



Explosion Characteristics of Water Gas for Fischer–Tropsch Process

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Abstract

Experimental study is presented for different CO-air and H₂-air mixtures at a maximum concentration range. CO concentration ranges from 12.5 ± 0.2 % vol. to 70.5 ± 0.2 % vol. and H₂ concentration ranges from 4.5 ± 0.2 % vol. to 76.0 ± 0.2 % vol. in a mixture with air at ambient atmospheric pressure (1 bar) and temperature (25°C). The explosion parameters of explosion pressure and maximum rate of pressure rise for water gas-air mixture were measured within the studied range, i.e. 0.30–2.13 at temperature of 25°C and pressure of 101 kPa. The experimental values of the maximum explosion pressure is compared with the mathematical modeling of this gas. The influence of initial concentration on the explosion characteristics were discussed.

Keywords: explosion modeling, explosion characteristics, carbon dioxide, hydrogen, water gas

Introduction

There is current interest in the production of alternative feedstock sources for the production of gas mixture composed of mainly hydrogen and carbon monoxide. Much of the research has focused on steam reforming or co-gasification processes with air and steam (Saad and Williams, 2017). Fischer-Tropsch synthesis (FTS) is considered one of the most attractive routes to convert syngas derived from coal, natural gas, and biomass into liquid fuels and chemicals. Among the catalysts containing active metals, iron-based catalysts have considerable merits, particularly when the FTS is performed with hydrogen-deficient syngas (H₂/CO ≤ 1.0); due to their potential activity for a water-gas shift (WGS) reaction as well as their high activity and low cost (Chun et al., 2014). In the FTS, the water gas is one of the most important reactants used to balance the H₂/CO ratio. It provides a source of hydrogen at the expense of carbon monoxide, which is important for the production of high purity hydrogen for use in ammonia synthesis. The focus of this contribution is the explosion characteristics and hazards arising from the water gas. Primarily, these are the hazards of fire and explosion induced by flammable components of water gas. In order to prevent explosions when storing and handling water gas it is necessary to know the explosion limits of individual gas components and its gas mixtures in mixture with air. However, water gas composition can vary significantly. Therefore, for each gas composition the explosion limits would have to be determined. This would require a considerable amount of time and effort. Due to this fact, the explosion limits of water gas are frequently referred to only by the hydrogen fraction of the gas mixture in the safety-rel-

evant literature. In reality as water gas consists of hydrogen and carbon monoxide and further residual gases the explosion limits are generally over or underestimated. The paper presents the results of an experimental evaluation of the safety characteristics for water gas multi-component mixture at elevated temperatures of 50°C, 100°C and 150°C.

Materials

All investigated chemicals are purchased from commercial companies with guaranteed mass fraction purity. The chemicals used are summarized in Table 1.

Test method

Experiments have been made according to EN 1839 and EN 15967. Procedure for water gas explosion starts with evacuation to pressure less than 0.4 bar to leave a space for the water gas. For example, the use of water gas concentration of 6 vol. % require the partial pressures of water gas to be added is 0.06 bar. Then the evacuation pressures should be 0.34 bar. PLC starts the experiment where 60 ms is counted as ignition delay time, and then the water gas is mixed by blowing dispersion air into the water gas mixture inside the chamber. After that, the mixture is ignited either by the electric discharge or by current source for pyrotechnic igniter. The explosion indices are then measured and calculated.

Experimental Apparatus

Experiments were done in 0.02 m³ chamber (CA 20L) made by OZM Research in accordance with EN 1839 and EN 15967. It is the stainless steel (1.4435) double-jacketed vessel

Tab. 1. Physical and safety properties of experimental materials

Tab. 1. Właściwości fizyczne i bezpieczeństwa materiałów eksperymentalnych

Component	Formula	Purity (mass %)	Company	LEL (vol %)	UEL (vol %)
hydrogen	H ₂	>99,8	Siad	4.0	77.0
carbon monoxide	CO	>99,9	Siad	11.0	76.0

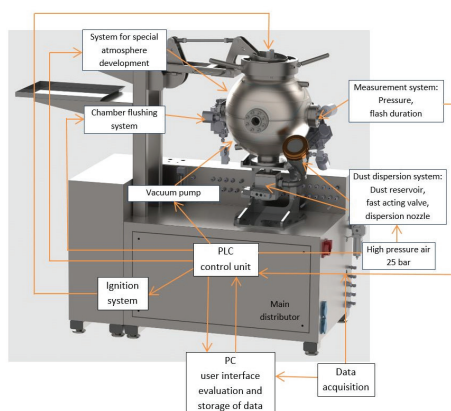


Fig. 1. Schematic introduction of the 20-L chamber system

Rys. 1. Schemat systemu komór 20-L

of spherical shape with an internal diameter of 336 mm. The vessel is provided with an opening of an inside diameter of 148 mm. The whole system is schematically introduced at Figure 1.

Highly dynamic temperature control system Presto A30 by JULABO is used for heating of the chamber. Permanent spark generator was made in accordance of EN 15967 with Tungsten electrodes with a distance of 6 mm. A pair of piezoelectric pressure sensors by Kistler, type 701A. Pressure range set for the sensors is 2.5 MPa and natural frequency 70 kHz. Data are recorded by four-channel data card with a sampling rate 50 kS/s/channel. PLC Siemens Simatic 1215 connected to PC used as a user interface automatically control whole procedure including fast acting valve timing. The chamber is equipped by thermocouple for temperature monitoring, especially for measurement of temperature in time of ignition. Correct gas mixture composition is assured by partial pressure method. Pressure transducer measures internal pressure.

Calculation procedure

For all concentrations of the water gas/air mixture, a calculation method of minimizing free Gibbs energy was used. The calculation procedure is described in (Skrinsky and Skrinska, 2014). For each equivalence ratio, the experimental explosion pressures (p_{ex}) were compared with the calculated adiabatic explosion pressures (p_g) under the assumption of chemical equilibrium reached in the flame front. As input parameters, the kinetic mechanisms and thermodynamic data sets (C_p , S_0 , H_0 , G_0) were used primarily from THERMO.dat databases of Explosion Pressure (Wolanski et al., 2004) and Thermdat.tdd from GASEQ (Morley, 2004) in CHEMKIN standard polynomial format. The results of adiabatic explosion pressure calculations were used to predict the initial values for experimental water gas/air measurement and are in Figure 6.

Results and discussion

Figures 2–5 plot explosion pressure (P_{ex}/P_0) and the rate of pressure rise (dP_{ex}/dt) versus equivalence ratio at ambient initial temperature (25°C) and ambient initial pressure (1.0 bar) for pure hydrogen and pure carbon monoxide, respectively.

Figures 2–5 shows experimental results for all the test runs. All the explosion pressure curves present a similar behavior that the pressure almost keeps constant at the initial stage of the flame propagation and then increases sharply until reaching its peak. It has been well established that a progressive change occurs in the variety of some explosion properties of gases when mixed them together. A very interesting example of such seeming differences is given by Figure 6–7 for different hydrogen-carbon monoxide-air mixtures. The search for the explosion parameters of the water gas was initiated in the $\Phi=0.30$ where the lower explosion limit have been expected.

The large uncertainties of the equilibrium calculations prevented from determination of precise explosion limits values. We consequently focused on the determination of maximum explosion parameters in the region between $\Phi=0.70$ –1.30. After several attempts consisting in adjusting the experimental apparatus, they were found close to the maximum explosion pressure predictions with the $P_{ex,max} - P_{AD,max} = 0.1$ bar(a).

Conclusion

Energy Research Centre, VŠB-TU Ostrava is aimed at fundamentally improving the understanding of gas mixtures oxidation processes, the risk assessment of such processes, their environmental efficiency and safety. The focus of this paper is to quantify the explosive properties of the water gas mixture for atmospheric initial temperatures and pressures.

The main conclusions are summarized as follows:

1. Explosion pressure, rate of explosion pressure rise and deflagration index of the water gas were deter-

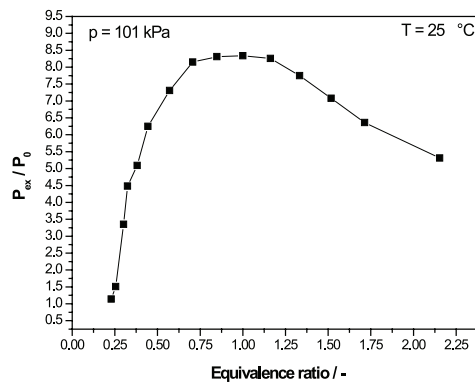


Fig. 2. P_{ex}/P_0 , versus equivalence ratio for H_2
 Rys. 2. P_{ex}/P_0 , a stosunek równoważności dla H_2

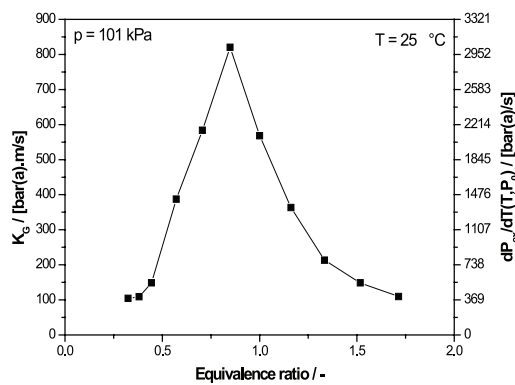


Fig. 3. $(dP/dt)_{ex}$ versus equivalence ratio for H_2
 Rys. 3. $(dP/dt)_{ex}$ versus stosunek równoważności dla H_2

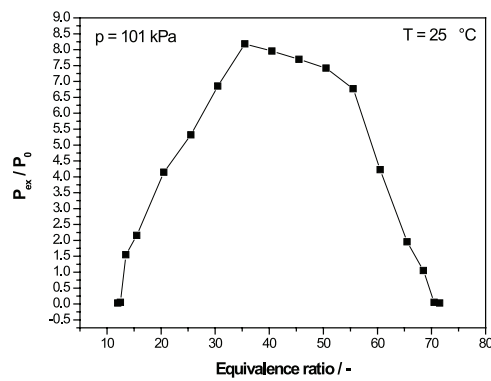


Fig. 4. P_{ex}/P_0 , versus equivalence ratio for CO
 Rys. 4. P_{ex}/P_0 , a stosunek równoważności dla CO

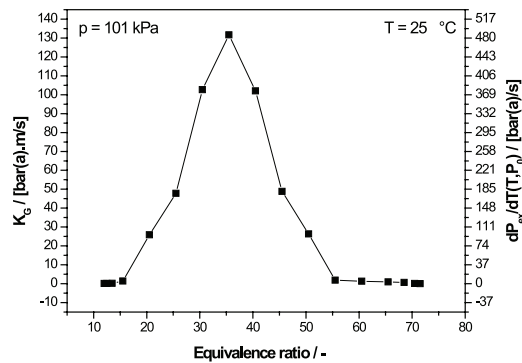


Fig. 5. $(dP/dt)_{ex}$ versus equivalence ratio for CO
 Rys. 5. $(dP/dt)_{ex}$ versus stosunek równoważności dla CO

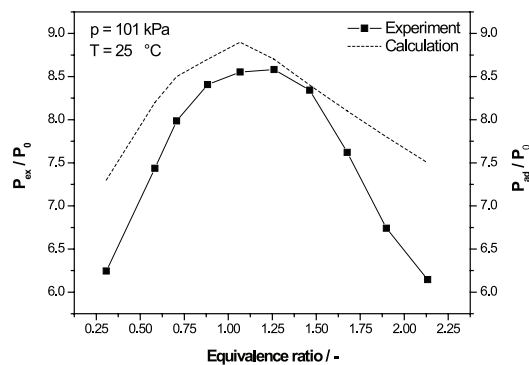


Fig. 6. P_{ex}/P_0 and P_{ad}/P_0 at $\Phi=0.30-2.15$, $P_0=0.1$ MPa and $T_0=25^\circ\text{C}$ for water gas-air mixtures
Rys. 6. P_{ex}/P_0 i P_{ad}/P_0 przy $\Phi = 0,30-2,15$, $P_0=0,1$ MPa i $T_0 = 25^\circ\text{C}$ dla mieszanin woda-gaz

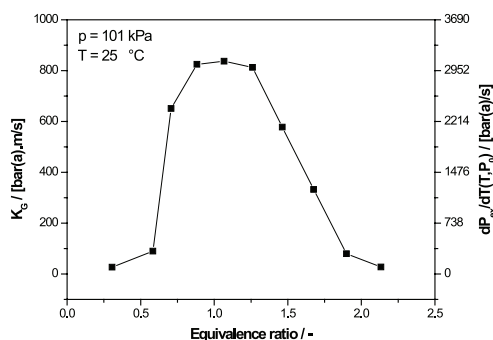


Fig. 7. $(dp/dt)_{ex}$ and K_G at $\Phi=0.30-2.15$, $P_0=0.1$ MPa and $T_0=25^\circ\text{C}$ for water gas-air mixtures
Rys. 7. $(dp/dt)_{ex}$ i K_G przy $\Phi = 0,30-2,15$, $P_0 = 0,1$ MPa i $T_0 = 25^\circ\text{C}$ dla mieszanin woda-gaz

mined in the 0.02 m^3 closed spherical chamber from the respective recorded pressure-time curves.

2. Explosion pressure, rate of explosion pressure rise and deflagration index of the water gas mixture reach maximum values near the stoichiometric concentration with an equivalent ratio $\Phi = 1.15$ within the studied range, i.e. $0.30-2.13$ at temperature of 25° and pressure of 101 kPa .
3. The maximum explosion pressure, p_{max} , was determined as the highest p_{ex} found for the mixture compositions investigated and is equal to 8.6 bar(a) .
4. The maximum rate of pressure rise $(dp/dt)_{max}$ reported is the highest $(dp/dt)_{ex}$ found for the mix-

ture compositions investigated and is equal to 3088 bar(a).m/s .

5. The deflagration index was calculated from the experimentally determined $(dp/dt)_{max}$ value and is equal to 837 bar(a).m/s .

Acknowledgements

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Charakterystyka wybuchowości gazu wodnego w procesie Fischera–Tropscha

Przedstawiono badania eksperymentalne dla różnych mieszanin CO-powietrze i H₂-powietrze w maksymalnym zakresie stężeń. Zakres stężenia CO wynosi od 12,5 ± 0,2% obj. do 70,5 ± 0,2% obj. i stężenie H₂ wynosi od 4,5 ± 0,2% obj. do 76,0 ± 0,2% obj. w mieszaninie z powietrzem o ciśnieniu atmosferycznym otoczenia (1 bar) i temperaturze (25°C). Parametry wybuchu – ciśnienia wybuchu i maksymalnej szybkości wzrostu ciśnienia dla mieszaniny woda-gaz mierzono w badanym zakresie, tj. 0,30–2,13 w temperaturze 25°C i ciśnieniu 101 kPa. Wartości eksperymentalne maksymalnego ciśnienia wybuchu porównuje się z modelem matematycznym tego gazu. Omówiono wpływ początkowego stężenia na charakterystykę wybuchu.

Słowa kluczowe: modelowanie wybuchu, charakterystyka wybuchu, dwutlenek węgla, wodór, gaz wodny