ДЕСТРУКЦИЯ УГЛЕВОДОРОДОВ МАСЛА В ВОДНЫХ РАСТВОРАХ В КИСЛОРОДНОМ ДИЭЛЕКТРИЧЕСКОМ БАРЬЕРНОМ РАЗРЯДЕ АТМОСФЕРНОГО ДАВЛЕНИЯ

В.И. Гриневич, В.В. Рыбкин, В.А. Любимов, А.А. Гущин

Владимир Иванович Гриневич, Владимир Александрович Любимов, Андрей Андреевич Гущин*

Кафедра промышленной экологии, Ивановский государственный химико-технологический университет, Шереметевский пр., 7, Иваново, 153000, Россия
E-mail: grin@isuct.ru, a_guschin@bk.ru *

Владимир Владимирович Рыбкин

Кафедра технологии приборов и материалов электронной техники, Ивановский государственный химико-технологический университет, Шереметевский пр., 7, Иваново, 153000, Россия
E-mail: rybkin@isuct.ru

*В статье приводятся результаты экспериментального исследования кинетики деструкции углеводородов масла (моторное минеральное масло М8), растворенного в воде под действием диэлектрического барьерного разряда в кислороде при атмосферном давлении. Диапазон начальных концентраций масла в водном растворе составлял (12-91) мг/л. Все эксперименты проводились при среднеквадратичных токе и напряжении 0,45 мА и 7,9 кВ. Частота приложенного напряжения составляла 50 Гц. При этом вложенная в разряд мощность равнялась 0,35 Вт/см³, а расход газа – 1 л/мин. Показано, что кинетика разложения формально описывается уравнением псевдопервого порядка по концентрации масла. Эффективная константа скорости разложения нефтепродуктов составила 0,0016 с⁻¹. В рассматриваемом диапазоне концентраций М8 в воде скорости деструкции изменялись в диапазоне (3,8÷28,9)·10⁻⁶ моль/(л·мин). Степень разложения масла достигала 80 %, а энергетический выход разложения составлял 0,16 молекулы на 100 эВ вложенной энергии. Исследована также кинетика образования озона и диоксида углерода. Полученные экспериментальные данные позволили определить степень полноты окисления масла, которая в максимуме составляла 54 % (по диоксиду углерода), что свидетельствует об образовании других углеродсодержащих соединений. Выявлена динамика изменения величины рН обрабатываемого раствора. В условиях эксперимента наблюдалось снижение рН с 6 до 4. Установлено, что концентрации озона, образующегося в объеме реактора, недостаточна для окислительной деструкции. Это говорит о присутствии в системе других активных частиц, участвующих в разрушении нефтепродуктов, таких как радикалы ОН*и атомарный кислород. Предложен возможный механизм процессов деградации нефтепродуктов в ДБР.*

Ключевые слова: моторное масло, очистка воды, диэлектрический барьерный разряд, кинетика

DESTRUCTION OF OIL HYDROCARBONS IN WATER SOLUTIONS WITH OXYGEN DIELECTRIC BARRIER DISCHARGE OF ATMOSPHERIC PRESSURE

V.I. Grinevich, V.V. Rybkin, V.A. Lyubimov, A.A. Gushchin

Vladimir I. Grinevich, Vladimir A. Lyubimov, Andreiy A. Gushchin *

Department of Industrial Ecology, Ivanovo State University of Chemistry and Technology, Sheremetievskiy ave., 7, Ivanovo, 153000, Russia
E-mail: grin@isuct.ru, a_guschin@bk.ru *

Vladimir V. Rybkin

Department of Microelectronic Devices and Materials, Ivanovo State University of Chemistry and Technology, Sheremetievskiy ave., 7, Ivanovo, 153000, Russia
E-mail: rybkin@isuct.ru

This paper reports the experimental study of destruction kinetics of oil hydrocarbons (engine oil of the M8 trademark) dissolved in water by dielectric barrier discharge in oxygen at the atmospheric pressure. The range of initial concentrations of oil in the aqueous solution was $(12-91)$ mg/l. All experiments were carried out under the applied voltage of 7.9 kV and discharge current of 0.45 mA (rms values) with a frequency of 50 Hz. The inputted power was 0.35 W/cm^3. The gas flow rate was 1 l/min. It was shown that the kinetics of oil decomposition can be formally described by the pseudo-first order law on oil concentration. The effective rate constant for decomposition of petroleum products was 0.0016 s^{-1}. The rate of destruction in the investigated concentration range of M8 was varied in the range $(3.8 - 28.9) \cdot 10^{-6}$ mol / (l·min). The oil decomposition degree achieved 80 %, and the decomposition energetic yield was 0.16 molecules per 100 eV of inputted energy. The kinetics of the formation of ozone and carbon dioxide was examined as well. The obtained experimental data allowed to determine the degree of completeness of oil oxidation, which at the maximum was 54% (for carbon dioxide), this results indicates the formation of other carbon-containing compounds. The dynamics of the change in the pH of the treated solution is revealed. Under the experimental conditions, the pH was reduced from 6 to 4. It was found that the concentration of ozone formed in the reactor was deficiency for oil oxidative degradation. This results confirms that in the system are formed other active particles involved in the destruction of petroleum products, such as the OH* radicals and atomic oxygen. The possible mechanism of degradation processes is discussed.

Key words: engine oil, water purification, DBD, kinetics

INTRODUCTION

Numerous studies published last ten years [1-5] on various aspects of high pressure non-equilibrium plasma created with gas discharges in water solutions or above their surface emphasize the increasing interest of researches to the given area of chemistry and physics of plasma. The reasons of that interest are the new possibilities, which provide these discharges for practical application. One of the promising directions of such discharge application is the use for organic substances degradation and removing ions of heavy metals

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(for example, Cr, Mn) contained in wastewaters. A plasma action is attractive since the plasma itself is a source of active species (for example, UV radiation, H_2O_2, molecules of singlet oxygen, oxygen and hydrogen atoms, $\cdot OH$ and $HO_2\cdot$ radicals etc.). These particles are capable to manifest both oxidative and reduction properties depending on conditions. Another important feature of processes in plasma is high rates at relatively low temperatures. This is due to the fact that plasma systems are non-equilibrium ones. The primary source of active species is not heat activation but the processes with participation of electrons. The latter gain the energy from external electric field and transform it colliding with atoms and molecules to the energy of excitation of various states and to dissociation. Further reactions of particles being formed result in the formation of other active particles. Degradation of many substances in aqueous solutions has already been studied. At the same time, we are not aware of the studies devoted to the degradation of oil and oil products. Due to the intensive human activity these compounds are very important pollutants of natural and industrial waters and soil. For this reason, the main goal of the given paper is to study the possibilities of oxygen DBD application to the degradation of engine oil. Furthermore, the investigation of degradation kinetics, kinetics of some products formation as well as the degradation degree will be presented.

EXPERIMENTAL

The scheme of the experimental set-up is shown in Fig. 1. Reactor body (1) of cylindrical form with 60 mm internal diameter was fabricated from a Pyrex tube. The bottom of the reactor cylinder was located on the tap from Teflon (2). The thickness of the dielectric barrier (6) between the lower electrode (4) from aluminum foil (thickness-20 μm, diameter – 60 mm) and the solution under the treatment was 2 mm. The reactor was hermetically closed with the Teflon cover (8) having two holds for the plasma-forming gas input and output. Upper electrode (3) of 30 mm diameter was fabricated from aluminum alloy. Technical grade oxygen (99.8%) was used. The gas flow rate was 1 l/min. The distance between the upper electrode and the solution surface was 3 mm. The solution volume was 100 ml.

A high voltage of an industrial frequency of 50 Hz was applied between electrodes for the discharge exciting. The applied voltage was measured with a high voltage probe (2000:1), and the discharge current was determined from the voltage drop over the resistor (100 Ω) connected in series into the ground circuit. Both waveforms were registered by the GW Instek GDS-2072 (Taiwan) digital two channels oscilloscope.

The inputted power was determined by the integrating the multiplication of both forms over the period. For all experiments, the rms values of voltage and current were 7.9 kV and 0.45 mA, respectively. The specific inputted power per one unit of discharge volume was 0.35 W/cm^3.
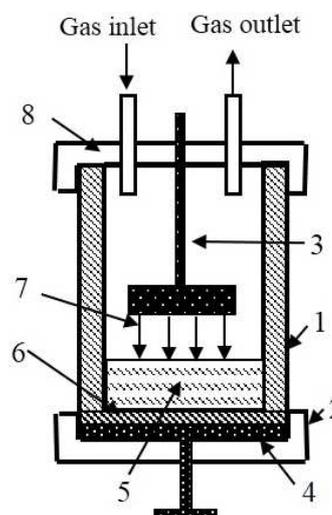

Fig. 1. Schematic diagram of the experimental set-up. 1 – reactor body, 2 – Teflon tap, 3 – upper electrode, 4 – lower electrode, 5 – solution, 6 – dielectric barrier, 7 – discharge, 8 – Teflon cover
Рис. 1. Схема экспериментальной установки. 1-корпус реактора, 2 – тефлоновая заглушка, 3-верхний электрод, 4-нижний электрод, 5-раствор, 6-диэлектрический барьер, 7-разряд, 8-тефлоновая крышка

As a model pollutant the engine oil of the M8 trademark was used. The M8 oil is a mineral all-season oil for medium-forced gasoline and diesel engines. This oil is prepared from the distillate component of thin fraction composition or from the mixture of distillate and residual components of petroleum oils with the addition of the effective composition of additives. According to the SAE classification on viscosity, M8 corresponds to class 20. According to API classification, M8 corresponds to the SD/CB type. The total weight composition is (83-87) % of carbon and (12-14) % of hydrogen. Furthermore, the oil contents small admixtures of oxygen, nitrogen, moisture, and noncombustible mineral substances [6].

For the determination of approximate molecular mass of petroleum and oil products some empirical relations can be used. One of them is the Craig's formula for oil fractions [7]

$$M = 44.29 \cdot \rho^{298} / (1.03 - \rho^{298}),$$
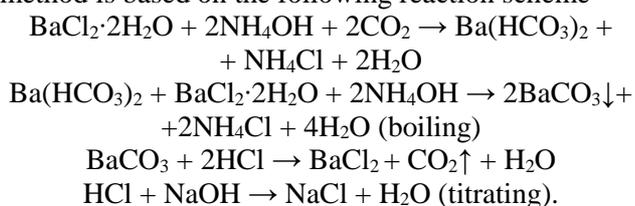
where ρ^{298} – the oil density (905 kg/m^3) at 298 K, M – the molar mass.

The calculation on this relation gives the approximate formula of M8 oil $C_{22}H_{38}$ and M = 302. The given values were used for further calculations.

The initial concentration of engine oil was varied from 12 to 91 mg/l. For each treatment time the fresh solution was used.

The concentration of oil products in water solutions was determined by gravimetric analysis [8]. Oil products were extracted from a sample with hexane followed by the extract purification from polar substances by passing through the column with a sorbent (aluminum oxide of II degree of activity (containing 3% of H_2O) and silica gel). The purified extractant was evaporated followed by the determination of the residue mass.

The CO_2 and CO concentrations were measured as follows. The gas evolving from the reactor entered into either two absorption vessels connected in series or only the second of them. In the first case, the first vessel contained the powder of potassium permanganate, an efficient oxidizer of CO to CO_2. This vessel can be shunted. The second vessel served for CO_2 determination by the method reported elsewhere [9]. This method is based on the following reaction scheme

$$BaCl_2 \cdot 2H_2O + 2NH_4OH + 2CO_2 \rightarrow Ba(HCO_3)_2 +$$
$$+ NH_4Cl + 2H_2O$$
$$Ba(HCO_3)_2 + BaCl_2 \cdot 2H_2O + 2NH_4OH \rightarrow 2BaCO_3\downarrow+$$
$$+2NH_4Cl + 4H_2O \text{ (boiling)}$$
$$BaCO_3 + 2HCl \rightarrow BaCl_2 + CO_2\uparrow + H_2O$$
$$HCl + NaOH \rightarrow NaCl + H_2O \text{ (titrating).}$$

The second vessel contained the ammonium solution of $BaCl_2$. A solution sample was boiled in a water bath to promote the precipitation of $BaCO_3$. The precipitate was filtered and then dissolved in a certain amount of hydrochloric acid. The unreacted acid was titrated by a solution of sodium hydrate. The results of measurements with one and two vessels allow estimating the concentration of CO_2 and CO separately.

The method of ozone concentration determination in outlet gas was based on the following reaction scheme [10]

$$O_3 + 2KI + H_2O \rightarrow O_2\uparrow + I_2 + 2KOH$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
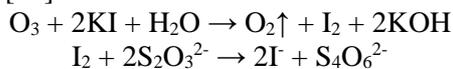
The outlet gas was passed through the vessel with 0.01 M solution of KI. I_2 being formed was titrated with a solution of sodium thiosulfate using starch solution as indicator.

The results of determination of ozone and CO_2 kinetics are treated in the following way. The change of component mass, dM, for the time dt can be written as

$$dM = \varphi(t) \cdot m \cdot J \cdot dt,$$

where $\varphi(t)$ – the mole fraction of component, m – the mass of one liter of component, J – the total gas flow rate(l/s). The measurement of time-dependence of M allows determining the $\varphi(t)$ followed by the calculation of the appropriate component concentration in the gas phase and calculation of the component flow and its formation or loss rate.

RESULTS OF MEASUREMENTS AND DISCUSSION

The M8 degradation kinetics and the degradation degrees, Y, are shown in Fig. 2. Kinetic curves are satisfactorily described ($R^2 > 0.98$) by the equations of the pseudo-first order with the rate constants, k_R, of (0.002 ± 0.0003), (0.0019 ± 0.0004), (0.002 ± 0.0002), and (0.0017 ± 0.0002) s^{-1} for curves 1, 2, 3, 4 respectively. The constant value of rate coefficients shows that concentrations of active species reacting with oil reach the stationary value. It is necessary to point out that the first order kinetic law is observed for the most of the studied compounds and discharge types [11, 12]. As can be seen, in the given case the effective rate constants do not depend on the initial concentration, neither on the degradation degree. Usually, the increase in concentration leads to the decrease in the rate constants [11, 13]. Evident explanation is that under large concentrations, the decomposition rate is limited by the formation rates of active species in discharge. Therefore, in this case the active species consumption in oil degradation has only a slight effect on the total loss rate of these active species.

Using these data we calculated the degradation rates and the energy efficiencies of degradation at treatment time t→0. The energy efficiency, α, was calculated as

$$\alpha = 1.6 \cdot 10^{-17} \cdot W \cdot V \cdot 6.02 \cdot 10^{23} / P,$$

where W – the degradation rate in mol/(l·s), $V = 0,1$ l – the solution volume, P – the discharge power in W.
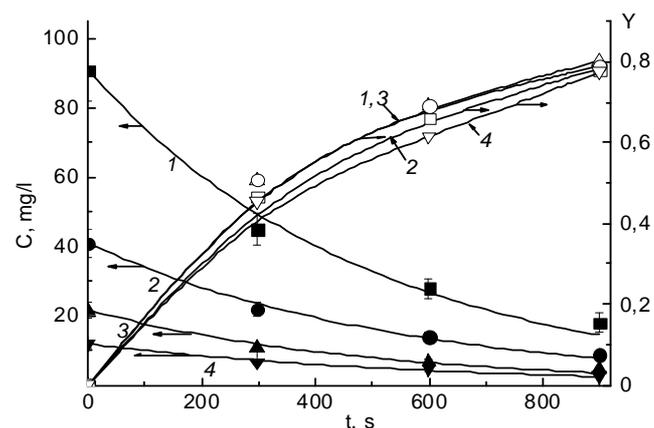
Fig. 2. The degradation kinetics and degradation degree, Y, at different concentrations of oil. 1-4 - the initial oil concentrations are 91, 41, 22, and 12 mg/l, respectively. Points – experiment, lines – calculations on the equation of the first order kinetic law
Рис. 2. Кинетика деградации и степень разложения, Y, при различных концентрациях масла. 1-4 – начальные концентрации масла – 91, 41, 22 и 12 мг/л, соответственно. Точки – эксперимент, линии – расчеты по уравнению первого кинетического порядка

The results are presented in the Table. The degradation efficiencies are close to those obtained for phenol water solution in other studies (10^{-3}-0.68 [11]). In study [14] devoted to the purification of real rain sewage by oxygen DBD the value of $\alpha = 0.05$ was obtained. A rather high degradation efficiency of ~80% was achieved after 15 min of processing.

Table
Initial degradation rates of oil, evolution rates of CO_2, and degradation energy efficiencies of oil
Таблица. **Начальные скорости разложения масла, скорости образования CO_2 и энергетические эффективности разложения**

Initial concentration, mg/l	Degradation rate, mol/(l·s)	Degradation energy efficiencies, molecules per 100 eV	CO_2 formation rate, mol/(l·s)
12	$(6.88\pm0.4)\cdot10^{-8}$	0.019	$(2.84\pm0.5)\cdot10^{-8}$
22	$(1.45\pm0.11)\cdot10^{-7}$	0.039	$(5.55\pm0.74)\cdot10^{-8}$
41	$(2.51\pm0.12)\cdot10^{-7}$	0.068	$(1.74\pm0.4)\cdot10^{-7}$
91	$(5.99\pm0.9)\cdot10^{-7}$	0.162	$(3.38\pm0.4)\cdot10^{-7}$

The final product of oxidative degradation of any organics is carbon dioxide. Here, CO_2 formation is observed as well. The kinetics of CO_2 accumulation in the gas phase is shown in Fig. 3, whereas the initial rates of CO_2 formation calculated using these data are presented in Table. Carbon monoxide formation was not observed. The comparison of the oil degradation rates and the CO_2 formation rates allows concluding that CO_2 is not the main degradation product. And the most part of the formed products remains in a solution. We have not determined the by-product composition yet. It will be the task of our further studies. However, using the data obtained at an oxidative degradation of other large molecules in air and oxygen discharges it is possible to anticipate the type of forming substances. Thus, the decomposition of phenol and its derivatives results in the formation of carboxylic acids and aldehydes [15, 16, 17]. The degradation of sodium lauryl sulfate ($C_{12}H_{25}SO_4Na$) [18] and sulfonol (C_nH_{2n+1}-Ar-SO_2ONa, n = 12-18) [19] leads to the formation of the same types of compounds. Independently on the discharge type, the solution treatment results in the solution pH decrease. For air discharges, it is explained by the formation of nitric and nitrous acids: the NO_3^- and NO_2^- ions are observed in the solution [20, 21, 17]. Under the treatment in oxygen discharges the pH dropping is observed as well [22, 15]. We think that the pH decrease is the result of carboxylic acids formation. In our case the growth of the solution acidity takes place (Fig. 4). The higher the initial concentration (more acids), the more the pH decrease. Since we did not detect nitrate and nitrite ions, the oil degradation must lead to acid formation.
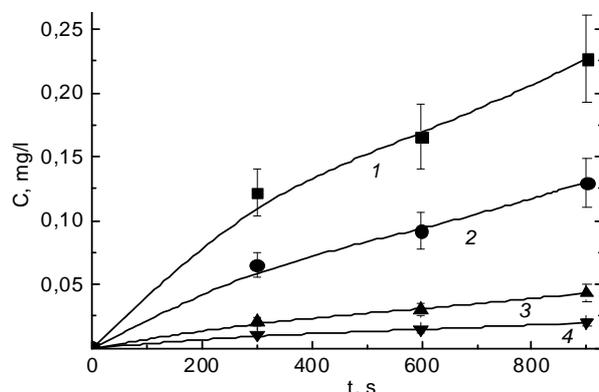

Fig. 3. The kinetics of carbon dioxide formation at different concentrations of oil. 1-4 - the initial oil concentrations are 91, 41, 22, and 12 mg/l, respectively
Рис. 3. Кинетика образования диоксида углерода при различных концентрациях масла. 1-4 – начальные концентрации масла – 91, 41, 22 и 12 мг/л, соответственно
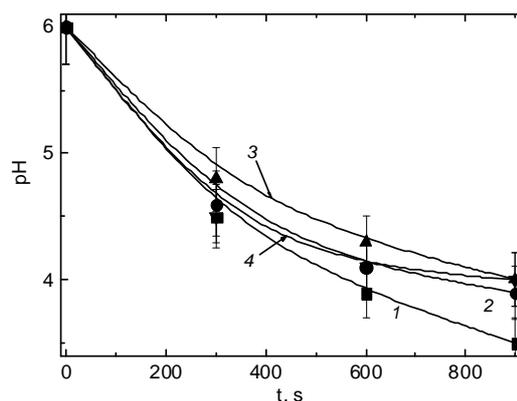

Fig. 4. The solution pH change at different concentrations of oil. 1-4 - the initial oil concentrations are 91, 41, 22, and 12 mg/l, respectively
Рис. 4. Изменение pH раствора при различных концентрациях масла. 1-4 – начальные концентрации масла – 91, 41, 22 и 12 мг/л, соответственно

Fig. 5. shows the kinetics of ozone accumulation in the gas phase. It can be seen that ozone reacts with oil since the ozone concentration becomes less in the presence of oil. Using these data and the gas flow rate we can estimate the ozone consumption rate on chemical reaction. It gives the value of ~$1.6\cdot10^{-6}$ mol/(l·s). A transformation of one oil molecule to CO_2 needs ~15 ozone molecules. Therefore, ozone is not capable to provide completely the oil oxidative destruction. Nevertheless, ozone can be responsible for the CO_2 formation.

Since the specific density of oil is less than this of water, the oil has to form a compact thin film on the water surface.
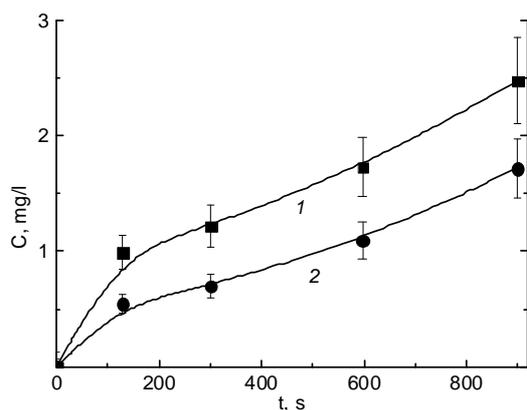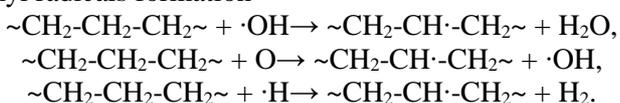
Fig. 5. The kinetics of ozone accumulation in a gas phase.
1 – distilled water, 2 – oil solution with the concentration of 41 mg/l
Рис. 5. Кинетика накопления озона в газовой фазе. 1 – дистиллированная вода, 2 – раствор масла с концентрацией 41 мг/л

Depending on the concentration, the estimated film thickness can be about 0.3-3 µm. Hence, the film can undergo the direct action of active species from the gas phase rather than the action of the particles, formed in the solution at the solvent (water) dissociation, or diffusing from plasma. Particularly, it is confirmed by the independence of the efficient rate constants on the initial concentration of oil. Except ozone, there is no available experimental data on concentrations of active species in plasma. There are data obtained by the modeling only. For pure O_2 these data were presented in study [23], whereas for the oxygen DBD in contact with the water electrode (gas is mixture of O_2 and H_2O) the appropriate data were obtained in [24]. According to [23] the main active particles in O_2 DBD were O_3, $O_2(a^1\Delta_g)$, and $O(^3P)$. In O_2 discharge with addition of H_2O besides above-mentioned particles the $\cdot OH$, $HO_2\cdot$ and H radicals are formed [24]. The possibilities of ozone formation were already discussed. Taking into consideration that $O_2(a^1\Delta_g)$ cannot react with unsaturated hydrocarbons the possible reaction pathway may be the following.

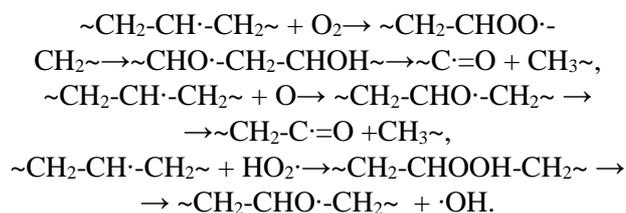Reactions of OH, O and H radicals result in alkyl radicals formation

$$\sim CH_2\text{-}CH_2\text{-}CH_2\sim + \cdot OH \rightarrow \sim CH_2\text{-}CH\cdot\text{-}CH_2\sim + H_2O,$$
$$\sim CH_2\text{-}CH_2\text{-}CH_2\sim + O \rightarrow \sim CH_2\text{-}CH\cdot\text{-}CH_2\sim + \cdot OH,$$
$$\sim CH_2\text{-}CH_2\text{-}CH_2\sim + \cdot H \rightarrow \sim CH_2\text{-}CH\cdot\text{-}CH_2\sim + H_2.$$
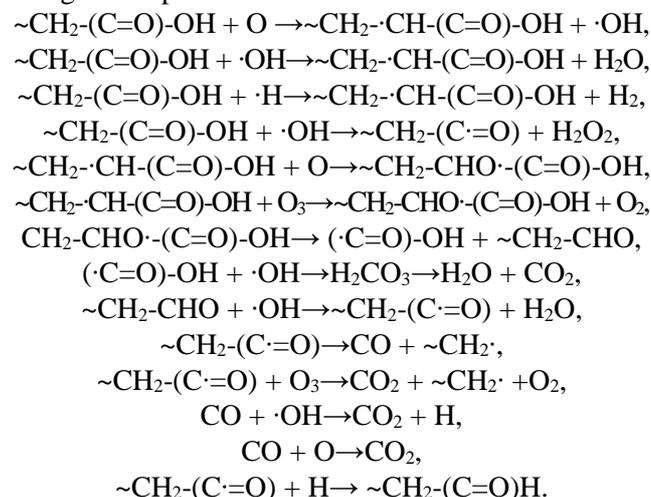
The alkyl radical reactions result in the formation of alkoxy radicals followed by their destruction accompanied by the chain scission and carboxyl radicals formation.

$$\sim CH_2\text{-}CH\cdot\text{-}CH_2\sim + O_2 \rightarrow \sim CH_2\text{-}CHOO\cdot\text{-}$$
$$CH_2\sim \rightarrow \sim CHO\cdot\text{-}CH_2\text{-}CHOH\sim \rightarrow \sim C\cdot=O + CH_3\sim,$$
$$\sim CH_2\text{-}CH\cdot\text{-}CH_2\sim + O \rightarrow \sim CH_2\text{-}CHO\cdot\text{-}CH_2\sim \rightarrow$$
$$\rightarrow \sim CH_2\text{-}C\cdot=O + CH_3\sim,$$
$$\sim CH_2\text{-}CH\cdot\text{-}CH_2\sim + HO_2\cdot \rightarrow \sim CH_2\text{-}CHOOH\text{-}CH_2\sim \rightarrow$$
$$\rightarrow \sim CH_2\text{-}CHO\cdot\text{-}CH_2\sim + \cdot OH.$$

The reactions of the carboxyl radicals can result in a formation of carboxylic acids.

$$\sim CH_2\text{-}C\cdot=O + \cdot OH \rightarrow \sim CH_2\text{-}COOH.$$

The formed carboxylic acids can be transformed to aldehydes with the molecular chain scission and gaseous products formation.

$$\sim CH_2\text{-}(C=O)\text{-}OH + O \rightarrow \sim CH_2\text{-}\cdot CH\text{-}(C=O)\text{-}OH + \cdot OH,$$
$$\sim CH_2\text{-}(C=O)\text{-}OH + \cdot OH \rightarrow \sim CH_2\text{-}\cdot CH\text{-}(C=O)\text{-}OH + H_2O,$$
$$\sim CH_2\text{-}(C=O)\text{-}OH + \cdot H \rightarrow \sim CH_2\text{-}\cdot CH\text{-}(C=O)\text{-}OH + H_2,$$
$$\sim CH_2\text{-}(C=O)\text{-}OH + \cdot OH \rightarrow \sim CH_2\text{-}(C\cdot=O) + H_2O_2,$$
$$\sim CH_2\text{-}\cdot CH\text{-}(C=O)\text{-}OH + O \rightarrow \sim CH_2\text{-}CHO\cdot\text{-}(C=O)\text{-}OH,$$
$$\sim CH_2\text{-}\cdot CH\text{-}(C=O)\text{-}OH + O_3 \rightarrow \sim CH_2\text{-}CHO\cdot\text{-}(C=O)\text{-}OH + O_2,$$
$$CH_2\text{-}CHO\cdot\text{-}(C=O)\text{-}OH \rightarrow (\cdot C=O)\text{-}OH + \sim CH_2\text{-}CHO,$$
$$(\cdot C=O)\text{-}OH + \cdot OH \rightarrow H_2CO_3 \rightarrow H_2O + CO_2,$$
$$\sim CH_2\text{-}CHO + \cdot OH \rightarrow \sim CH_2\text{-}(C\cdot=O) + H_2O,$$
$$\sim CH_2\text{-}(C\cdot=O) \rightarrow CO + \sim CH_2\cdot,$$
$$\sim CH_2\text{-}(C\cdot=O) + O_3 \rightarrow CO_2 + \sim CH_2\cdot + O_2,$$
$$CO + \cdot OH \rightarrow CO_2 + H,$$
$$CO + O \rightarrow CO_2,$$
$$\sim CH_2\text{-}(C\cdot=O) + H \rightarrow \sim CH_2\text{-}(C=O)H.$$

CONCLUSION

It was shown that the application of an oxygen dielectric barrier discharge under atmospheric pressure provides rather high degradation efficiency, degradation rates and low energetic degradation cost of engine oil in water solution.

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