

Engancement in the oxidative stability of commercial gasoline fuel by the goethite nanoparticles

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Abstract

It is well-established that traces of the transition metals strongly accelerate the gasoline oxidation significantly decreasing the gasoline storage time. This paper explores the opposite effect of the goethite nanoparticles on the oxidative stability of the commercial gasoline. The goethite nanoparticles were obtained in a colloidal solution by a simple thermal decomposition of iron(II) oleate. The size and the structure of the nanoparticles are confirmed by TEM, Mössbauer spectroscopy, and elemental analysis. Model study of the benzyl alcohol oxidation shows that the goethite nanoparticles significantly inhibit the oxidation process. Study of the effect of the goethite nanoparticles on the induction period of the commercial gasoline reveals a significant elongation of the induction period. It highlights that the goethite nanoparticles are capable to enhance the storage time of a gasoline. The effect may be associated with a quenching of free radicals by the goethite nanoparticles.

Keywords: Goethite nanoparticles, Oxidative Stability, Induction period

Introduction

Automotive gasoline is a motor fuel extensively used in spark-ignition engines. Compounds presented in a gasoline fuel are susceptible to oxidation by the atmospheric oxygen forming undesirable oxidation products between the production and final use of a gasoline [1,2]. The formation of the oxidation products results in a degradation in properties of a gasoline. Additives are frequently added to gasoline to address oxidative stability and other issues [3]. Among various additives, the phenolic antioxidants are of special interest because they are able to directly seize peroxy radicals formed during the oxidation, thus breaking the auto-oxidation chain reaction. The two different types of antioxidants used in gasoline are phenylenediamines and various phenols [3,4].

It is well-established that traces of the transition metals strongly accelerate the gasoline oxidation, catalyzing the decomposition of hydroperoxides into radical species, in particular, those suffering a transfer of one electron, such as copper, iron, cobalt, and manganese ions, which are the most effective [5–8]. The presence of the metallic species in automotive fuels is generally undesirable because it is associated with corrosion, metal deposition on engine parts, and poor fuel performance as a result of oxidative decomposition reactions [6,9].

On the other hand, the metal oxide nanoparticles of the sizes in the range of 1-20 nm are widely used in various fields of science and technology because they show unique properties [10–13]. The metal-containing nanoparticles have already shown a capability to inhibit chemical reactions [14–16]. Group VIII metal nanoparticles, e.g., platinum and palladium, accelerate the rate of the radical chain reactions [17,18]. Among various metal-containing nanoparticles, the iron-containing nanoparticles have found wide applications as catalysts, drug delivery system, high-density memory devices, and others [19]. Based on the literature data, there is a reason to believe that the iron-containing nanoparticles can also change the rate of the radical chain oxidation processes.

This study shows the effect of the goethite nanoparticles on the rate of the radical chain oxidation of

benzyl alcohol with atmospheric oxygen. The goethite nanoparticles with average size of 7.1 nm are found to inhibit the benzyl alcohol oxidation. These model studies allowed us to reveal that the goethite nanoparticles effectively enhance the oxidative stability of the commercial gasoline.

Materials and methods

The preparation of the FeOOH nanoparticles colloidal solution was performed according to a modification of the procedure described earlier [20]. The procedure is based on the iron(II) oleate thermal decomposition. The average nanoparticles size was determined by a transmission electron spectroscopy (TEM). The structural characteristics of the nanoparticles were found by the Mössbauer and Fourier transform infrared spectroscopies. The total iron content was measured by a photochemical method and the oxygen pulse titration method.

The initiated oxidation of benzyl alcohol was studied volumetrically according to the procedure described elsewhere [21,22]. The benzyl alcohol, chlorobenzene, and azobisisobutyronitrile used in the oxidation reaction were purified by the standard procedure [23]. The conditions of the reaction were chosen as follows: the temperature was kept at 50°C, the oxygen pressure was $P(O_2) = 0.1$ MPa, the concentration of benzyl alcohol was 4.82 mol/L, and the rate of the initiation reaction was $W_i = 2.98 \cdot 10^{-8}$ mol/(L·s). The rate of the oxidation was evaluated from the amount of oxygen consumed, which was measured volumetrically. The rate of the oxidation was determined by the procedure described elsewhere [24].

The fresh gasoline used in this study was provided by a local refinery and fulfilled specified quality requirements. The physical and chemical properties of the gasoline are presented in Table 1.

The oxidative stability of gasoline was measured by the induction period test according to the standard procedure [25]. The test method covers the determination of the stability of gasoline in finished form only, under accelerated oxidation conditions. According to the standard procedure, the 50 mL of gasoline is oxidized in a pressure vessel with the oxygen pressure at 700 kPa and heated at a temperature of 100°C. The pressure was recorded continuously until the breakpoint is reached. The time required for the sample to reach this point is the observed induction period. The induction period was determined as an elapsed time between starting the test and the breaking point, which is defined as a pressure drop of 10 % below the maximum pressure as detected in the pressure versus time curve. We tested two samples of gasoline. One sample is a fresh gasoline, whereas the second sample is the gasoline containing 0.007 % of the goethite nanoparticles.

Results and discussion

Fig. 1(a) shows a TEM image of the FeOOH nanoparticles prepared by the thermal decomposition of the iron(II) oleate. The average size of the FeOOH nanoparticles is found to be 7.1 nm. The corresponding size distribution of the nanoparticles shows that the size distribution is almost normal. The sample is characterized by a narrow width of the particle size distribution with the standard deviations less than 15 %. Fig. 1(b) presents Mössbauer spectrum of the FeOOH nanoparticles giving the isomer shift of 0.37 mm·s⁻¹ and the quadrupole splitting of -0.26 mm·s⁻¹. These values correspond to the goethite (α -FeOOH) [26]. Based on the elemental analysis and pulse O₂ titration methods, it was found that the iron content in nanoparticles is 63.0 %.

Fig. 2 gives the dependence of the rate of the benzyl alcohol oxidation on the goethite concentration and on the bulk Fe₂O₃ concentration. The rate of the oxidation without iron-containing compounds was found $W_0 = 2.0 \cdot 10^{-6}$ mol/(L·s). The bulk iron oxide does not change the oxidation rate of the benzyl alcohol for the studied concentrations. Contrary, the oxidation rate falls almost monotonically down with increasing the goethite nanoparticles concentration. The oxidation of the benzyl alcohol is fully suppressed by the goethite nanoparticles at the concentration $C_{FeOOH} = 0.35$ g/L. As a matter of fact, the

goethite nanoparticles used in the oxidation are the α -FeOOH nanoparticles stabilized by oleic acid and hexane in a colloidal solution. Effect of the oleic acid and hexane on the oxidation rate of the benzyl alcohol was separately tested under the same conditions. Neither oleic acid nor hexane does not change the rate of the oxidation and its value remains constant $W_0 = 2.0 \cdot 10^{-6}$ mol/(L·s).

Our studies show that a presence of the goethite nanoparticles with the size of 7.1 nm results in an inhibiting the chain oxidation of the benzyl alcohol. The liquid-phase oxidation of benzyl alcohol by molecular oxygen is the radical process that occurs via a formation of the intermediate free benzyl radicals (Bn^\bullet) and benzyl peroxy radicals ($BnOO^\bullet$) [27,28]. It includes reactions of the chain initiation, the chain generation, the chain propagation, the chain branching, and the chain termination. The inhibition of the oxidation process by nanoparticles may occur as a result of the appearance of the additional reaction that involves interaction between the goethite nanoparticles and the Bn^\bullet or $BnOO^\bullet$ radicals. Therefore, based on the obtained results, we assume that the goethite nanoparticles are capable to react with Bn^\bullet or $BnOO^\bullet$ radicals. It opens up the possibility to inhibit by the goethite nanoparticles the oxidation of various organic compounds and the complex hydrocarbon mixtures, e.g., the automotive gasoline.

The oxidative stability is one of the most important characteristics of the automotive gasoline. The stability of the gasoline to oxidation with the goethite nanoparticles was tested by the standard method. The results are presented in Fig. 3. The induction period goes up to 405 min in the presence of the goethite nanoparticles in the gasoline. Therefore, the goethite nanoparticles in the concentration of 0.007 % enhance the gasoline stability. It is unexpectable that the iron-containing nanoparticles presenting in the gasoline behave as an antioxidant preventing the gasoline oxidation. Fig. 4 shows the dependence of the induction period on the goethite concentration. The results demonstrate increasing the induction period for the gasoline exposed to increasing concentrations of the goethite nanoparticles. Therefore, increasing the concentration of the goethite nanoparticles increases the storage time for the automotive gasoline.

The main antioxidants used in the industry that prevent automotive gasoline from oxidation are the aromatic compounds, particularly, hindered phenols, aromatic amines, and diamines, or mixtures of aromatic diamines (e.g., phenylenediamines) and alkyl phenols. They are able to directly seize peroxy radicals formed during oxidative degradation, thus breaking the auto-oxidation chain reaction. A mechanism is based on interrupting this chain of reactions (removing free radical intermediates), preventing the formation of hydroperoxides, peroxides, soluble gums, or insoluble particulates. Our findings show that the iron-containing nanoparticles, contrary to the bulk iron-containing solids, exhibit a similar effect on the gasoline oxidation by the air oxygen.

It is well-known than the traces of transition metals, particularly, iron, strongly accelerate the gasoline oxidation, catalyzing a decomposition of hydroperoxides into radical species [5–8]. As a result, a presence of the various metals in the automotive gasoline is undesirable. Our study shows that, contrary to this opinion, the iron-containing nanoparticles are capable to effectively inhibit the oxidation of organic compounds. The inhibition may occur as a result of the appearance of the additional reactions in the termination step of the oxidation mechanism. Probably, for the benzyl alcohol oxidation, there is an interaction between the goethite nanoparticles and reactive $BnOO^\bullet$ radicals. Moreover, it allows us to assume that the goethite nanoparticles inhibit the oxidation processes in gasoline according to the similar mechanism. The goethite nanoparticles interact with peroxy radicals preventing a formation of hydroperoxides and peroxides. As a result, the goethite nanoparticles significantly enhance the oxidative stability of the automotive gasoline.

Conclusion

The goethite nanoparticles material was prepared using the thermal decomposition method. The size and

structure of the prepared material were confirmed by TEM, Mössbauer spectroscopy, and elemental analysis. The goethite nanoparticles exhibit a significant inhibition activity in the radical chain oxidation reaction which has been shown by our studies for the benzyl alcohol oxidation. Based on these studies, we reveal that the use of the goethite nanoparticles was shown to improve the oxidative stability of the commercial gasoline. Increasing the goethite concentration up to 0.06 g/L increases the gasoline induction period up to 600 min., i.e. almost two times. Therefore, using the goethite nanoparticles as an antioxidant additive may significantly enhance the gasoline storage period. It is worth noting that goethite is the main component of a rust. Therefore, our results show that not only the goethite nanoparticles but also the nano-rust have a capability to enhance the oxidative stability of gasoline. That opens a new avenue for a design of new generation of antioxidants. A new advance in the fuel storage may be also provided by a technique for a preparation of the storage containers covered by the nano-rust.

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References

- [1] Jeon C-H, Park C-K, Na B-K, Kim J-K. Properties of Gasoline Stored in Various Containers. *Energies* 2017;10:1307. doi:10.3390/en10091307.
- [2] Zhong B-J, Zheng D. A chemical mechanism for ignition and oxidation of multi-component gasoline surrogate fuels. *Fuel* 2014;128:458–66. doi:10.1016/j.fuel.2014.03.044.
- [3] Groysman A. Corrosion in Systems for Storage and Transportation of Petroleum Products and Biofuels. Dordrecht: Springer Netherlands; 2014. doi:10.1007/978-94-007-7884-9.
- [4] Corporan E, Edwards T, Shafer L, DeWitt MJ, Klingshirn C, Zabarnick S, et al. Chemical, Thermal Stability, Seal Swell, and Emissions Studies of Alternative Jet Fuels. *Energy & Fuels* 2011;25:955–66. doi:10.1021/ef101520v.
- [5] Pereira RCC, Pasa VMD. Effect of Alcohol and Copper Content on the Stability of Automotive Gasoline. *Energy & Fuels* 2005;19:426–32. doi:10.1021/ef049849h.
- [6] Teixeira LSG, Souza JC, dos Santos HC, Pontes LAM, Guimarães PRB, Sobrinho E V., et al. The influence of Cu, Fe, Ni, Pb and Zn on gum formation in the Brazilian automotive gasoline. *Fuel Process Technol* 2007;88:73–6. doi:10.1016/j.fuproc.2006.08.008.
- [7] Kennerly GW, Patterson WL. Kinetic Studies of Petroleum Antioxidants. *Ind Eng Chem* 1956;48:1917–24. doi:10.1021/ie50562a042.
- [8] Ali ME, Rahman MM, Sarkar SM, Hamid SBA. Heterogeneous Metal Catalysts for Oxidation Reactions. *J Nanomater* 2014;2014:1–23. doi:10.1155/2014/192038.
- [9] Cassella RJ, Brum DM, Lima CF, Fonseca TCO. Direct determination of Cu and Fe in jet fuel by electrothermal atomic absorption spectrometry with injection of sample as detergent emulsions. *Fuel* 2011;90:1215–20. doi:10.1016/j.fuel.2010.12.008.
- [10] Grassian VH. When Size Really Matters: Size-Dependent Properties and Surface Chemistry of Metal and Metal Oxide Nanoparticles in Gas and Liquid Phase Environments. *J Phys Chem C* 2008;112:18303–13. doi:10.1021/jp806073t.
- [11] Sundaram D, Yang V, Yetter RA. Metal-based nanoenergetic materials: Synthesis, properties, and

- applications. *Prog Energy Combust Sci* 2017;61:293–365. doi:10.1016/J.PECS.2017.02.002.
- [12] Joo SH, Zhao D. Environmental dynamics of metal oxide nanoparticles in heterogeneous systems: A review. *J Hazard Mater* 2017;322:29–47. doi:10.1016/J.JHAZMAT.2016.02.068.
- [13] Nam KM, Seo WS, Song H, Park JT. Non-native transition metal monoxide nanostructures: unique physicochemical properties and phase transformations of CoO, MnO and ZnO. *NPG Asia Mater* 2017;9:e364. doi:10.1038/am.2017.38.
- [14] Pavlov V, Xiao Y, Willner I. Inhibition of the Acetylcholine Esterase-Stimulated Growth of Au Nanoparticles: Nanotechnology-Based Sensing of Nerve Gases. *Nano Lett* 2005;5:649–53. doi:10.1021/nl050054c.
- [15] Tada H, Kiyonaga T, Naya S. Rational design and applications of highly efficient reaction systems photocatalyzed by noble metal nanoparticle-loaded titanium(IV) dioxide. *Chem Soc Rev* 2009;38:1849. doi:10.1039/b822385h.
- [16] Guo J-Z, Cui H, Zhou W, Wang W. Ag nanoparticle-catalyzed chemiluminescent reaction between luminol and hydrogen peroxide. *J Photochem Photobiol A Chem* 2008;193:89–96. doi:10.1016/j.jphotochem.2007.04.034.
- [17] Henglein A, Giersig M. Reduction of Pt(II) by H₂: Effects of Citrate and NaOH and Reaction Mechanism. *J Phys Chem B* 2000;104:6767–72. doi:10.1021/jp000801o.
- [18] Chen G, Huynh D, Felgner PL, Guan Z. Tandem Chain Walking Polymerization and Atom Transfer Radical Polymerization for Efficient Synthesis of Dendritic Nanoparticles for Bioconjugation. *J Am Chem Soc* 2006;128:4298–302. doi:10.1021/ja0573864.
- [19] Kharisov BI, Rasika Dias H V., Kharissova O V., Manuel Jiménez-Pérez V, Olvera Pérez B, Muñoz Flores B. Iron-containing nanomaterials: synthesis, properties, and environmental applications. *RSC Adv* 2012;2:9325. doi:10.1039/c2ra20812a.
- [20] Bychko IB, Kalishin EY, Strizhak PE. Effect of the size of Fe@Fe₃O₄ nanoparticles deposited on carbon nanotubes on their oxidation-reduction characteristics. *Theor Exp Chem* 2011;47:219–24. doi:10.1007/s11237-011-9207-9.
- [21] Kovtun G, Kameneva T, Hladyi S, Starchevsky M, Pazdersky Y, Stolarov I, et al. Oxidation, Redox Disproportionation and Chain Termination Reactions Catalysed by the Pd-561 Giant Cluster. *Adv Synth Catal* 2002;344:957–64. doi:10.1002/1615-4169(200210)344:9<957::AID-ADSC957>3.0.CO;2-V.
- [22] Zhao J, Zhang R, Misawa K, Shibuya K. Experimental product study of the OH-initiated oxidation of m-xylene. *J Photochem Photobiol A Chem* 2005;176:199–207. doi:10.1016/j.jphotochem.2005.07.013.
- [23] Armarego WLF, Chai CLL. *Purification of Laboratory Chemicals*. Butterworth-Heinemann; 2012.
- [24] Azatyan VV, Denisov E. *Inhibition of chain reactions*. CRC Press; 2000.
- [25] ASTM D525. *Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method)*. Annu. B. Stand. ASTM Int., West Conshohoken, Pennsylvania; 2014.
- [26] Murad E, Johnston JH. Iron oxides and oxyhydroxides. In: Long GJ, editor. *Mössbauer Spectrosc. Appl. to Inorg. Chem.*, Plenum Publishing Corporation; 1987, p. 507–82.
- [27] Mallat T, Baiker A. Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts. *Chem Rev*

2004;104:3037–58. doi:10.1021/cr0200116.

[28] Skibida IP, Sakharov AM. Molecular oxygen as environmental acceptable, selective and the most strong oxidant in liquid-phase oxidation. *Catal Today* 1996;27:187–93. doi:10.1016/0920-5861(95)00186-7.

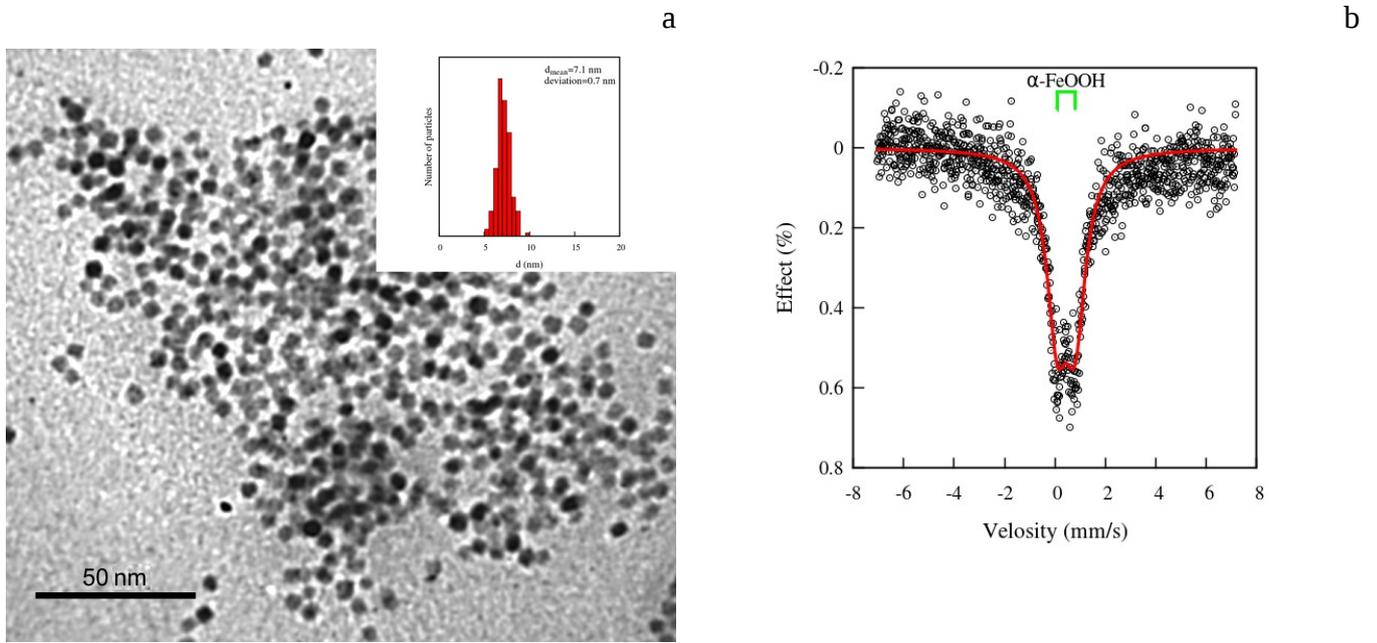


Fig. 1. (a) TEM image of the colloidal solution of the goethite nanoparticles. Inset – size distribution of the nanoparticles. (b) Mössbauer spectrum of the goethite nanoparticles

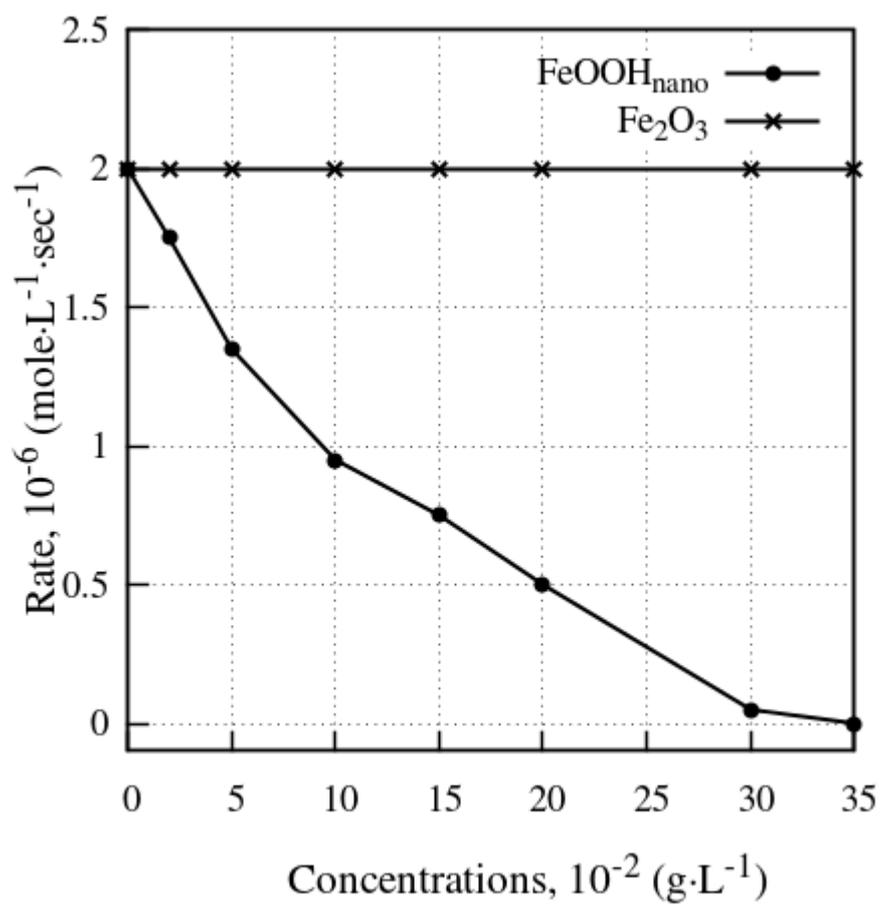


Fig. 2. Dependence of the oxidation rate of the benzyl alcohol on the concentration of the goethite nanoparticles

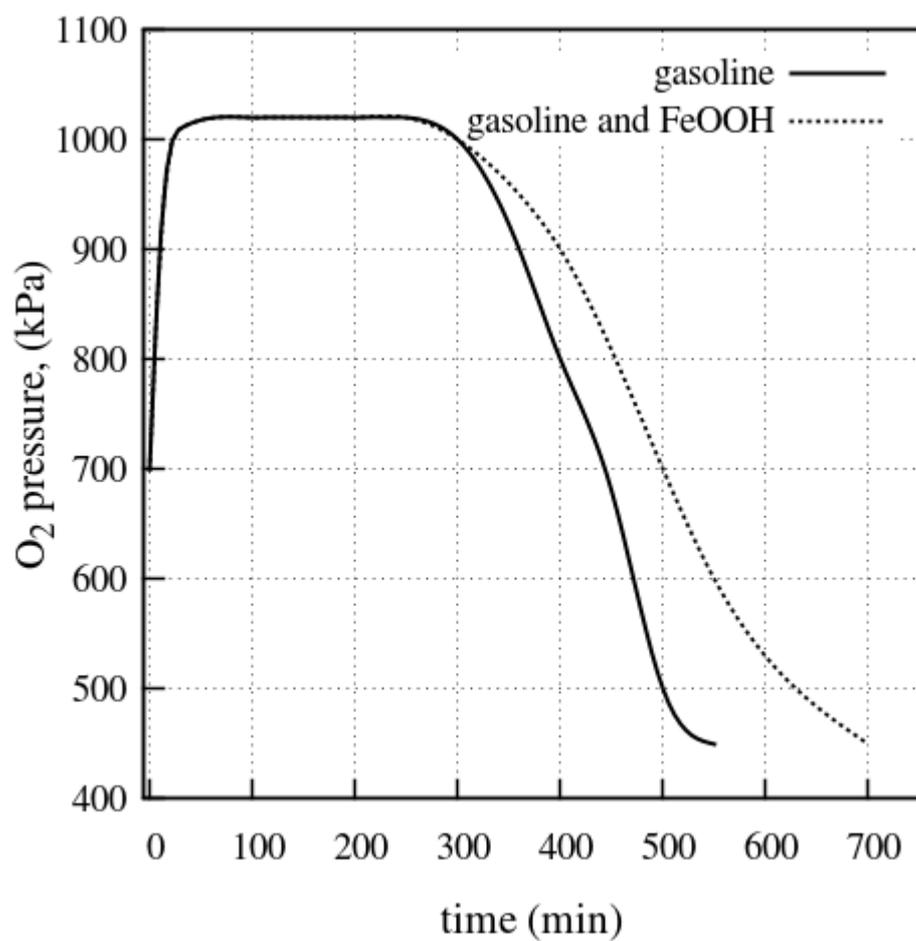


Fig. 3. The time dependencies of the O₂ pressure for the fresh gasoline (line) and mixture gasoline and goethite nanoparticles (dotted). The goethite nanoparticles content in gasoline are 0.007 %

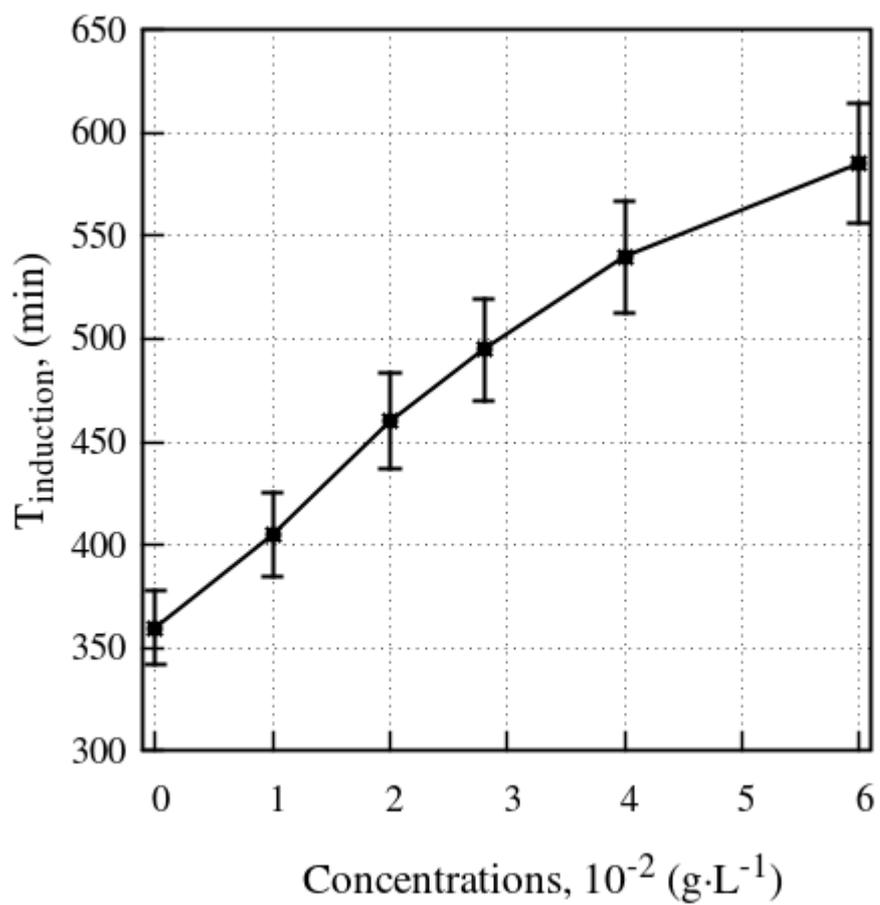


Fig. 4. The dependence of the induction period (T_{ind}) on the concentration of the goethite nanoparticles

Table 1. The dependence of the induction period (T_{ind}) on the concentration of the goethite nanoparticles

Properties of the Ukrainian Gasoline

Characteristic	Value
Octane number	
-research octane number	95.2
-motor octane number	83.3
Pressure (kPa)	64.90
Lead content (mg/m^3)	lower 5
Destiny at 15°C (kg/m^3)	742.3
Distillation class fraction	
-at 15°C evaporated, max (% v/v)	25.0
-at 100°C evaporated, max (% v/v)	50.0
-at 150°C evaporated, max (% v/v)	80.0
-final boiling point, maximum (°C)	202
-maximum distillation residue (%)	1.2
Sulfur content (mg/kg), max	35
Olefin content (vol %)	8.57
Aromatic content (vol %)	32.9
Benzene content (vol %)	0.56
Oxygene content (vol %)	0.73
Methanol content (vol %)	0
Ethanol content (vol %)	0
Isopropyl alcohol content (vol %)	0
Isobutyl alcohol content (vol %)	0
tert-butyl alcohol content (vol %)	0
Ether (5 or more C atoms) (vol %)	4.0
Other oxygenates (vol %)	0
Manganese content (mg/m^3)	0
Oxidation stability, min	370
Washed gums ($mg/100cm^3$), max	1.0
Copper corrosion (50°C, 3h), max	1
Color	yellow