derived on the base of available experimental data suggested to bring the simulation results closer to the actual findings. This approach can be useful for analysis of methanol steam reforming when detailed kinetic data are unavailable.

The simulation results show that the maximum hydrogen production can be achieved under the reforming temperature of approximately 300°C, when full methanol conversion takes place. The moderate temperature of methanol reforming makes it possible to utilize the ICE exhaust gases heat for sustaining the endothermic reactions in the reformer.

The difference between the maximal achievable values of energy efficiency for methanol and ethanol steam reforming is not significant (0.66 for methanol compared with 0.59 for ethanol). However, for methanol it can be achieved under much lower temperature. This is a significant benefit of methanol over ethanol in the view of the TCR concept realization. This concept can be realized most efficiently in a hybrid propulsion system, where cold start and transient operation problems can be successfully overcome due to availability of additional energy source.

ACKNOWLEDGEMENTS

Financial support of the Israel Science Foundation, Ministries of Energy & Water Resources and Environmental Protection is highly appreciated. Authors are grateful to Ms. Ron Karasenti and Mr. Tamir Bengio for their valuable help in calculations carrying out.

REFERENCES

- [1] International Energy Agency, Energy technology perspectives 2010: scenarios & strategies to 2050, OECD/IEA, Paris, France, 2010.
- [2] IPCC - Intergovernmental Panel on Climate Change, IPCC Fourth Assessment Report, UN IPCC, Geneva, 2007.
- [3] Berggren, C. and Magnusson, T., 2012, Reducing automotive emissions - The potentials of combustion engine technologies and the power of policy, *Energy Policy*, 41, 636–643.
- [4] Tartakovsky, L., Gutman, M. and Mosyak, A., Energy efficiency of road vehicles – trends and challenges. In *Energy Efficiency: Methods, Limitations and Challenges* edited by Santos Cavalcanti, E. F. and Barbosa, M. R., Nova Science Publishers, New-York, 63-90, 2012.
- [5] Kobayashi, S., Plotkin, S., Kahn Ribeiro, S., 2009, Energy efficiency technologies for road vehicles, *Energy Efficiency*, 2, 125-137.
- [6] Taylor, A.M.K.P., 2008, Science review of internal combustion engines, *Energy Policy*, 36, 4657–4667.
- [7] Chakravarthy, V.K., Daw, C.S., Pihl, J.A., Conklin, J.C., 2010, Study of the theoretical potential of thermochemical exhaust heat recuperation for internal combustion engines, *Energy Fuels*, 24, 1529–1537.
- [8] Tartakovsky, L., Baibikov, V., Gutman, M., Mosyak, A., Veinblat, M., 2011, Performance analysis of SI engine fuelled by ethanol steam reforming products, SAE Technical Paper 2011-01-1992.
- [9] Carapellucci, R., 2009, A unified approach to assess performance of different techniques for recovering exhaust heat from gas turbines, *Energy Convers. Management*, 50, 1218–1226.
- [10] Cocco, D., Tola, V., Cau, G., 2006, Performance evaluation of chemically recuperated gas turbine (CRGT) power plants fuelled by di-methyl-ether (DME), *Energy*, 31, 1446–1458.
- [11] Verkhivker, G., Kravchenko, V., 2004, The use of chemical recuperation of heat in a power plant, *Energy*, 29, 379–388.
- [12] Ivanic, Z., Ayala, F., Goldwitz, J.A., Heywood, J.B., 2005, Effects of hydrogen enhancement on efficiency and NO_x emissions of lean and EGR-diluted mixtures in a SI engine, SAE Technical Paper 2005-01-0253.
- [13] Galloni, E., Minutillo, M., 2007, Performance of a spark ignition engine fuelled with reformat gas produced on-board vehicle, *Int. J. Hydrogen Energy*, 32, 2532-2538.
- [14] Joensen, F., Rostrup-Nielsen, J.R., 2002, Conversion of hydrocarbons and alcohols for fuel cells, *J. Power Sources*, 105, 195-201.
- [15] Choi, K.S., Choi, I.J., Hwang, S.J., Kim, H.M., Dorr, J. L., Erickson, P.A., 2010, An experimental study of methanol autothermal reformation as a method of producing hydrogen for transportation applications, *Int. J. Hydrogen Energy*, 35, 6210-6217.
- [16] Zhou, W., Tang, Y., Pan, M., Wei, X., Chen, H., Xiang, J., 2009, A performance study of methanol steam reforming microreactor with porous copper sintered felt as catalyst support for fuel cell, *Int. J. Hydrogen Energy*, 34, 9745–9753.

- [17] Chang-Wei, J.I., Deng, F.S., Korte, S., Fang, Z.J., Wang, S.F., He, H., 2009, Apparatus design and experimental study of methanol steam catalytic reforming for H₂ production using engine exhaust heat, *J. of Beijing University of Technology*, 35.
- [18] Choi, K.S., Kim, H.M., Dorr, J. L., Yoon, H.C., Erickson, P.A., 2008, Equilibrium model validation through the experiments of methanol autothermal reformation, *Int. J. Hydrogen Energy*, 33, 7039-7047.
- [19] Cui, W., Li, L., Jen, T.C., 2005, Numerical simulation of steam reforming of methanol in micro-channel reactor. Paper IMECE2005-82467, Proc. ASME Conference, 19365-19369.
- [20] Purnama, H., Ressler, T., Jentoft, R.E., Soerijanto, H., Schlögl, R., Schomäcker, R., 2004, CO formation/selectivity for steam reforming of methanol with a commercial CuO/ZnO/Al₂O₃ catalyst, *Applied Catalysis A: General*, 259, 83-94.
- [21] Sá, S., Silva, H., Brandão, L., Sousa, J. M., Mendes, A., 2010, Catalysts for methanol steam reforming—a review, *Applied Catalysis B: Environmental*, 43-57.
- [22] Sá, S., Sousa, J. M., Mendes, A., 2011, Steam reforming of methanol over a CuO/ZnO/Al₂O₃ catalyst part II: A carbon membrane reactor, *Chemical Engineering Science*, 66(22), 5523-5530.
- [23] Mingheng, L., Duraiswamy, K., Knobbe, M., 2012, Adsorption enhanced steam reforming of methanol for hydrogen generation in conjunction with fuel cell: Process design and reactor dynamics, *Chemical Engineering Science*, 67(1), 26-33.
- [24] Tartakovsky, L., Mosyak, A., Zvirin, Y., 2013, Energy analysis of ethanol steam reforming for internal combustion engine. *International Journal of Energy Research*, 37, 259-267.
- [25] Brinkman, N.D., Stebar, R.F., 1985, Comparison of methanol and dissociated methanol illustrating effects of fuel properties on engine efficiency- experiments and thermodynamic analyses, SAE Technical Paper 850217.
- [26] Sato, T., Tanaka, M., Agawa, K., 1986, A Study on the reformed-methanol engine, SAE Technical Paper 861237.
- [27] Wang, W., Wang, Y.Q., 2008, Thermodynamic analysis of steam reforming of ethanol for hydrogen generation, *International Journal of Energy Research*, 32(15):1432–1443.
- [28] Agrell, J., Birgersson, H., Boutonnet, M., 2002, Steam reforming of methanol over a Cu/ZnO/Al₂O₃ catalyst: a kinetic analysis and strategies for suppression of CO formation, *Journal of Power Sources*, 106, 249–257.
- [29] Agrell, J., Boutonnet, M., Fierro, J.L.G., 2003, Production of hydrogen from methanol over binary Cu/ZnO catalysts. Part II: catalytic activity and reaction pathways, *Applied Catalysis A: General*, 253, 213–223.
- [30] Wang, L.C., Liu, Y.M., Chen, M., Cao, Y., He, H.Y., Wu, G.S., Dai, W.L., Fan, K.N., 2007, Production of hydrogen by steam reforming of methanol over Cu/ZnO catalysts prepared via a practical soft reactive grinding route based on dry oxalate-precursor synthesis, *Journal of Catalysis*, 246, 193–204.
- [31] Jones, S.D., Neal, L.M., Everett, M.L., Hoflund, G.B., Hagelin-Weaver, H.E., 2010, Characterization of ZrO₂-promoted Cu/ZnO/nano-Al₂O₃ methanol steam reforming catalysts. *Applied Surface Science*, 256, 7345–7353.
- [32] Jones, S.D., Neal, L.M., Hagelin-Weaver, H.E., 2008, Steam reforming of methanol using Cu-ZnO catalysts supported on nanoparticle alumina. *Applied Catalysis B: Environmental*, 84, 631–642.
- [33] Bree, J.P., Ross, J.R.H., 1999, Methanol reforming for fuel-cell applications: development of zirconia containing Cu-Zn-Al catalysts, *Catalysis Today*, 51, 521-533.
- [34] Tartakovsky, L., Baibikov, V., Veinblat, M., 2013, Comparative performance analysis of SI engine fueled by ethanol and methanol reforming products, SAE Technical Paper 2013-01-2617.