REGRESSION EQUATIONS FOR CALCULATING THE SOLUBILITY OF HYDROGEN IN LIQUID FUELS

The efficiency of combustion of liquid fuels in heat engines is determined by their hydrocarbon composition. The rate of combustion and the completeness of combustion depend on the hydrocarbon composition of the fuel. One of the ways to increase the efficiency of combustion of fuel is to use fuel-hydrogen mixtures. The use of such mixtures gives prerequisites for low-temperature self-ignition of fuel droplets (about 590 °C). Preheating of the fuel gives the possibility of "explosive" combustion with increasing of the temperature up to 2500 K in 0.02 – 0.04 ms. This leads to the intensification of heavy fuel combustion. The use of fuel-hydrogen mixtures allows to obtain a low level of harmful emissions with flue gases and to reduce emissions: CO and CH – not less than 15%, CO2 – not less than 20%. A promising direction for the creation of such mixtures is the direct dissolution of hydrogen in liquid fuel. This simplifies the flow of the fuel-hydrogen mixture into the combustion chamber of the heat engine or into the cylinders of the internal combustion engines. Analysis of previous studies showed the possibility of obtaining a single form of regression dependence for calculations of the dissolution of hydrogen in liquid fuels. The processing of the literature data and the results of our own research gave a set of regression equations for calculating the solubility of hydrogen in liquid fuels: gas, diesel, fuel oil, LVGO, HVGO, GDAR, ABVB. The obtained regression dependencies show that with increasing average molecular weight the solubility of hydrogen in the fuel decreases. These regression dependencies make it possible to obtain baseline data for the design of fuel systems for supplying fuel and hydrogen mixtures to combustion chambers of heat engines. Studies of hydrogen-diesel have shown a decrease in the flash fuel temperature by 10 – 15 °C by comparison with pure fuel. For heavy fuels, this level of reduction of the fuel round is not sufficient. Therefore, it is necessary to conduct further studies on the intensification of the process of dissolution of hydrogen in heavy fuels. This will significantly reduce energy costs for the organization of the combustion process.

Key words: hydrogen, fuel, solubility, regression dependences.

INTRODUCTION. The combustion efficiency of liquid fuels in thermal installations is determined primarily by the hydrocarbon composition of the fuel. The combustion rate
and completeness of combustion depend on the hydrocarbon composition of the fuel. Therefore, the intensification of fuel combustion processes is an urgent task to improve the efficiency of heat engines.

One way to solve this problem is to use hydrogen-fuel mixtures [1]. The experimental results show that at low concentrations of hydrogen in fuel – air mixtures an abnormal increase in the completeness of fuel combustion is observed. The intensification of the combustion processes of fuel - air mixtures with hydrogen additives is confirmed by the data [2–4].

Research [1–4] was conducted on internal combustion engines, in which the fuel supply system was modernized. Hydrogen was supplied to the engine cylinders simultaneously with the supply of liquid fuel. This required the provision of a hydrogen pressure in the supply system exceeding the pressure of compressed air in the cylinder. This reduces the reliability of the internal combustion engine.

The obtained data [1] on the intensification of the process of burning liquid fuel with small additions of hydrogen to the fuel – air mixture allow us to make an assumption about the possibility of using fuel-hydrogen mixtures in heat engines. In this case, we can consider the process of obtaining fuel-hydrogen mixtures by pre-dissolving hydrogen in fuel. This simplifies the supply of fuel-hydrogen mixture to the combustion chamber of a heat engine or to the internal combustion engine cylinders.

Studies of the solubility of hydrogen in liquid fuel [5–10] allow us to conclude that the use of fuel-hydrogen mixtures in heat engines is promising. However, the process of dissolving hydrogen in liquid fuel is not well understood. The possibility of using hydrogen-fuel mixtures in heat engines requires additional research.

The solubility of hydrogen in liquid fuel substantially depends on the hydrocarbon and fractional compositions of the fuel. These parameters depend on the oil field and the characteristics of the rectification process. In addition, the constant hydrocarbon and fractional composition of the fuel is extremely difficult to ensure during operation of the heat engine. Therefore, it is advisable to have integral characteristics for estimating the amount of hydrogen dissolved in liquid fuel when it is saturated with hydrogen.

The aim of the work is to obtain regression dependences for calculating the saturation of light fuels (diesel fuel and kerosene) with hydrogen at atmospheric pressure and a temperature of up to 60 °C.

**EXPERIMENT AND DISCUSSION OF THE RESULTS.** Liquid fuel is a multicomponent mixture of organic substances Henry's law [11] for a multicomponent mixture, taking into account the Wohl’s expansion [12], can be represented as:

\[
\ln(H_{2,M}) = x_1 \cdot \ln(H_{21}) + x_2 \cdot \ln(H_{23}) - a_{13} \cdot x_1 \cdot x_3
\]

where \(H_{2,M}\) – Henry’s constant for a gas 2; \(x_1\) and \(x_2\) – share of solvents 1 and 3 in the mixture, respectively; \(H_{21}\) and \(H_{23}\) – Henry’s constants for individual solvents, respectively; \(a_{13}\) – the interaction parameter of the solvents from Wohl’s expansion of the excess chemical potential of the ternary mixtures.

Improving the modeling of hydrogen solubility in heavy oil cuts using an Augmented Grayson-Streed (AGS) approach...
gives a significant deviation from experimental data [7]. This is due to the difficulty in determining the exact proportions of organic matter in the fuel.

Another important factor is the achievement of an equilibrium state between the gas and liquid phases. The intensity of mass transfer between phases during the absorption of hydrogen by fuel is described by Fick's law [13]:

$$J = D \cdot \left( \frac{dc}{dn} \right),$$

where $J$ is the diffusion flux; $D$ is the diffusion coefficient of hydrogen in fuel; $c$ is the concentration of hydrogen in fuel; $n$ is position in the fuel layer.

The rapid achievement of equilibrium between the phases can be achieved with $D \to \infty$ or contact time $\tau \to \infty$. Parameters ($D$ and $\tau$) values cannot be reached equal to infinity in real experiments. Therefore, the experiment time [10] was determined based on the ratio of the dissolution time of a fixed volume of hydrogen at the beginning $\tau_b$ of the experiment to the time of dissolution of the same volume of hydrogen at the end of the experiment $\tau_e$ as $\tau_e / \tau_b = 15$ – based on the recommendations [14].

The value of the dosed hydrogen volume was taken equal to 0.01 $\pm$ 0.0002 L. The time of complete dissolution of hydrogen bubbles was recorded. During the experiment, the data obtained were entered into a program for calculating the dynamics of hydrogen dissolution. As a result of the calculation, a graph of hydrogen solubility and a regression dependence of solubility were obtained. An example of processing experimental data is shown in fig. 1: the abscissa axis is the logarithm of the time of dissolution of hydrogen in the fuel ($\log(\tau)$); the ordinate axis is the logarithm is the amount of dissolved hydrogen in the fuel ($\log(m)$); the vertical line is the predicted maximum amount of hydrogen in the fuel.

The graph (fig.1) showed the hydrogen solubility curve and the predicted limit value of the concentration of hydrogen in the fuel. The experiment ended when the solubility of hydrogen became equal to 0.97 from the equilibrium.

Based on the foregoing, it becomes appropriate to obtain regression equations for calculating the solubility of hydrogen in each fuel grade based on a regression analysis of experimental data [6–8, 10] and own experiments. Relevant physical properties for these fuels are given in table 1.

The data on hydrogen solubility in fuels (table 1) are summarized in the temperature range $T = 293 – 653$ K and pressures $P = 0 – 10$ MPa by the following regression dependence:

$$R(P, T) = A \cdot B$$

$$A(T) = a_0 + a_1 \cdot T + a_2 \cdot T^2$$

$$B(P) = b_0 + b_1 \cdot P + b_2 \cdot P^2$$
Regression equations for calculating the solubility of hydrogen in liquid fuels

Table 1
Characterization of fuels and experimental conditions

| Name of fuel, source          | Density, kg/l | T, K    | P, MPa |
|------------------------------|---------------|---------|--------|
| Kerosene (K) [6]             | 0.840         | 298–573 | 4.7–30 |
| Fuel oil (FO) [6]            | 0.930         | 473–573 | 10.0–30|
| Light Virgin Gas Oil (LVGO) [7] | 0.892       | 353–653 | 2.2–11 |
| Heavy Virgin Gas Oil (HVGO) [7] | 0.973      | 353–653 | 1.0–11 |
| GuDao Atmospheric Residuum (GDAR) [7] | 0.922       | 353–653 | 0.9–11 |
| Athabasca Bitumen Vacuum Bottoms (ABVB) [7] | 1.050       | 353–653 | 0.9–10 |
| Diesel fuel (DF) [10]        | 0.847         | 295–333 | Atmospheric |
| Fuel oil [10]                | 0.937         | 295–333 | Atmospheric |

Table 2
The coefficients in equation (3)

| Fuel     | a0   | a1   | a2   | b0   | b1   | b2   |
|----------|------|------|------|------|------|------|
| K [6]    | 1.69 | -7.0×10^{-3} | 1.19×10^{-5} | 0.55 | 0.46 | 1.54×10^{-3} |
| FO[6],[10] | 0.45 | -2.75×10^{-5} | 5.9×10^{-6} | 2.00 | 0.55 | 5×10^{-5} |
| LVGO [7] | 3.4  | -0.011 | 8.53×10^{-6} | 0.40 | 1.49 | 0.013 |
| HVGO [7] | 3.77 | -0.011 | 7.88×10^{-6} | 0.40 | 0.77 | 0.042 |
| GDAR [7] | 2.6  | -6.22×10^{-3} | 4.81×10^{-6} | 0.083 | 0.954 | -0.036 |
| ABVB [7] | 3.7  | -0.012 | 7.9×10^{-6} | 0.113 | 0.85 | -0.026 |
| DF [10]  | 3.3  | -0.0105 | 8.2×10^{-6} | 0.45 | 1.49 | 0.013 |

Table 3
The solubility of hydrogen in various fuels at atmospheric pressure and T = 298 K

| Parameter          | K    | DF   | FO   | LVGO | HVGO | GDAR  | ABVB |
|--------------------|------|------|------|------|------|-------|------|
| Solubility, l/l    | 0.363| 0.405| 0.309| 0.0359| 0.198| 0.097 | 0.099|
| Mean molar mass, g/mol | 162 | 144  | 310  | 250  | 350  | 1678  | 1700 |

The coefficients in equation (3) are shown in table 2. The error in determining the amount of hydrogen dissolved in the fuel according to the given regression does not exceed ± 8.3%. What is quite acceptable for the predictive assessment and design of fuel systems for such mixtures [15].

A graphical interpretation of experimental data processing in the form of paired regression (the dependence of hydrogen solubility on temperature and pressure) for LVGO [7] is shown in fig. 2.
Table 3 presents data on the solubility of hydrogen in various fuels at atmospheric pressure and \( T = 298 \text{ K} \). The data in Table 3 show that the solubility of hydrogen in the liquid fuel depends on the average molecular weight of the fuel. As the average molecular weight of the fuel increases, the solubility of hydrogen in it decreases. The amount of dissolved hydrogen in light grades of fuel is quite sufficient to reduce the flash point by 10 – 15 K. Further increase of the concentration of hydrogen in light fuel is not appropriate based on the safety requirements of the heat engine.

CONCLUSIONS. The obtained regression equations allow us to predict the solubility of hydrogen in liquid fuel. Light grades of fuel do not require special preparation before the process of dissolution of hydrogen at atmospheric pressure. For heavy fuels it is necessary to develop methods of intensification of the process of dissolution of hydrogen in the fuel.

Fig.2. The dependence of hydrogen solubility on temperature and pressure) for LVGO [7].

\[ \text{Solubility of Hydrogen} \]

\[ \frac{100}{P} \]

\[ T \]

\[ 0 \rightarrow 600 \]

\[ 1 \rightarrow 12 \]

\[ 300 \rightarrow 500 \]

\[ 400 \rightarrow 600 \]

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Regression equations for calculating the solubility of hydrogen in liquid fuels

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Efficiency of burning liquid fuels in thermal power units depends primarily on the hydrocarbon composition of the fuel. The rate of combustion and completeness of combustion depend on the hydrocarbon composition of the fuel. Therefore, the intensification of the combustion process is an urgent task in the development of thermal engines. One of the ways to improve the efficiency of combustion is the use of liquid hydrogen mixtures. This simplifies the delivery of liquid hydrogen fuel to the combustion chamber of the thermal engine or to the cylinders of the engine. Analysis of literature data and results of own research showed the possibility of obtaining the solubility of hydrogen in liquid fuels: kerosene, diesel fuel, fuel oil, LVGO, HVGO, GDAR, ABVB, analysis of the obtained regression dependences showed that with an increase in the average molecular mass of the fuel, its solubility decreases. The obtained regression dependences allow obtaining the initial data for the design of fuel systems of liquid hydrogen fuel mixtures in thermal engines.

**References**

1. Bortnikov L.N., Rusakov M.M., Petrov R.E. Activation by hydrogen of the combustion of hydrocarbon fuels. *Newsletter of sciences TSU*. 2012. 4 (22): 137. [in Russian].

2. Pavlov D.A., Bortnikov L.N. Research the performance engine at hydrogen additive in heterogeneous formation FAM. *Newsletter of sciences TSU*. 2012. 4 (22): 183. [in Russian].

3. Novoselov S.V. Use of hydrogen as a motor fuel. *Thermal Engineering*. 1996:27. [in Russian].

4. Siroti A.A., Radchenko N.I., Shcherbak Yu.G. Profitability of ship medium-speed diesel with application of small additives of hydrogen to the diesel fuel, working according to the screw characteristic. *Aerospace technical and technology*. 2014. 6 (113): 89. [in Russian].

5. Gonigberg M.G. Chemical equilibrium and reaction rate at high pressures. M. *Publishing House of the Academy of Sciences of the USSR*. 1960. [in Russian].

6. Vishnevsky N.E., Glukhov N.P., Kovalev I.S. Machine and apparatus with a sealed
electric drive. (Leningrad: Mechanical engineering, 1977).
7. Torres I. R., de Hemptinne J.-C., Machin I. Improving the Modeling of Hydrogen Solubility in Heavy Oil Cuts Using an Augmented Grayson Streed (AGS) Approach. *Oil & Gas Science and Technology – Rev. IFP Energies nouvelles*, 2013. **68**(2):217.
8. Adrian A. Rodriguez Pinos. Modeling of Hydrogen Consumption and Process Optimization for Hydrotreating of Light Gas Oils. (*University of Saskatchewan*, 2017).
9. Humberto Aguilar-Cisneros, Veronica Uribe-Vargas, Bernardo Carreon-Calderon, Jose Manuel Dominguez-Esquivel, Mario Ramirez de-Santiago Hydrogen Solubility in Heavy Undefined Petroleum Fractions Using Group. *Contributions Methods. Oil & Gas Science and Technology – Rev. IFP Energies nouvelles*, 2017. **72**(2): 11.
10. Leybovych L., Yevstigneyev Y.V. Solubility of hydrogen in mixtures of liquid fuels at atmospheric pressure. *International periodic scientific journal. Modern engineering and innovative technologies*. 2018. **3**(5): 46.[in Russian].
11. Sander R. Compilation of Henry's law constants (version 4.0) for water as solvent, *Atmos. Chem. Phys.* 2015. **15**: 4399.
12. Steven L. Jackson. Extension of Wohlf's ternary asymmetric solution model to four and *n* component. *American Mineralogist*. 1989. **74**: 1.
13. Conlisk A. Terrence. Essentials of Micro- and Nanofluidics: With Applications to the Biological and Chemical Sciences. 2013. *Cambridge University Press*. 537.
14. Gladkaya A. V., Vinogradov O. L. Entire functions of exponential type deviating least from zero with a weight. *Abstracts of the international conference “Comlex analysis & related topics”*. St. Petersburg, 2014. 13.
15. Rules for Construction of Power Boilers. *ASME Boiler and Pressure Vessel Code*. 2010. 341.

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