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Hydrogen Enriched Hydrocarbons as New Energy Resources – as Studied by Means of Computer Simulations

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ABSTRACT

During several recent years an increasing interest concerning behavior of various gaseous or liquid hydrocarbons mixtures with neat gaseous hydrogen is observed. The phase equilibria as well as flow properties have been studied and some practical implementations indicated. The main practical idea consists in a possibility to use such mixtures as a replacement for pure hydrocarbons actually used as the energy source. Application of hydrogen enriched mixtures seem to be a temporary solution for gradual decarbonization of energy resources. The advantage of such approach may consist in much smaller requirements for investment in various aspect of infrastructure needed for handling the fuels. The present work is devoted to computer simulation of carbon dioxide emissions for several scenarios based on different compositions of hydrogen mixtures with hydrocarbons. The simulations include estimation of calorific value of the mixture and composition of exhaust gases emitted after its combustion. The simulation, based on s.c. logistic function, evaluates several variants of time dependence of new fuels implementation, and consequently time dependence of changes in composition of emissions to atmosphere. The simulation can be used for choosing the ways of practical implementation management.

Keywords: hydrogen, methane, hydrogen-methane fuels, mathematical modeling, technology management.

INTRODUCTION

Global warming appears to be the main concern of humanity during the recent decades. The decarbonization of technological processes, as well as the processes of everyday life, mainly related to obtaining and using energy, seems to be a remedy for threats [1]. Many possible routes to achieve decarbonization of energy sources such as the use of alternative, renewable resources have been undertaken [2]. The possible ways include solar, water flow, wind energy [3], also generation from biomass [4, 5]. Among others a version already discussed for several year is the addition of hydrogen to natural gas. The main principles of this approach are given in the papers [6, 7]. The report mentioned gives an extensive review of the properties of methane-hydrogen mixtures. Several papers are devoted to physicochemical properties of the mixtures. Interesting research is given in [8], the paper analyses thermodynamic interactions between hydrogen and hydrocarbons in various conditions of temperature and pressure. Experimental studies on virial coefficients related to the mixtures of hydrogen and ethane are presented in the theses [9]. Subsequent paper [10] presents viscosity data for neat methane and hydrogen as well as their mixtures. Already many years ago the PVT data for mixtures of methane with hydrogen have also been published [11, 12] and later [13]. All these publications give insight into thermodynamic behavior and phase equilibria in the discussed system. They indicate that gaseous hydrogen can be mixed with methane gas without problems at practically all concentrations. More difficult situation occurs when any of the components are liquid. There is a very big difference between melting temperature of both liquified gases. When the methane is in liquid form it is kept at not very low pressure, what due to Henry's law causes low concentration of hydrogen in liquid methane. In opposite situation when hydrogen is in liquid form the methane freezes to solid – what prevents transportation in pipes. Behavior of the mixture CH_4/H_2 is also reported in [14], where transport of hydrogen methane mixtures in network pipes, their behavior in consumer equipment domestic or industrial as well as probability of explosion characteristics (and ignition probability) of the mixtures are discussed. Many works are related towards behavior of CH_4/H_2 mixtures in the internal combustion engine, e.g. [15, 16]. The papers [17, 18], give a review of several phenomena occurring during combustion of the gas mixture in the engine. It also describes the design of the engine with direct injection of hydrogen into combustion chamber of the engine. Such solution can be used for liquid form of fuel gases. Similar studies are also performed in papers [19,20]. Various other fuels for internal combustion engines were also studied in the papers [21]. Transport of hydrogen methane mixtures in network pipes, their behavior in consumer equipment domestic or industrial as well as probability of explosion characteristics (and ignition probability) are discussed in the work [22]. The deep studies on hydrogen transport in the existing pipelines were reported in [23]. The work presented several reasons of hazards for human and property safety associated with phenomena connected with e.g. corrosion of steel pipes that might lead to explosion. Experimental studies on fire safety connected with the use of CH_4/H_2 in buildings were performed in the works [15, 24]. The paper [25] shows practical examination of feasibility of the use the mixture for fueling of city bus. Feasibility of hydrogen-methane application in practice is also recognized by some manufacturers of appliances already claiming that their products are ready for conversion to such fuel. Also the CH_4/H_2 is already used as a fuel in public bus transportation in some cities [7].

The presented above extract from the literature brings following conclusions:

- The CH_4/H_2 mixture can be easily transported with normal technical means designed for natural gas [11];
- The mixture can be used in domestic and technical appliances as well as in internal ignition engines in automobiles; some sources also predict large increase of hydrogen application as an energy carrier;
- The shift from natural gas to CH_4/H_2 mixture does not require substantial investments in the infrastructure;
- The fire and explosion risks associated with the use of this flammable mixture of gases is not higher than in the case of use classical natural gas.

There are already examples of practical use of the CH_4/H_2 mixture e.g. for fueling of city busses. There is quite wide expectation that use of CH_4/H_2 mixture will positively contribute to CO_2 emission abatement.

This last statement arises some doubts since various methods of hydrogen production are associated with various amounts of carbon dioxide emissions. This concerns both hydrogen production by various approaches to chemical reforming of hydrocarbons, hydrocarbon pyrolysis, and electrolysis of water. Consequently it seems worth to analyze the effect of those emissions on the results of CH_4/H_2 mixture.

The aim of present work is to analyze the dependence of carbon dioxide emission associated with combustion of CH_4/H_2 mixture as function of its composition and compare the result with the CO_2 emission rising during production of hydrogen present in the mixture. The secondary goal is to attempt modeling the time dependence of natural gas replacement with CH_4/H_2 mixture.

METHODS

The methods applied to the present topic is purely theoretical based on mathematical modeling and computer simulation. The composition of the mixture is defined by the assumption that constant total volume of the mixture is created by mixing hydrogen with methane by taking in the first sample 5 volume parts or hydrogen with 95 parts of methane, and increasing amount of hydrogen by 5 parts in subsequent samples correspondingly decreasing amount of methane. Therefore concentration of the mixtures can be easily expressed in volume fraction u_v (1).

$$u_{v_i} = \frac{v_i}{\sum v_i} \quad (1)$$

where: u_{v_i} – is volume fraction of component *i*,
v_i– volume of component *i*.

Mass fractions according to the formula (2):

$$u_{m_1} = \frac{\rho_1 v_1}{\rho_1 v_1 + \rho_2 v_2} \quad (2)$$

where: $\rho_i = \frac{M_i}{V_i}$ – density of gas *i*,
M_i – molecular mass of the component *i*,
$V_i = 22.41\ \mathrm{g/dm^3}$ – molar volume of the component *i*.

For each concentration the density of gas mixture was computed as (3):

$$\rho_{mix} = \frac{\rho_1 v_1 + \rho_2 v_2}{v_1 + v_2} \quad (3)$$

The lower heating value (LHV) of the gas mixture was computed under assumption of additivity. The two values LHVm [J/kg] and LHVv (J/m³) were obtained for each composition of the mixture (4a, 4b).

$$LHV_{m\,mix} = u_{mH2} * LHV_{mH2} + u_{mCH4} * LHV_{mCH4} \quad (4a)$$

$$LHV_{v\,mix} = u_{vH2} * LHV_{vH2} + u_{vCH4} * LHV_{vCH4} \quad (4b)$$

Values of LHV for pure components are presented in Table 1.

Further computations were made considering annual consumption of natural gas in Poland being about $20*10^6$ m³. This value was converted to corresponding energy equal $7{,}96*10^8$ MJ. As a next step the volume and mass of the CH_4/H_2 gas mixture needed to obtain the mentioned earlier amount of energy consumed in form of natural gas. Finally, by means of standard stoichiometric procedure the amount of CO_2 emitted during production of the amount of hydrogen incorporated into mixtures of different concentrations were computed. In computations the value 7.1 kg CO_2/1/kgH_2 was according to the publication [26].

Additionally, the logistic function was applied to estimate potential time dependence of practical implementation of CH_4/H_2 mixture. The logistic function was used in the form (5):

$$N(t) = \frac{K}{1 + \left(\frac{K - N_0}{N_0}\right) exp\left(-B(t - M)\right)} \quad (5)$$

where: $N(t)$ – the cumulative amount of gas in time t,
K – carrying capacity, what means the maximum (asymptotic) amount of gas,
N_0 – is an initial amount (assumed in order to avoid negative values in the initial run of the function),
B_b – parameter defining the average rate of implementation process,
M_b – position of the curve of time scale.

The parameters used are presented in Table 2.

RESULTS AND DISCUSSION

Figure 1. presents computed dependencies of measures of content together with computed density of mixtures as functions of hydrogen volume fraction.

It is seen on the Figure 1 that densities of the mixtures of different concentrations shows linear dependence upon volume fractions. Mass fractions obviously show nonlinear dependence upon volume fractions of each components.

Figure 2 shows computed dependencies of low calorific value on volume fraction of hydrogen in the mixture. The values related to volume represent linear decrease with an increase of hydrogen concentration. The plot of values related to mass concentration of hydrogen shows

Table 1. Properties of mixture components

Fuel	Density At 0°C, 1 bar	Higher heating value (HHV)		Lower heating value (LHV)	
	[kg/m³]	[MJ/kg]	[MJ/m³]	[MJ/kg]	[MJ/m³]
Hydrogen	0.09	141.7	12.7	120	10.8
Methane	0.716	55.5	39.8	50	35.8

Table 2. Parameters of logistic function accepted for computations

Parameter	A	B	C	D
B	0.4	0.2	0.3	0.2
M	3	1	1	5
K	0.3	0.3	0.3	0.3
N_0	0.01	0.01	0.01	0.01

nonlinear increase with the increase of hydrogen concentration. Such results are physically expectable. The observed behavior results of very low density of hydrogen as compared with methane, and very high calorific value related to the mass.

Figure 3 illustrates the results of stoichiometric computations of the mass of methane and corresponding mass of carbon contained in methane in the total amount of gas mixture theoretically carrying 7.96*10^8 MJ of energy (the amount estimated from actual consumption of natural gas in Poland. Obviously the amount of methane as well as carbon reaches zero when hydrogen volume fraction becomes one. The amount of carbon

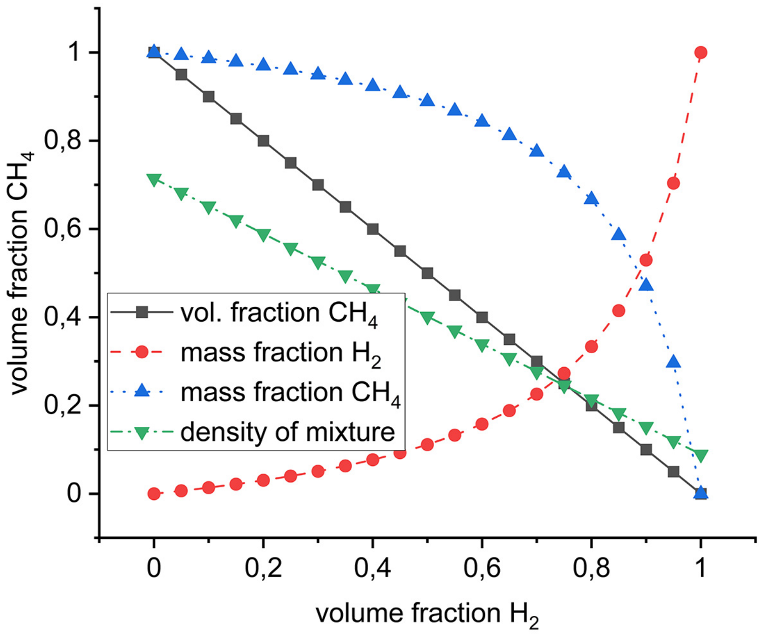

Fig. 1. Relations between volume and mass fractions and density of mixtures H_2/CH_4

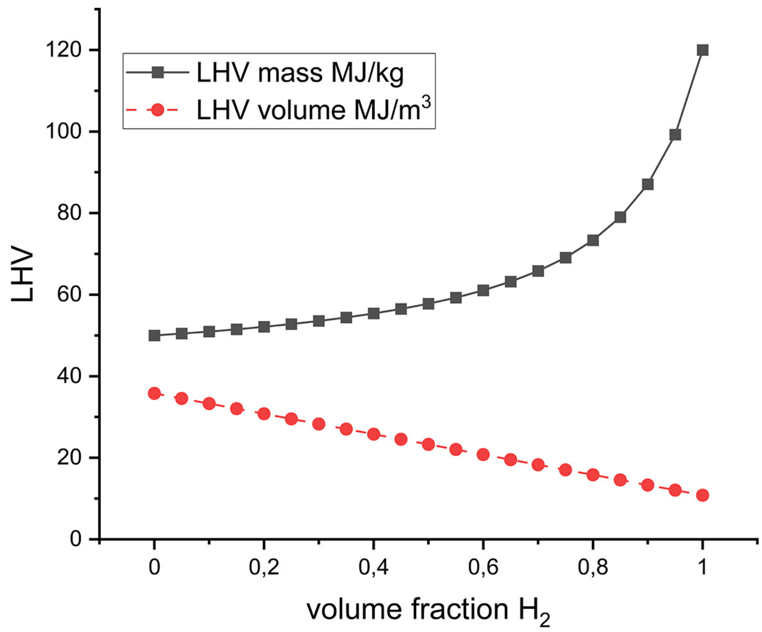

Fig. 2. Dependencies of low calorific values upon composition of the mixture

contained in the mixture seems to be proportional to the amount of mixture. The amount of methane is more evidently dependent upon hydrogen concentration.

The plots shown on Figure 4 illustrate the total amount of carbon dioxide emitted by CH_4/H_2 mixture containing the amount of energy that correspond to natural gas consumption in Poland. The maximum being about 40Gg CO_2 correspond to neat methane. The amount of emitted carbon dioxide decreases with an increase of volume fraction of hydrogen obviously reaching zero when the burned gas is pure hydrogen. This result, however indicates only the amount of carbon dioxide emitted during the combustion of CH_4/H_2 gas mixture. It is well known that hydrogen has to be obtained either from water or from other compounds containing this component e.g. hydrocarbons or carbohydrates existing in nature. the process of obtaining hydrogen

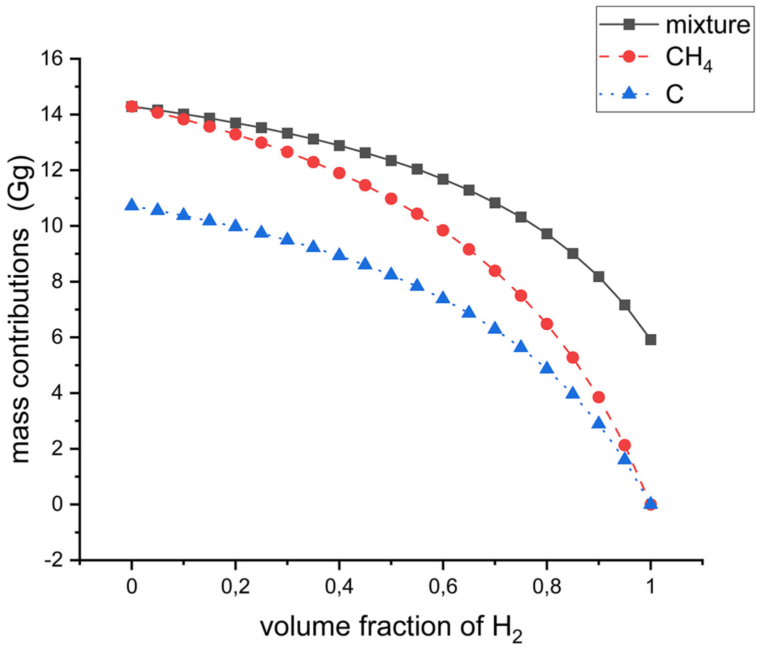

Fig. 3. Mass of the methane and carbon in the total amount of gas fulfilling demand of Poland as a function of hydrogen volume fraction

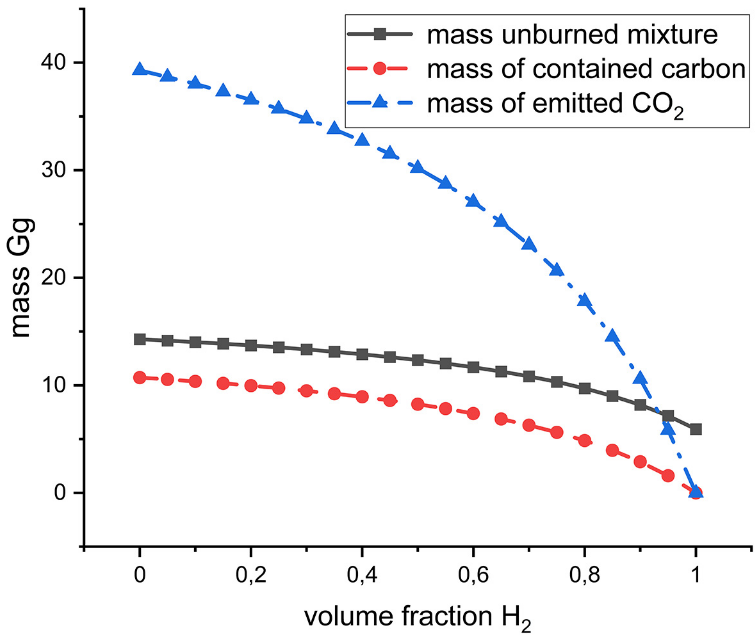

Fig. 4. Mass of emitted CO_2 related to the total mass of gas mixture consumed in Poland

is always associated with carbon dioxide emissions. On average, in world production, obtaining 1 kg of hydrogen is associated with the emission of 7.2 kg carbon dioxide.

The data presented on Figure 4 enable computation of mass CO_2 associated with hydrogen production. Results of this estimation are given in Figure 5 together with amount of savings of this emission due to the implementation of the mixture. The savings, were computed as a difference between emission from combusting of neat methane and CH_4/H_2 mixtures of different concentrations.

In addition to the mentioned dependencies Figure 5 contains the plot of the function describing the amount of carbon dioxide emitted due to production the amount of hydrogen that has to be added to the CH_4/H_2 mixture of appropriate concentration. It can be seen that the curve for emissions related to production of hydrogen slightly outweigh the curve of savings. This means that the implementation of hydrogen methane mixture

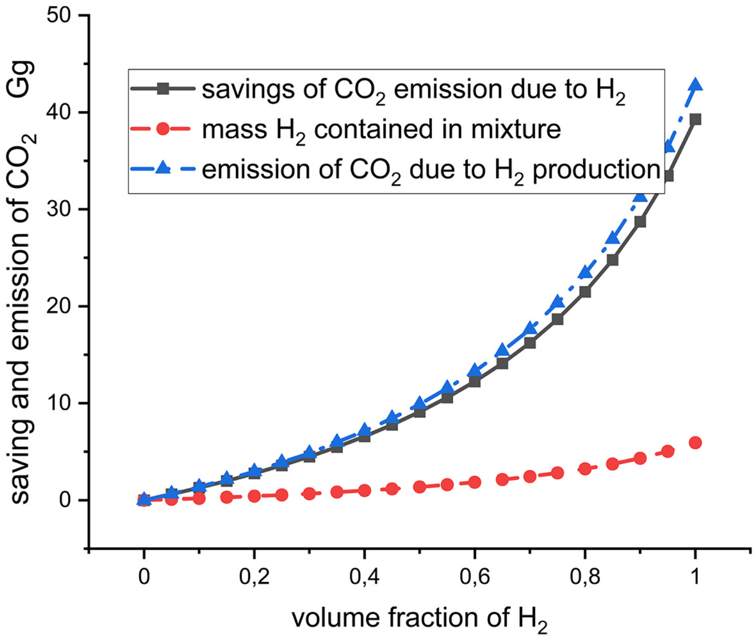

Fig. 5. Savings of CO2 achieved by implementation of various concentrations of the mixture CH_4/H_2

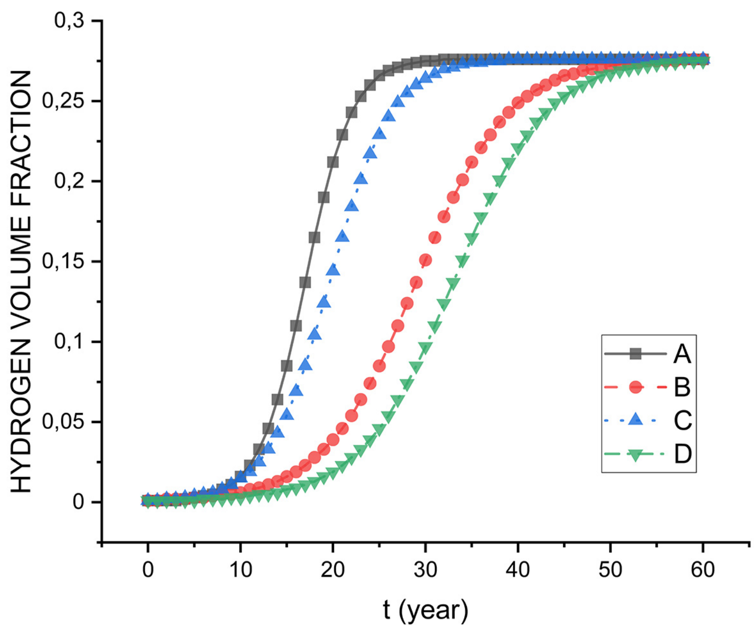

Fig. 6. Logistic function describing hypothetical courses of implementation of technology and possible variants of preceding development of innovations enabling implementation of planned processes

may have positive effect only in situation when technology used for hydrogen production emits less carbon dioxide than actual global average (which is also Polish average). This is a challenge to global hydrogen production industry.

The transition from using pure natural gas to CH_4/H_2 blends cannot be an immediate one. Its implementation requires some time to pass. However, this time may be shorter than the introduction of a completely new technology for obtaining or using energy. The implementation of such a transition depends on many constraints, often occurring in a field of technology other than the introduced innovation. The feasibility assessment may be based on mathematical modeling using a logistic function. Fig. 6 shows an example of such a function for several assumed parameter values. Based on currently available data, it is not yet possible to determine realistic parameter values for specific planned processes.

This issue requires further research, which should lead to the possibility of forecasting the course of implementing technological innovations also in the area of obtaining and using energy.

CONCLUSIONS

The performed research indicates that replacement of neat natural gas (methane) in the gas network with CH_4/H_2 mixture has the potential to reduce CO_2 emissions during combustion of gas in various devices in industry and everyday life including at least partially road transport.

Such a change does not require significant investments in the infrastructure, so it can be introduced in a relatively short time and at low financial costs. Therefore it can be considered as an early step leading to CO_2 emission mitigation.

The mixture can also be used in road transportation as replacement for CNG. In the case of LNG the Hydrogen should be used separately being directly injected into combustion chamber.

The possibility of introducing the CH_4/H_2 mixture in place of pure methane, however, requires the prior introduction of new, low-emission hydrogen production technologies based on alternative energy sources, biotechnological or similar processes.

Further research on modelling of the courses of mutually dependent innovation processes should bring solutions enabling decisions and formulating priorities of technology management.

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