



## TECHNICAL NOTE

# Energy analysis of ethanol steam reforming for hybrid electric vehicle

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## SUMMARY

Thermodynamic equilibrium of ethanol steam reforming is studied using the Gibbs free energy minimization method. The reaction paths of ethanol steam reforming are simulated using Chem-CAD software. Appropriate optimization of reactants ratio and reaction conditions is performed, to achieve the composition of ethanol steam reforming products, which will be favorable as an internal combustion engine (ICE) fuel. The effects of process variables, such as temperature and water:ethanol molar ratio are discussed. Numerical investigations are conducted to analyze energy performance of steam reforming of ethanol for ICE. Realization of ethanol steam reforming at high temperature leads to an increase in efficiency of the process. The optimal conditions are obtained as follows: 1100K, water:ethanol molar ratio of 1.2. Copyright © 2011 John Wiley & Sons, Ltd.

## KEY WORDS

ethanol steam reforming; thermodynamic analysis; Gibbs free energy minimization; hybrid propulsion system; energy efficiency

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## 1. INTRODUCTION

The internal combustion engine (ICE) is the main power plant in most modern transportation systems. As such, it is responsible for a substantial part of petroleum fuel consumption as well as environmental pollution. This fact provides a powerful incentive to design more fuel-efficient engines, to economize on depleting petroleum. The risk of economic dependence on expensive oil has strengthened the support for the development of renewable fuel technologies. Biofuels, for example, represented 49% of the growth in non-OPEC oil supply in 2007 and are expected to rise at a later time [1].

It is well known that one of the best ways to improve fuel efficiency of ICE is to increase its compression ratio. This parameter is, nevertheless, bounded from above by the so-called knock limit. Until recently, this drawback in the way of increasing compression ratio was solved by the use of a fuel additive called tetraethyl lead (TEL), which is supposed to act as a self-ignition inhibitor by adsorbing at the surface of its molecules the active radicals in front of the flame front, thus effectively preventing knock. Unfortunately, because of its high molecular stability, TEL exhausted into the atmosphere turned out to be a dangerous pollutant. In the last decades, because of increased public awareness to air pollution problems, TEL was practically banned from use in most of the industrialized nations. An alternative way to prevent

knock without using TEL is to add a modest amount of methanol to gasoline [2], but it is not yet an economically viable alternative to gasoline [3]. One of the main drawbacks of methanol is relatively high toxicity and corrosivity. Its production is essentially based on reforming of non-renewable fossil fuels, mostly natural gas. Therefore, its use will realize fossil carbon into the atmosphere.

Ethanol appears as an attractive alternative to methanol because it is much less toxic and corrosive [4] and is already used as versatile fuel that offers a high octane number and low photochemical reactivity. Moreover, bioethanol can be produced in large quantities from biomass fermentation and, therefore, can be considered as a renewable energy source [5,6].

A significant advantage of this alcohol over fossil fuel-based systems is that it is CO<sub>2</sub> neutral. Carbon dioxide released into the atmosphere during ethanol combustion is absorbed during the growth of the biomass. Thus, ethanol appears as one of the best candidates that can be used for hydrogen generation. However, previous studies have focused on hydrogen generation for fuel cells [7,8]. Compared with the strict requirement for high-purity hydrogen for fuel cells, ICE is much more flexible and can effectively burn different mixtures of hydrogen, carbon monoxide, and other gases. This characteristic greatly reduces the cost of energy obtained from renewable fuels.

The main goal of this study is to optimize reaction conditions of steam reforming of ethanol (SRE) to achieve the composition of SRE products, which will be favorable as an ICE fuel.

## 2. SYSTEM DESCRIPTION

The schematic layout of a typical onboard alcohol steam reforming system is known and based on the previous studies [9] that considered the concept of ICE fueled by methanol decomposition products (MDPs). The typical scheme is shown in Figure 1. According to this scheme, the exhaust heat that would have been wasted is used for heating and decomposition of liquid methanol. It was shown that the MDP fuel has about 20 and 14% higher heating value than liquid methanol and methanol vapor, respectively [9]. Unfortunately, an onboard reformer cannot work efficiently in a wide range of engine operation regimes typical for a conventional road vehicle, especially at transient modes and cold-start conditions. In case of a hybrid propulsion system, which always has an additional energy source, these shortcomings can be easily overcome.

Tartakovsky and Zvirin [10] presented a hybrid propulsion system based on an ICE fueled by ethanol decomposition products. The hybrid concept is a known series scheme: a vehicle is driven by an electric motor(s) powered by a storage system of energy, supplied by charging from an electricity network or/and by an ICE through a generator. The ICE runs in an on-off mode, at optimal operation point, and is fed by products of ethanol decomposition, SRE, (mainly hydrogen and carbon monoxide) emerging from the onboard catalytic reformer. Using the SRE products as a fuel for ICE makes possible to eliminate the known problems of onboard hydrogen storage and to reduce expenses substantially compared with the use of fuel cells. Using the scheme of series hybrid (Figure 2) allows the engine to be operated in an on-off mode at constant, optimal regime. Excess energy produced by the engine at lower load driving conditions is accumulated by the energy storage system of the hybrid. The engine is automatically switched off, and only electric propulsion is used in the case of a full-charge state of the energy storage system. Engine operation at the constant optimal regime contributes to an additional significant rise in efficiency and reduction in pollutants emission.

Table I includes the results of a qualitative comparison of the proposed hybrid concept and some other fuel-vehicle propulsion systems. Performance parameters of a hybrid vehicle with a gasoline engine are taken as base values for this comparison. Some options have multiples of '+' or '-', to distinguish between various levels of change in parameter value for more than three considered cases. The applied signs mean the following: '+ + +'—the best, '+ +'—significantly better, '+'—better, '0 +'—close or slightly better, '0'—taken as a base value or close to it, '-'—worse, '- -'—significantly worse, and '- - -'—the worst.

For example, energy consumption (EC) of ethanol ICE is better than gasoline counterpart—one '+' designated; EC of hydrogen ICE is better than ethanol counterpart (and significantly better than gasoline ICE)—two '+' designated; for SRE ICE for motor vehicle, the similar level of EC is estimated because a significant improvement because of SRE is partially diminished by the need of addition of liquid ethanol to make possible engine's operation at cold starts and transient regimes; SRE ICE for hybrid vehicle allows the best EC between the considered cases—three '+' designated.

Simultaneous use of '+' and '-' is used for 'tailpipe emissions' parameter, to mention reduction in emission of some pollutants together with increase in emission of others. For example, using the liquid ethanol as a fuel enables the reduction of benzene, 1,3 butadiene, and organic matter hydrocarbon equivalent emissions together with a lower photochemical reactivity of emitted pollutants [11]. However, it leads to increase in non-methane organic gases and aldehyde emissions. Therefore, '+ -' was designated to the ethanol ICE case.

As can be seen from Table I, the main advantages of using liquid ethanol as an alternative fuel are the possibilities to improve engine efficiency, to reduce emissions of some pollutants and, of course, to contribute to the solution of the problem of energy supply security. Improvement in engine performance can be achieved with ethanol because of its excellent antiknock performance (allowing an increase of the engine's thermal efficiency), lower flame temperature and luminosity (leading to lower heat losses), and high latent heat of vaporization, which makes the achievement of higher volumetric efficiency possible. If hydrogen is considered as a fuel for ICE, its storage onboard a vehicle and cost of its production, as well as absence of fueling infrastructure, remain major technological challenges.

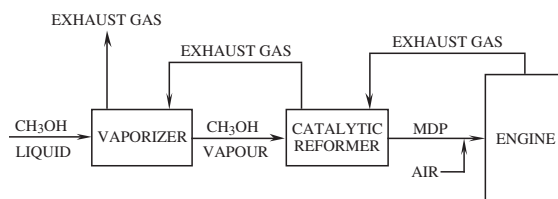


Figure 1. Scheme of onboard methanol decomposition system.

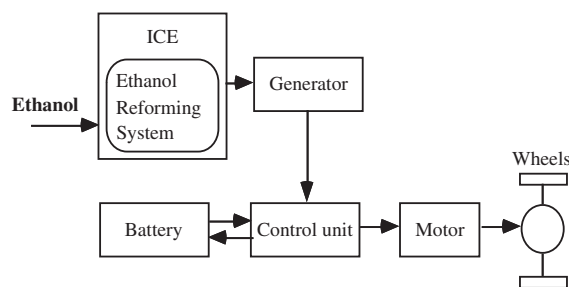


Figure 2. Scheme of the series hybrid propulsion system with onboard ethanol decomposition.

Using the SRE as an automotive fuel allows, as mentioned above, consolidation of the benefits of liquid ethanol cost and onboard storage with engine feeding by a gaseous non-corrosive hydrogen-enriched fuel. A comparison about engine durability in Table I relates to the issue of the engine durability worsening in case of using alcohol fuels because of their high corrosivity and washing away of lubricant film during cold start, [11]. SRE application makes possible use of renewable and easy-to-store onboard liquid alcohol together with engine feeding by gaseous mixture and therefore preventing durability worsening. However, implementation of SRE in a conventional motor vehicle with multi-regime engine places the appropriate requirements on fuel and control systems. A catalytic reformer is needed to operate efficiently in a wide range of ethanol flow rates and exhaust gases temperatures (as a result of engine load and speed changes). There is a requirement and a serious problem to ensure engine cold start and warm-up because, at low temperatures, the catalytic reformer will not operate efficiently. The requirement to address any momentary change in engine load leads to a serious complication of the fuel and control systems. To enable satisfactory engine operation in the whole range of working regimes, different amounts of ethanol should be added to the SRE fuel, thus reintroducing the drawbacks of liquid ethanol fuel.

The proposed system opens new possibilities to achieve great advantages of the known idea of onboard ethanol decomposition, by combining it with the hybrid vehicle concept. The benefits follow from the availability of an energy storage device and the operation of the ICE at optimal

steady-state regime and may lead to the elimination of current shortcomings of multi-regime fuel systems with ethanol decomposition. Among the problems that may be eliminated, or at least minimized, are the following: undesirable chemical reactions in the catalytic reformer, which usually lead to the reduction of hydrogen yield and rise of soot formation with subsequent increase of radiation heat losses; cold start and warm-up problems (the reformer may be electrically preheated from an energy storage device); and problems that follow from the requirement to address any momentary change of needed fuel amount, taking into account the residence time of the fuel in the catalytic reactor. As a result of these advantages, the fuel and control systems can be made much simpler, effective, and less expensive, and of course, better fuel economy may be achieved.

### 3. THERMODYNAMIC CONSIDERATIONS

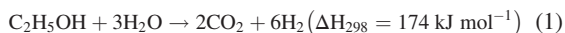
#### 3.1. Modeling and simulation methodology

Ethanol can be converted into gas containing hydrogen through steam reforming (SRE). The thermodynamics of ethanol SRE has been widely discussed in the literature [12–15]. The possible reaction pathways of SRE can be described by 20 equations [15]. The most important of them are presented below. The equilibrium calculations employing the minimization of total Gibbs free energy were carried out using the Chem-CAD software package.

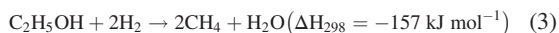
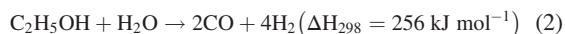
Table I. Qualitative assessment of various fuel vehicle systems.

Parameter	Gasoline ICE for hybrid vehicle	Ethanol ICE for hybrid vehicle	Hydrogen ICE for hybrid vehicle	SRE ICE for motor vehicle	SRE ICE for hybrid vehicle
Tailpipe emissions	0	+	+++	++	++
Energy consumption	0	+	++	++	+++
Cold startability	0	--	+	--	0+
Engine durability	0	-	0	-	0
Onboard fuel storage	0	0	---	0	0
Fuel cost	0	0+	---	0+	0+

The sufficient steam supply reaction, Equation (1), is strongly endothermic and produces only hydrogen and carbon dioxide, if ethanol reacts in the most desirable way. It is an ideal pathway by which the highest hydrogen yield may be achieved.



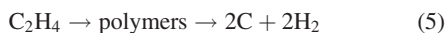
Hydrogen in lower amounts, CO, and undesirable products are formed during insufficient steam supply reactions, Equations (2)–(5):



Ethanol can dehydrate to ethylene according to Equation (4):



A possible route of carbon formation is ethylene polymerization, Equation (5):



The lack of detailed kinetic data (reaction rates, residence time, known intermediate species, etc.) has determined a modeling of the steam reforming. Therefore, the simulation has been run with a Gibbs reactor that simulates a chemical reactor by solving the heat and mass balances on 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 [15].

The total Gibbs free energy of a system is given by the sum of  $i$  species:

$$G^t = \sum_{i=1}^N n_i G_i^0 + RT \sum_{i=1}^N n_i \ln \frac{f_i}{f_i^0} \quad (6)$$

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 of species  $i$ . For reaction equilibrium in gas phase,  $G_i^0 = \Delta G_{f_i}^0$  is assumed.

When solid carbon (graphite) is involved in the system, the minimization function of Gibbs energy is as follows:

$$\sum_{i=1}^{N-1} n_i \left( \Delta G_{f_i}^0 + RT \ln \frac{y_i \phi_i P}{P^0} + \sum \lambda_k a_{ik} \right) + (n_C \Delta G_{f_C(s)}^0) = 0 \quad (7)$$

where  $y_i$  is the gas phase mole fraction,  $\phi_i$  is the fugacity coefficient of species  $i$ ,  $P$  is the pressure of system,  $P^0$  is the standard-state pressure of 101.3 kPa,  $\lambda_k$  is the Lagrange multiplier,  $a_{ik}$  is the number of atoms of the  $k$  element present in each molecule of species,  $n_C$  is the moles of carbon,

and  $\Delta G_{f_C(s)}^0$  is the standard Gibbs function of formation of solid carbon.

The equilibrium calculations employing the Gibbs energy minimization were performed with the Chem-CAD professional software package. The programs are capable of simulating single-phase or multi-components in equilibrium. Equilibrium constants,  $K_p$ , of Equations (3)–(5) versus temperature were determined from the Van't Hoff reaction [15].

High equilibrium constants of Equations (3), (4),  $\ln(K_p) \approx 30$ –40 mean complete conversion of ethanol in the temperature range of 800–2000 K.

The caloric equation of state is

$$H_i = H_{i0} + \int_{T_0}^T C_{p_i} dT \quad (8)$$

which describes the relation between the species' enthalpies and their specific heat capacities  $C_{p_i}$ .

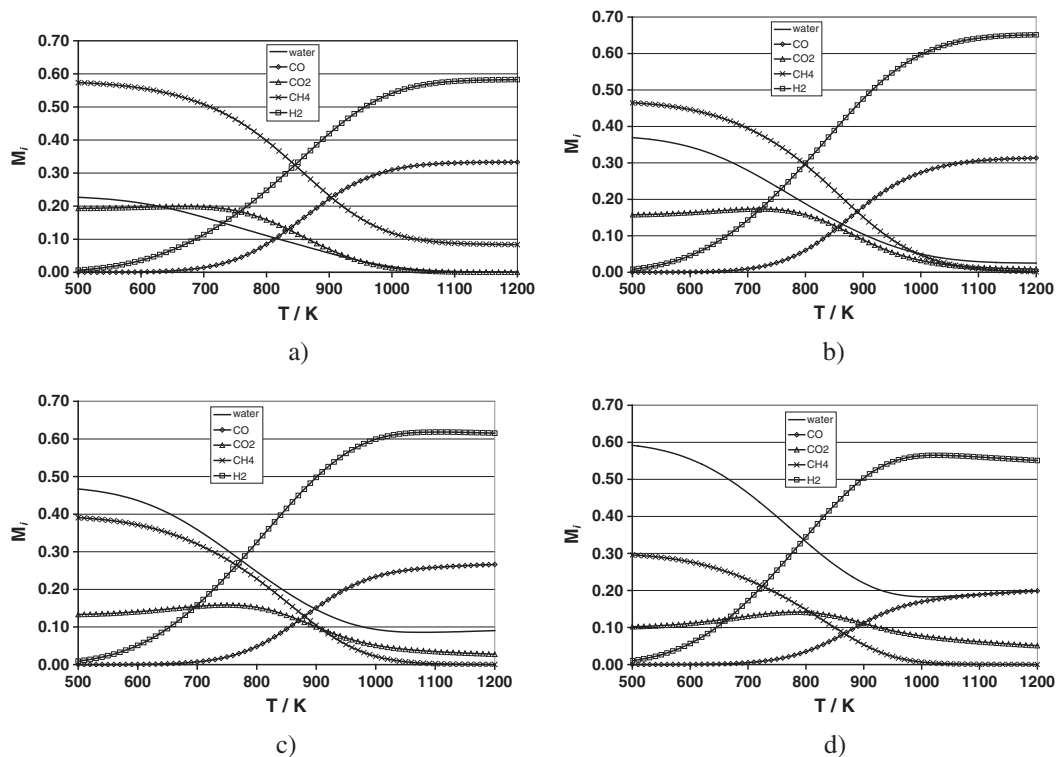
### 3.2. Results

Previous numerical calculations were focused on thermodynamic analysis of hydrogen production from ethanol with respect to fuel cell applications, and the effect of operating parameters on hydrogen yield has been examined, [4,8,12]. Previous numerical calculations were focused on thermodynamic analysis of hydrogen production from ethanol with respect to fuel cell applications, and the effect of operating parameters on hydrogen yield has been calculated [4,8,12]. In the present study, the effect of operating parameters on enthalpy of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  was examined with relation to using as fuel for ICE.

Mol fractions,  $M_i$  (moles of given product,  $i$ , to total moles of products,  $M$ ) of ethanol decomposition products in steam reformer at atmospheric pressure, various water: ethanol (W/E) ratios, and different reaction temperatures are shown in Figure 3. At given W/E, the yield of hydrogen first increases sharply with rise of temperature and then practically stabilizes in the range of  $T=1000$ – $1200$  K. These results agree with those reported in [14,15]. Carbon monoxide yield approaches to 0% when the temperature is 500 K. It increases with increasing temperature depending on W/E ratio. For example, in the range  $T=1100$ – $1200$  K at  $W/E=1.2$   $M_{\text{CO}} \approx 30\%$ , and at  $W/E=3.0$  CO yield drops down to  $M_{\text{CO}} \approx 20\%$ . Decrease in equilibrium yield of carbon monoxide from SRE with increase of W/E also was reported in [15].

In the range of  $T=1000$ – $1200$  K,  $M_{\text{CO}_2}$  can be kept low and changes from about 0–5% with rise of W/E from 0.6 to 3.0. In the range  $T=1000$ – $1200$  K,  $M_{\text{CH}_4}$  drops down from about 11 to 0% with increase of W/E from 0.6 to 3.0. The same trend was observed by Wang and Wang [15].

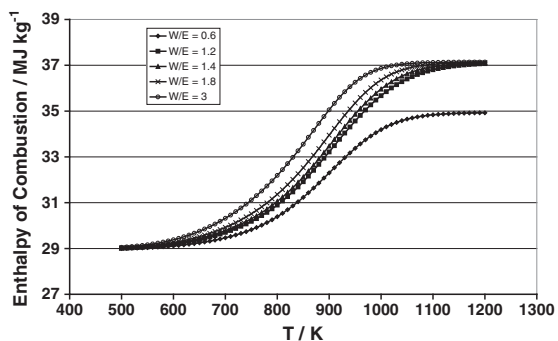
Equations (1) and (2) are dominant at temperatures above 800 K, [16]. This result is very important because according to Equation (5), existence of  $\text{C}_2\text{H}_4$  in steam reforming products leads to carbon formation. When fuels, such as hydrocarbons, ethanol, and methanol, are used, there is a



**Figure 3.** Composition of SRE products at various W/E ratios depending on temperature: (a) W/E=0.6; (b) W/E=1.2; (c) W/E=1.8; and (d) W/E=3.

risk of carbon deposition [17]. It was shown in the study [15] that the carbon (graphite) is absent in the temperature range 600–2000K and the W/E range of 3–20.

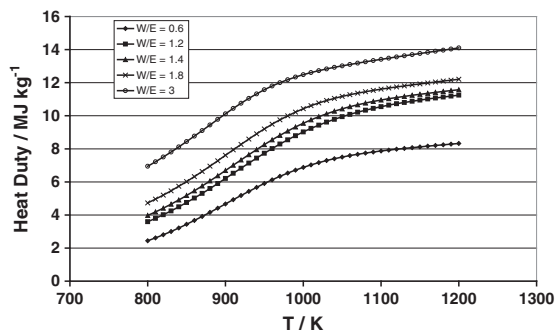
Figure 4 shows enthalpy of combustion of SRE products (megajoules per kilogram of ethanol) at different W/E ratios and temperatures. Increase of SRE products enthalpy is observed with an enhancement of temperature and steam:ethanol molar ratio (W/E). At  $T \geq 1100\text{K}$  and  $W/E > 1.2$ , enthalpy of SRE products is about 21% higher than that of dehydrated ethanol. On the other hand, an increase of this parameter is associated with an increase in so-called heat duty ( $H_d$ ) to heat the reactor to a temperature necessary for achievement of high ethanol conversion. The



**Figure 4.** Enthalpy of combustion of SRE at different W/E ratios and temperatures.

heat duty is the sum of the heat of reaction, latent heat, and sensible heat. Increase in W/E leads to an increase of the heat required for water evaporation. Figure 5 shows heat duty (megajoules per kilogram of ethanol) required to heat primary water/ethanol proportions (W/E) to the dissociation point (T).

As was shown above, the SRE for hydrogen and CO production involves a complex multiple reaction system, and the dissociation products are affected by many undesirable side reactions. Therefore, the total enthalpy of combustion of dissociated products depends in a complex manner on the process variables. To analyze efficiency of the steam reforming process, it is necessary to know the



**Figure 5.** Heat duty dependence on temperature and W/E ratio.



effect of these variables on total enthalpy of combustion and heat duty. The energy efficiency is a very important system parameter [18]. This efficiency is defined as the ratio of the difference between enthalpy of combustion of SRE products,  $H_{\text{comb}}$ , and enthalpy of primary reactants,  $H_{\text{in}}$ , to the heat duty (enthalpy),  $H_d$ .

$$\eta = (H_{\text{comb}} - H_{\text{in}})/H_d \quad (9)$$

Figure 6 shows the energy efficiency of SRE as a function of the W/E ratio in the reformer at the temperature range of 800–1200K.

It was found that  $\eta$  reaches the maximum value of about 0.59 at temperature  $T=1100\text{K}$  and  $W/E=1.2$ .

## 4. DISCUSSION

### 4.1. Economic and environmental indicators for fuel cell and motor vehicles

Chemical storage of hydrogen in liquid fuels is considered to be one of the most advantageous for the fuel cell applications [7–9]. Fuel cells produce electric power through an electrochemical process, in which hydrogen energy is converted to electricity. Several different liquid and solid media can be used to facilitate the fuel cell electrochemical reactions. These media are phosphoric acid, molten carbonate, solid oxide, and polymer electrolyte membrane (PEM). Each medium consists of a distinct fuel cell technology and unique performance characteristics. The overall efficiency of fuel cells is impacted by the ratio of the parasitic power consumed by the auxiliary components to the stack power. For example, the electrical efficiencies of PEM fuel cells are in the range of 23–40% [19].

However, there are more losses to be considered. Typically, automotive PEM fuel cells consume more of the rated stack power output to provide power to pumps, blowers, controllers, and so on. Depending on the chosen drive train technology, the DC power is converted to

frequency modulated AC or to voltage adjusted DC, before motors can provide motion for wheels. Energy is always lost in the electric system between fuel cell and wheels. The overall electric efficiency of the electric drive train can hardly be better than 90%. Fuel cells need hydrogen of high purity, which is always a challenge, if SRE is used for onboard hydrogen production. Together with hydrogen, normally, other components, such as CO, and  $\text{CO}_2$ , are produced (see Figure 3). Their yields are changed depending on W/E ratio and temperature, as was discussed above. Because CO also is a fuel, it may be used directly for the ICE feeding. However, carbon monoxide is known as the poison for fuel cells. Therefore, a route for removing carbon monoxide in case of fuel cell use is necessary, which complicates the system and reduces its overall efficiency [20]. Fuel cells today are much more expensive than an equivalently sized ICE.

Moore *et al.* [21] present results of an energy analysis for load following versus battery hybrid direct hydrogen fuel cell vehicles. Hybridizing is generally assumed to be a viable technique for improving the vehicle efficiency—largely based on the ability to recover and reuse regenerative braking energy. Simulation results showed that for hybrid vehicles, the increase in efficiency is about 1% for federal highway cycle (HIWAY, US) and about 4% for federal urban driving schedule (FUDS, US). Calculated vehicle efficiency is about 38 and 25% for HIWAY, US, and FUDS, US, respectively.

Hybridizing the ICE is generally assumed to be a viable technique for improving the vehicle energy use and efficiency—largely based on the ability to recover and reuse regenerative braking energy. However, there also are negative aspects of hybridization, including additional complexity, additional packaging constraints, and potentially higher cost—especially when the hybrid design is configured for maximum recovery and reuse of regenerative braking energy. Balancing these negative attributes are potential benefits of hybridization, for example, improvement in start-up performance, efficiency improvement for the system, and use of renewable fuels produced from biomass fermentation. The overall environmental impact of vehicle use also should be taken into account. The battery-hybrid designs may be selected for hybrid propulsion system. Utilization of the series hybrid scheme together with a benefit of ICE operation at the optimal regime will require an appropriate dimensioning of the battery pack and usually requires the use of larger battery compared with the parallel hybrid scheme.

The most important parameters of the battery pack are as follows: good power performance and energy density, high charge and discharge efficiency, and excellent cyclability. Currently, Li-ion phosphate batteries present the most favorable combination of the above parameters and also the most adequate safety features. There is an option in the selection of the configuration of power source. Essentially, the issue is as follows: to implement a pack composed of a smaller amount of high capacity cells or to implement a battery pack composed of a substantial

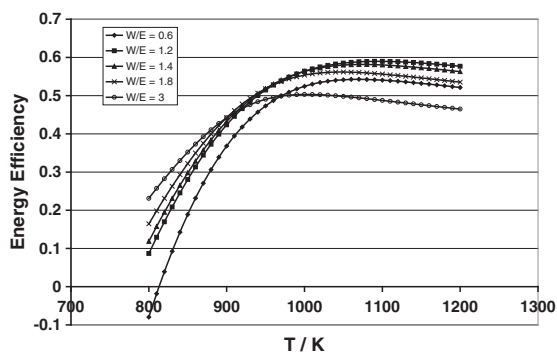


Figure 6. Energy efficiency of the SRE as a function of temperature and W/E ratio.

amount of considerably small cells. There are several points in favor of the latter power source configuration. A battery pack composed of a large number of small cells has an advantage over a battery pack with a small number of big cells from the safety point of view—in the case of such a power source configuration, an internal short or external damage of a few cells are local events and do not result in the thermal runaway of the pack (or its substantial part) as a whole. It is reasonable to expect a normal battery pack of 50kWh (one-charge travel is about 200km). The overall dimensions may be estimated as close to  $58 \times 58 \times 65$  cm [22].

The very important issue is power source temperature sustainability. Whereas many brands of the Li-ion batteries are workable at the temperatures as high as 50, 65, and even 75°C, the Li-ion cell life span substantially reduces at the operating temperatures of 45°C and above. This point brings up the understanding of the necessity of a battery pack thermal control system for keeping the battery below 40–45°C in all operating conditions.

Economic and environmental comparison of conventional (ICE powered) hybrid and fuel cell vehicles was performed by Granovskii *et al.* [23]. The following criteria were taken to be key economic characteristics of vehicles: vehicle price (including the price for changing batteries for hybrid and electric vehicles), fuel costs (which are related to vehicle lifetime), and driving range (which defines the number of refueling stations required). According to this comparison, the hydrogen fuel cell vehicles are not beneficial over conventional and hybrid vehicles. ICE-powered vehicles offer low initial cost, easy start-up, proven reliability, and good part-load characteristics and recovery potential. The emissions of ICE can be controlled by exhaust catalysts and through better control of the combustion process.

#### 4.2. Distinct features of steam reforming of ethanol for internal combustion engines

The aim of SRE for fuel cell applications is to reach maximum pure hydrogen production together with prevention of other product formation. It has been shown that an enhancement of the reaction temperature leads to an increase in the obtained H<sub>2</sub> yields. High temperatures and high W/E ratios are needed to obtain the highest H<sub>2</sub> production from ethanol. Thermodynamic analysis shows that ethanol steam reforming at T > 650K, atmospheric pressure, and W/E up to 10 are required to maximize H<sub>2</sub> production and minimize the formation of CO and carbon deposition [12–15]. In the viewpoint of thermodynamics, the favorable condition of SRE for fuel cells is to obtain theoretical molar ratio of ethanol feed and hydrogen produced ( $6 \times M_{E, in}$ ) where M<sub>E, in</sub> is the molar rate of ethanol at reformer inlet.

The aim of SRE for ICE feeding is to reach maximal energy efficiency  $\eta$  by way of appropriate optimization of the reaction temperature and W/E ratio. Here, it is assumed that the products formed in SRE reformer are directly used

in ICE. Therefore, the SRE reforming temperature and temperature of the gaseous fuel at the engine inlet are the same, which is actually not true because of the heat losses. Figure 6 shows that  $\eta$  increases with temperature change from 900 to 1100K and reaches the maximum value at the temperature T=1100K and W/E=1.2. As can be seen from the SRE product composition calculations for different temperatures and W/E (see Figure 3), the mol fractions of CH<sub>4</sub> and CO<sub>2</sub> at T=1100K and W/E=1.2 reach their minimum and increase with further rise of W/E. For fuel cell applications, the optimum W/E ratio is recommended to be 3–6 [13,24]. Therefore, initial amounts of water required onboard for ICE SRE can be greatly reduced compared with SRE for fuel cell applications. Taking into account that an increase of W/E leads to the rise of energy required for water evaporation, a conclusion about additional energy saving compared with fuel cell vehicle can be made.

#### 4.3. Comparison of engine fueled by liquid ethanol with reformed ethanol engine

The experimental results obtained recently by Fubing *et al.* [25] indicate that it is feasible that the reformed ethanol is supplied to the engine. However, operating parameters and the performance of steam reactor were not given in this paper. It should be stressed that the waste heat from the exhaust can be recovered and used as energy source for ethanol and water evaporating and subsequent ethanol steam reforming. However, the efficiency of the engine can be improved by feeding it with SRE fuel only under certain conditions, as it is shown in Figures 4–6.

It was shown in this study that the SRE products under optimized reforming conditions may contain about 60% H<sub>2</sub> (see Figure 3). The properties of hydrogen contribute to more efficient combustion of SRE fuel in the engine. Table II compares selected combustion-related properties of H<sub>2</sub> with those of ethanol as were compiled from standard chemical engineering reference works and material safety data sheets [26]. Hydrogen has a wide flammability range in comparison with ethanol, which makes it easier to start an engine. As a result, a hydrogen-rich mixture can be combusted in an ICE over a wide range of fuel–air mixtures. The hydrogen flame speed is much higher than that of ethanol. This means that hydrogen-rich engines can more closely approach the thermodynamically ideal engine cycle.

Composition of the SRE products for the optimal reforming conditions T=1100K and W/E=1.2 and their auto-ignition temperatures are given in Table III. All main

**Table II.** Comparative properties of ethanol and hydrogen.

Property	Ethanol	H <sub>2</sub>
Flammability limits (volume %)	LFL 3, UFL 19	LFL 4, UFL 75
Auto ignition temperature (°C)	365	574
Laminar flame speed (ms <sup>-1</sup> )	0.25–0.4	1.9–2.7

**Table III.** Composition of the SRE products ( $M_i$  %) and their auto-ignition temperatures ( $^{\circ}\text{C}$ ) at  $T=1100\text{K}$ ,  $W/E=1.2$ .

Product	$\text{H}_2$	$\text{CO}$	$\text{CH}_4$
Concentration	65	30	$\approx 5$
Auto-ignition temp.	574	609	580

SRE products have relatively high auto-ignition temperatures ( $574\text{--}609^{\circ}\text{C}$ ), which are much higher than that of ethanol ( $365^{\circ}\text{C}$ ). This has important implications, when a hydrogen–CO–air mixture is compressed. The high auto-ignition temperature allows higher compression ratios to be used in an engine fed by the SRE fuel with an appropriate gain in the engine's thermal efficiency.

## 5. CONCLUSIONS

Ethanol as a fuel presents clear advantages as an alternative to the fossil fuels used in the transportation sector: renewable production, economical benefits for agriculture and rural areas, and improvement of energy supply security. At the same time, the logistics for its distribution is the same as for fossil fuels, so it does not need an expensive new infrastructure. A major concern with onboard ethanol reforming for fuel cell applications is that the gas fed to the fuel cell stack is no longer pure hydrogen but rather a mixture of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and some others. Compared with a fuel cell case, this gaseous mixture could be an excellent fuel for ICE, especially taking into account a possibility of utilization of exhaust gases energy for undertaking the endothermic reaction of ethanol steam reforming. Unfortunately, onboard reformer cannot work efficiently at a wide range of engine operation regimes typical for road vehicle, especially at transient modes and cold-start conditions. In case of a hybrid propulsion system, which always has an additional energy source, these shortcomings can be easily overcome.

A numerical study has been conducted to analyze the energy aspects of ethanol steam reforming for ICE. The reaction paths of ethanol steam reforming were simulated using Chem-CAD software. Appropriate optimization of reactants ratio and reaction conditions have been performed, to achieve the composition of SRE products, which will be favorable as an ICE fuel. It was found that the optimal energy efficiency of SRE together with the highest hydrogen yield is achieved at the following reforming conditions:  $T=1100\text{K}$  and  $W/E=1.2$ .

## NOMENCLATURE

AC	= alternating current
$C_p$	= specific heat capacity ( $\text{Jkg}^{-1}\text{K}^{-1}$ )
DC	= direct current
$E$	= molar flow rate of ethanol at inlet ( $\text{mols}^{-1}$ )
FUDS, US	= federal urban driving schedule, US

$H$	= enthalpy ( $\text{MJkg}^{-1}$ )
HIWAY, US	= federal highway cycle, US
ICE	= internal combustion engine
LFL	= lower flammability limit
$M$	= mol fraction
MC	= molten carbonate
MDP	= methanol decomposition products
NMOG	= non-methane organic gases
OMHCE	= organic matter hydrocarbon equivalent
PA	= phosphoric acid
PEM	= polymer electrolyte membrane
SO	= solid oxide
SRE	= steam reforming of ethanol
$T$	= temperature ( $\text{K}$ , $^{\circ}\text{C}$ )
TEL	= tetraethyl lead
UFL	= upper flammability limit
$W$	= molar flow rate of water at inlet ( $\text{mols}^{-1}$ )

### Greek symbols

$\Delta H_{298}$	= heat of reaction at the temperature of 298 K and pressure 101.3 kPa ( $\text{kJ mol}^{-1}$ )
$\eta$	= efficiency

### Subscripts

$\text{CH}_4$	= methane
CO	= carbon monoxide
$\text{CO}_2$	= carbon dioxide
comb	= combustion
$d$	= heat duty
$E$	= ethanol
$i$	= given product
in	= inlet

## REFERENCES

1. The Petroleum Economist Forum of Biofuels. London, UK, November 18–19 2008.
2. Naegeli DW, Yost DM, Moulton DS, Owens EC, Chui GL. The measurement of octane numbers for neat methanol and reference fuel blends. SAE Paper 892038, SAE Transactions. 1989.
3. Hagen DL. Methanol as a fuel: a review with bibliography. SAE Paper 770792. 1977.
4. Ioannides J. Thermodynamic analysis of ethanol processors for fuel cell applications. *J. Power Sources* 2001; **92**(1–2):17–25.
5. Sorensen B. Renewables and hydrogen energy technologies for sustainable development. *Int. J. Energy Research* 2008; **32**(5):367–368.
6. Turner J, Sverdrup G, Mann MK, Maness PC, Kroposki B, Ghirardi M, Evans RJ, Blake D. Renewable hydrogen production. *Int. J. Energy Research* 2008; **32**(5):379–407.



7. Klouz V, Fierro V, Denton P, Katz H, Lisse JP, Bouvot-Mauduit S, Mirodatos C. Ethanol reforming for hydrogen production in a hybrid electric vehicle: process optimization. *J. Power Sources* 2002; **105**(1): 6–34.
8. Joensen F, Rostrup-Nielsen JR. Conversion of hydrocarbons and alcohols for fuel cells. *J. Power Sources* 2002; **105**(2):195–201.
9. Brinkman ND, Stebar RF. Comparison of methanol and dissociated methanol illustrating effects of fuel properties on engine efficiency- experiments and thermodynamic analyses. *SAE Paper 850217, SAE Transactions* 1985; **94**.
10. Tartakovsky L, Zvirin Y. Internal combustion engine for a hybrid vehicle fueled by ethanol decomposition products. Proceedings of 31<sup>st</sup> Israeli Conference on Mechanical Engineering, Tel-Aviv, Israel, June 2–3 2010.
11. Zvirin Y, Gutman M, Tartakovsky L. Fuel Effects on Emissions. In Handbook of Air Pollution from Internal Combustion Engines: Pollutants Formation and Control, Sher E (ed.). Academic Press, 1998; 548–651.
12. Garcia EY, Laborde MA. Hydrogen production by the steam reforming of ethanol: thermodynamic analysis. *Int. J. Hydrogen Energy* 1991; **16**(5):307–312.
13. Vasudeva K, Mitra N, Umasankar P, Dhingra SC. Steam reforming of ethanol for hydrogen production: thermodynamic analysis. *Int. J. Hydrogen Energy* 1996; **21**(1):13–18.
14. Vadya PD, Rodrigues AE. Insight into steam reforming of ethanol to produce hydrogen for fuel cells. *Chem Eng J* 2006; **117**(1):39–49.
15. Wang W, Wang YQ. Thermodynamic analysis of steam reforming of ethanol for hydrogen generation. *Int. J. Energy Research* 2008; **32**(15):1432–1443.
16. Wang W, Wang Y, Liu Y. Production of hydrogen by ethanol steam reforming over nickel-metal oxide catalysts prepared via urea- nitrate combustion method. *Int. J. Energy Research* 2011; **35**(6):501–506.
17. Colpan CO, Dincer I, Hamdullahpur F. A review on micro-level modeling of planar solid oxide fuel cells. *Int. J. Energy Research* 2008; **32**(4):336–355.
18. Abuadala A, Dincer I. Efficiency evaluation of dry hydrogen production from biomass gasification. *Thermochimica Acta* 2010; **507**(8):127–134.
19. Elgowainy A, Wang MQ. Fuel Cycle Comparison of Distributed Power Generation Technologies. Center of Transportation Research, Argonne National Laboratory November 2008: 1–25.
20. Perna A. Hydrogen from ethanol: theoretical optimization of a PEMFC system integrated with a steam reforming processor. *Int. J. Hydrogen Energy* 2007; **32**(12):1811–1819.
21. Moore RM, Hauer KH, Ramaswamy S, Cunninham S. Energy utilization and efficiency analysis for hydrogen fuel cell vehicles. *J. Power Sources* 2006; **159**(2): 1214–1230.
22. Selman JR, Al Hallaj S, Uchida I, Hirano Y. Cooperative research on safety fundamentals of lithium batteries. *J. Power Sources* 2001; **97–98**:726–732.
23. Granovskii M, Dincer I, Rosen MA. Economic and environmental comparison of conventional, hybrid, electric and hydrogen fuel cell vehicles. *J. Power Sources* 2006; **159**(2):1186–1193.
24. Sahoo DR, Vajpai S, Patel S, Pant KK. Kinetic modeling of steam reforming of ethanol for the production of hydrogen over Co/Al<sub>2</sub>O<sub>3</sub> catalyst. *Chemical Engineering* 2007; **125**(2):139–147.
25. Fubing Y, Gesheng L, Xiaohong G. Study on reformed Ethanol Engine. Proceedings of ISES World congress, Beijing, China, September 18–24 2007; 2418–2421.
26. Combustible Material. In CSE PSM Symposium. : Edmonton, Alberta, 2007.