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AMMONIA AS A SUSTAINABLE FUEL

AMONIAK JAKO ZRÓWNOWAŻONE PALIWO

Abstract: An ammonia evaluation as a potential sustainable fuel in comparison with other fuels was made. Values of laminar burning velocity ammonia at ambient and elevated temperatures 20, 100, 200, 250 °C and pressure 100 and 500 kPa using the data from SAFEKINEX project were estimated.

Keywords: ammonia flammability, burning ammonia-air mixtures, laminar burning velocity

Introduction

With the increasing global population and dwindling energy resources, there is a need to search for alternative energy sources and carriers. They must be able to satisfy the world's growing demand for energy, generating the least possible amount of greenhouse gases and pollutants into the environment. Energy storage in the form of electricity is still a big challenge, on which the researchers from around the world are working. Therefore, only the synthesis of simple chemical compounds, like ammonia and using them as an energy carrier give the possibility of reduction of greenhouse gases emission in the near future [1–4].

Ammonia is a large-scale synthesis product, widely used in many industries [5]. Its global production in 2013 was estimated to approx. 140 million Mg [6]. It is mainly used for agricultural purposes as well as for the production of explosives, synthetic fibers, detergents and pharmaceuticals. The process of its production by Haber-Bosch method, requires a high temperature (~500 °C) and very high pressure (15–30 MPa). The raw material for the process is the most a natural gas [7]. Estimated carbon dioxide emission during ammonia synthesis from natural gas is *ca.* 1.87 Mg of CO₂/Mg NH₃.

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Such a large amount of carbon dioxide emitted, the complexity and technical difficulties of the Haber-Bosch process, are forcing to look for alternative sources of hydrogen, as well as search for new, better ammonia synthesis process [6–8].

Ammonia as an energy carrier

The biggest advantage of ammonia and a high interest of it as a potential fuel are caused by its possible of non CO₂-emission during the synthesis and the combustion process [1, 4]. The combustion is a very complicated process, which progresses with participation of a lot of intermediate products and elementary reactions [9, 10]. The main products of ammonia combustion in the air are: nitrogen, water steam and nitrogen oxides. The amount of nitrogen oxides depend on the kind of mixture and conditions of the process [11]. If the concentration of nitrogen oxides was significant, it might be proposed the selective catalytic reduction as a method to remove them from exhaust gases. The reagent to remove nitrogen oxides might also be ammonia [12].

For the last years hydrogen has been considered as the most promising fuel, but because of its low critical temperature the research about the new and more effective methods of its storage are still in progress [13]. For application a fuel in transportation sector, a very important are: mass and volume of fuel tank, distance range and rate of its fill/regeneration. Low volume energy density of hydrogen creates an advantage of ammonia as a transportation fuel. Compressed ammonia to 1 MPa indicates volume energy density (13.6 GJ m⁻³) bigger than metal hydrides under pressure 1.4 MPa (3.6 GJ m⁻³) and also bigger than even actual used fuels, like compressed natural gas to 25 MPa (10.4 GJ m⁻³). Ammonia can be also the direct source of hydrogen in fuel cells

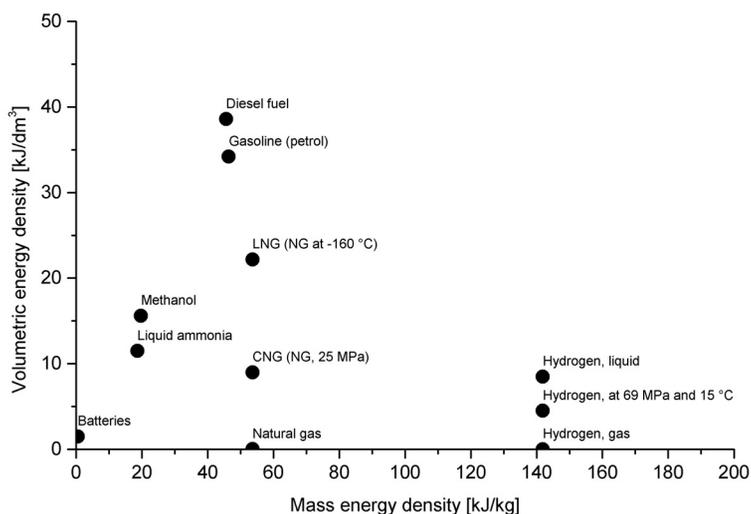


Fig. 1. The comparison of volumetric energy density and gravimetric energy density for different fuels and ammonia [2]

and in the spark-ignition engine [2]. Volume density energy in dependence on mass density energy was shown on the Fig. 1.

Synthesis ammonia by Haber-Bosch method is related inseparably with the hydrogen production process. Currently, the most common methods of hydrogen production are steam reforming of natural gas, partial oxidation of hydrocarbons and coal gasification. It means, that almost entire currently produced hydrogen comes from production process, in which fossil fuels are used. The CO₂-free fuel cannot emit significant amount of greenhouse gases during using of fuel and also during its production. It forces to produce hydrogen and ammonia only with using nuclear or renewable energy [7, 14].

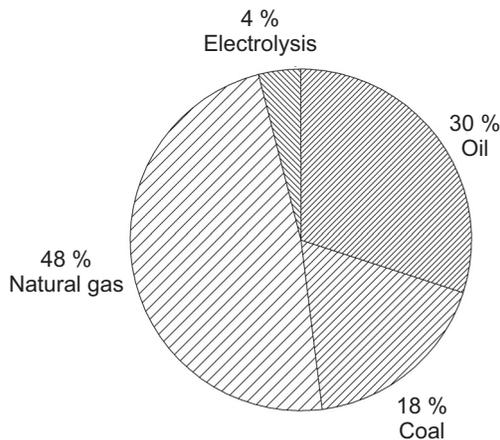


Fig. 2. The participation of different fuels in hydrogen production [7]

In comparison with metal hydrides (H_2 cont. *c.a.* 25 kg/m³) content of hydrogen in liquid ammonia (condition: 20 °C and 0.86 MPa) is above four times bigger (*c.a.* 108 kg/m³). The consideration of ammonia as a fuel has to include not only its directly combustion in engine, but also possibility of recovery hydrogen from ammonia – at least a part of it in order to increase value of laminar burning velocity [2, 15].

Ammonia cannot be directly used in the spark ignition engine. Despite of its high octane number (110–130), the values of laminar burning velocity of ammonia-air mixtures are too low. The solution of this problem can be an addition of an another fuel with high laminar burning velocity, like *eg* hydrogen. The sufficient amount of hydrogen to increase properties of the combustion can be prepared by thermal or catalytic ammonia decomposition at the expense of some of the energy from its combustion. The cooling effect during the evaporation of ammonia at an appropriate concept of technology can significantly improve the performance of a heat engine [2, 3, 11].

The advantage of ammonia as an energy carrier are also the already existing infrastructure of manufacturing, distribution and more than 100 years of experience in the synthesis, storage and marketing. Ammonia can be stored under similar conditions as propane, *ie* at a pressure of *approx.* 0.8 MPa at ambient temperature. In case of leakage, it is dispersed due to the lower density in comparison to the air [2, 16].

Dangers connected with commercial using of ammonia

Ammonia is a toxic, flammable, colorless gas with a characteristic, suffocating odor. It is easily perceptible in air above 20 ppm concentration. There are known few of severe disasters connected with a production and storage of ammonia [17]. The most significant danger in production and distribution of ammonia is its toxicity and flammability in mixture with the air [16].

In comparison with others fuels, the flammability limits of ammonia under normal conditions are relatively narrow (16–25 % vol.), and autoignition temperature is high (651 °C). Eg. the flammability limits of others fuels respectively are: hydrogen (4–75 % vol.), methane (5–15 % vol.), gasoline (1.4–7.6 % vol.) and gas oil (0.6–5.5 % vol.) [2]. The most significant indexes of explosiveness of gases are: maximal pressure during explosion P_{ex} , maximum rate of pressure rise $(dP/dt)_{ex}$, deflagration index K_G , explosion and detonation limits, minimal ignition energy E_{min} , and autoignition temperature T_s . Maximum rate of pressure rise during explosion and deflagration index are considered as the indices, which the best show dynamic (violence) explosion of gases [18, 19].

In respect to the mathematical notation, the rate of pressure rise $(dP/dt)_{ex}$ is defined as the maximum value of first derivative with respect to time during the explosion mixture of a precisely determined composition. The rate of pressure rise is dependent from a vessel volume. To describe the explosion phenomena is applied deflagration index K_G , which was presented by expression (1); V is a vessel volume:

$$K_G = \left(\frac{dP}{dt} \right)_{ex} V^{\frac{1}{3}} \quad (1)$$

Laminar burning velocity S_L shows the violence and gas dynamics of the combustion process and it is applied to evaluation of the substance as a potential fuel. During obtaining maximal rate of pressure rise, laminar burning velocity can be approximated by the expression (2); R – vessel diameter, P_{ex} – maximal pressure during explosion, P_i – initial pressure, P – measured pressure, γ – heat capacity ratio (C_p/C_v), dP/dt – current pressure rise. The following expression has been derived for the spherical reactor [20]:

$$S_L \approx \frac{R}{3(P_{ex} - P_i)} \left(\frac{P_i}{P} \right)^{\frac{1}{\gamma}} \left[1 - \left(\frac{P_i}{P} \right)^{\frac{1}{\gamma}} \frac{P_{ex} - P}{P_{ex} - P_i} \right]^{-\frac{2}{3}} \frac{dP}{dt} \quad (2)$$

In Tables 1 and 2, rates of pressure rise $(dP/dt)_{ex}$ for ammonia, obtained by Federal Institute for Materials Research and Testing (BAM) were shown. The research were carried out in cylindrical reactor (6 dm³; initial pressures: 100 and 500 kPa; initial temperatures, T_i : 20, 100, 200 and 250 °C) in within the European project SAFEKINEX [18, 21].

Table 1

The values $(dP/dt)_{ex}$ at initial pressure $P_i = 100$ kPa [21]

T_i [°C]	$(dP/dt)_{ex}$ [100 kPa/s] (values in brackets show concentration of ammonia in mole percent)								
	20	1.87 (15 %)	1.82 (18 %)	3.83 (19 %)	12.29 (21 %)	22.74 (23 %)	30.28 (25 %)	4.37 (30 %)	1.60 (35 %)
100	3.01 (15 %)	3.2 (17 %)	9.52 (19 %)	35.56 (21 %)	41.26 (23 %)	36.03 (25 %)	8.50 (30 %)	3.15 (35 %)	
200	9.48 (15 %)	16.23 (17 %)	39.62 (19 %)	71.73 (21 %)	71.12 (23 %)	72.45 (25 %)	31.8 (30 %)	11.37 (35 %)	
250	11.71 (15 %)	18.52 (17 %)	41.83 (19 %)	48.35 (21 %)	45.92 (23 %)	42.01 (25 %)	30.67 (30 %)	10.96 (35 %)	3.09 (40 %)

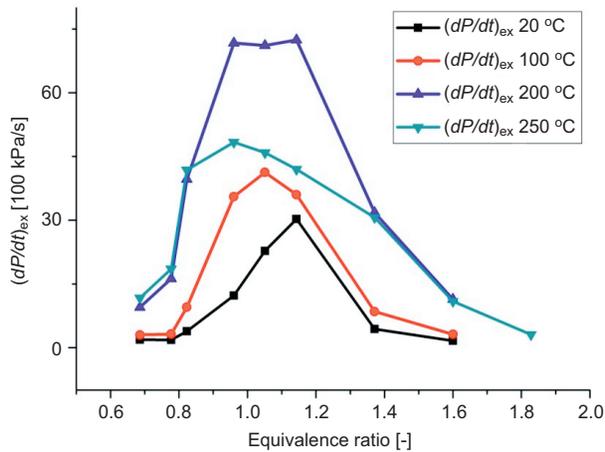
Fig. 3. $(dP/dt)_{ex}$ vs equivalence ratio at in different initial temperature, $P_i = 100$ kPa [21]

Table 2

The values $(dP/dt)_{ex}$ at initial pressure $P_i = 500$ kPa [21]

T_i [°C]	$(dP/dt)_{ex}$ [100 kPa/s] (values in brackets show concentration of ammonia in mole percent)								
	20		63.33 (17 %)	106.32 (19 %)	142.75 (21 %)	204.33 (23 %)	134.02 (25 %)	15.01 (30 %)	5.27 (35 %)
100	21.6 (15 %)	88.77 (17 %)	118.59 (19 %)	226.86 (21 %)	287.77 (23 %)	237.04 (25 %)	83.91 (30 %)	2.31 (35 %)	
200	71.77 (15 %)	117.79 (17 %)	162.45 (19 %)	186.42 (21 %)	232.54 (23 %)	191.03 (25 %)	114.41 (30 %)	22.09 (35 %)	3.56 (37 %)
250	28.54 (15 %)	56.51 (17 %)	126.62 (19 %)	264.1 (21 %)	301.94 (23 %)	324.31 (25 %)	151.89 (30 %)	63.13 (35 %)	

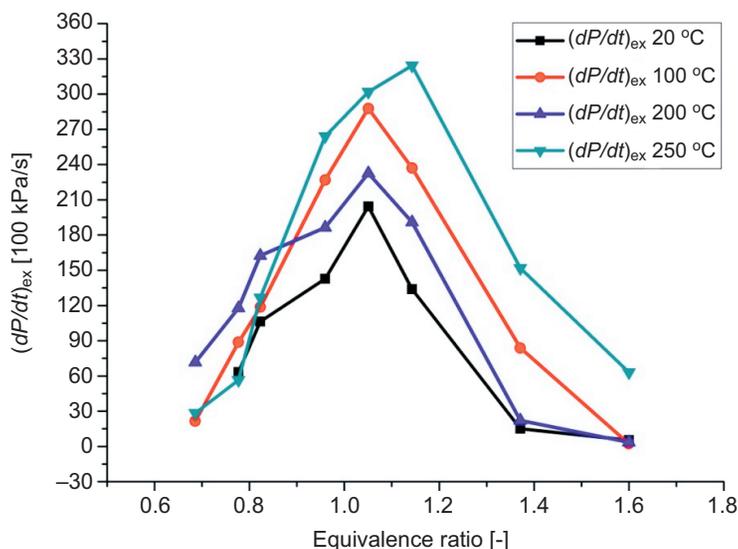


Fig. 4. $(dP/dt)_{ex}$ vs equivalence ratio at in different initial temperature, $P_i = 500$ kPa [21]

To estimate the value of laminar burning velocity in the point of maximum pressure rise were assumed that the maximum pressure rise was reached while the flame front had not reached the wall of reactor. The data from SAFEKINEX project for ammonia [12] and expression (2) to estimation S_L values were used. The obtained values of laminar burning velocity for initial pressure 100 and 500 kPa respectively in Table 3 and 4 were listed.

Table 3

The estimated values of $S_{L,ex}$ at initial pressure $P_i = 100$ kPa

T_i [°C]	$S_{L,ex}$ [m/s]								
	(values in brackets show concentration of ammonia in mole percent)								
20	— (15 %)	0.116 (18 %)	0.133 (19 %)	0.086 (21 %)	0.051 (23 %)	0.064 (25 %)	0.072 (30 %)	— (35 %)	
100	— (15 %)	— (17 %)	0.053 (19 %)	0.149 (21 %)	0.125 (23 %)	0.127 (25 %)	0.091 (30 %)	— (35 %)	
200	0.107 (15 %)	0.130 (17 %)	0.206 (19 %)	0.301 (21 %)	0.230 (23 %)	0.267 (25 %)	0.160 (30 %)	0.077 (35 %)	
250	0.138 (15 %)	0.161 (17 %)	0.270 (19 %)	0.238 (21 %)	0.202 (23 %)	0.230 (25 %)	0.174 (30 %)	0.089 (35 %)	— (40 %)

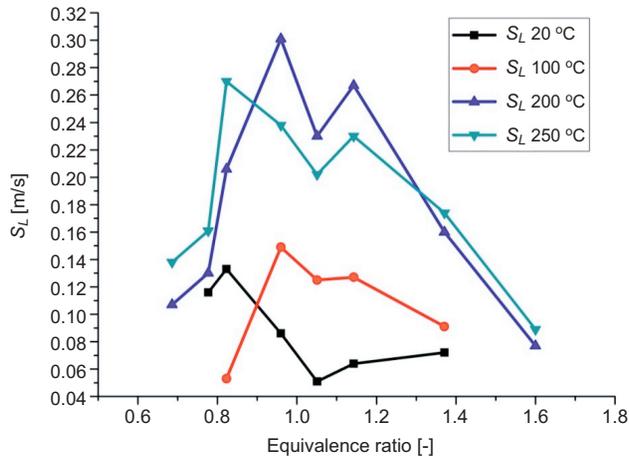


Fig. 5. $S_{L, ex}$ vs equivalence ratio at different initial temperature, $P_i = 100$ kPa

Table 4

The estimated values of $S_{L, ex}$ at initial pressure $P_i = 500$ kPa

T_i [°C]	$S_{L, ex}$ [m/s] (values in brackets show concentration of ammonia in mole percent)								
	20		0.053 (17 %)	0.052 (19 %)	0.068 (21 %)	0.072 (23 %)	0.060 (25 %)	0.045 (30 %)	— (35 %)
100	0.066 (15 %)	0.085 (17 %)	0.066 (19 %)	0.123 (21 %)	0.123 (23 %)	0.119 (25 %)	0.064 (30 %)	— (35 %)	
200	— (15 %)	0.113 (17 %)	0.144 (19 %)	0.163 (21 %)	0.197 (23 %)	0.162 (25 %)	0.089 (30 %)	0.048 (35 %)	— (37 %)
250	0.059 (15 %)	0.116 (17 %)	0.199 (19 %)	0.224 (21 %)	0.250 (23 %)	0.291 (25 %)	0.150 (30 %)	0.089 (35 %)	

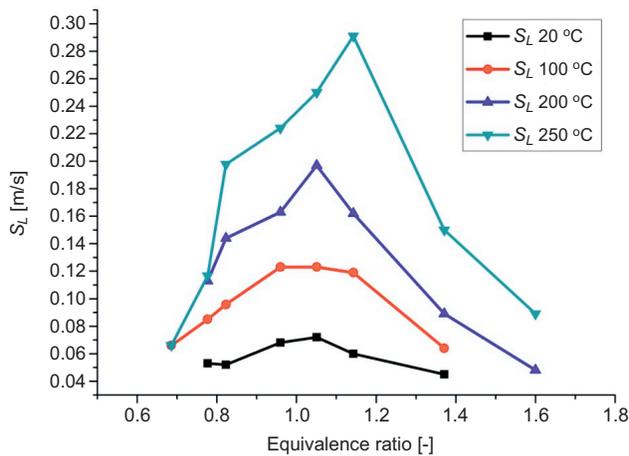


Fig. 6. $S_{L, ex}$ vs equivalence ratio at different initial temperature, $P_i = 500$ kPa

Conclusions

Ammonia can be considered as a potential fuel in the short and long term perspective of using it. It has low values of laminar burning velocity but this is not major issue to apply it in spark-ignition engines – *eg* short term solution. Ammonia can also be a hydrogen's precursor in fuel cells – *eg* long term solution. It must be kept in mind that above sample solutions would be reasonable if the energy used to produce ammonia came from renewable sources.

The greatest challenge for ammonia applying in the public space as an energy carrier is its strong toxicity. Simultaneously, there only have been noticed few cases of deadly poisoning, caused by release of ammonia from refrigeration systems into the public space [22].

The explosiveness research of the substances present in public space are always important in aspect of safety. Projects as SAFEKINEX give very important, in aspect of safety data for many substances present in the public space under different conditions.

It is important to underline that the obtained values of laminar burning velocity could contain gross errors, especially under initial conditions 100 kPa and 20 °C. Despite this, the obtained values are consistent with data in standard conditions in available science literature [23].

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Abstrakt: W pracy dokonano oceny przydatności amoniaku jako potencjalnego paliwa w odniesieniu do paliw konwencjonalnych. Wykorzystując dane z projektu SAFEKINEX, oszacowano także wartości prędkości spalania laminarnego amoniaku w temperaturze 20, 100, 200, 250 °C przy ciśnieniu 100 i 500 kPa.

Słowa kluczowe: palność amoniaku, spalanie mieszanki amoniak-powietrze, prędkość spalania laminarnego

