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Desulfurization of raw naphtha cuts using hybrid systems based on acoustic cavitation and advanced oxidation processes (AOPs)

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ABSTRACT

A combination of dual-frequency acoustic cavitation (acoustic cavitation) and UV assisted advanced oxidation processes (AOPs) reaction system was developed for desulfurization of raw naphtha used to produce aviation fuels. Various types of oxidants in hybrid systems including hydrogen peroxide, acetic acid, acetone, air and ozone were compared. At optimum oxidant to sulfur compounds molar ratio (rox) of 5.0, the hybrid process of acoustic cavitation /acetic acid/hydrogen peroxide (acoustic cavitation/peracetic acid) was the most effective treatment process with synergistic index of 7.55 and desulfurization efficiency of 100% (highest reaction rate constant of 0.1337 min-1) for all sulfur compounds present in naphtha within the short reaction time of 30 min. At rox of 0.5 and 1.0, the synergy coefficients of 3.77 and 5.41 corresponding to the desulfurization efficiencies of 93.07 and 95.10% were obtained in 180 min, respectively. Comparatively, at the rox of 5.0, the efficiency of acoustic cavitation combined with hydrogen peroxide alone and acetic acid alone was 63.68 and 47.36%, respectively. Alternative treatment process of acoustic cavitation /UV/acetone/water can be used for the complete desulfurization (100%) of specific sulphur compounds including dibutyl sulfide, di-tert butyl disulfide, 1,4-butanedithiol and benzyl thiol considering the optimum acetone to water ratio of 2:1. All acoustic cavitation-based treatment systems followed the pseudo first order kinetic model. The most expensive process was ozone-aided acoustic cavitation with treatment costs exceeding 100 USD m-3. The peracetic acid-based system was the most economic process with a treatment cost of 15 USD/m^3 with electric energy consumption of 100.17 kWh/m^3.

1. Introduction

Cavitation technologies are considered as very effective methods for the transformation and degradation of hazardous chemical compounds, widely found in various wastewaters. Cavitation is defined as the formation, growth, and subsequent collapse of bubbles into the liquid media in regions of very low pressure, which leads to the formation of highly reactive radicals responsible for the degradation of contaminants present in the liquid media [1]. Cavitation-based treatment processes are found to be very applicable for the decomposition of different types of pollutants in wastewater such as inorganic and organic acids [2], pesticides [3], pharmaceuticals [4], volatile organic compounds (VOCs) [5] volatile sulfur compounds (VSC) [6], benzene, toluene, ethylbenzene, xylenes (BTEXs) [7], organic dyes [8], etc. Among abovementioned contaminants, VSC are malodour contaminants present in industrial wastewaters which are very harmful to the aquatic environments. Several treatment techniques have been applied for the elimination of VSC from aquatic phase [9]. Among different chemical approaches, cavitation phenomenon has been successfully applied for the removal of VSC from industrial effluents. Complete oxidation of sulfide ions (2000 mg S^{2-}/L) present in bitumen effluents as well as complete VSC decomposition was achieved within a short reaction time of 30 min when combined process of cavitation/advanced oxidation processes (AOPs) was utilized [6]. The presence of sulfur compounds such as thiophene, substituted benzo and dibenzothiophenes, thiols and sulfides in crude oil makes the control of sulfur compounds emission difficult as

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this type of emission is spontaneous [10]. It relates mainly to a “breathing” of the storage tanks (emissions at tank filling as well as daily variations of the temperature). From 1st January 2020, the maximum sulfur content of marine fuels is reduced to 0.5%, globally. Reduction of sulfur dioxide concentration around Sulphur Oxides Emissions Control Areas (SECAs) leads to improving the health of people living around SECAs regions, but no significant change in the economic sector is observed yet [11].

Desulfurization processes like oxidative desulfurization (ODS), hydrodesulfurization (HDS), and adsorptive desulfurization (ADS) are of great approaches to attain low sulfur content in fuels and overcoming the environmental pollution related to the sulfur emissions throughout the world [12]. HDS is based on sulfur removal from a sulfur compound by reaction with hydrogen followed by the formation of H_2S [13]. Extreme operating conditions such as high temperatures (300–350 °C), high pressures (50–100 atm), and high hydrogen consumption make this method non-economic with high investment costs. Unlike the HDS method, ODS can occur under mild conditions (ambient pressure and temperature $<$ 100 °C). ODS converts sulfur-containing compounds into polar compounds that can be separated using extraction solvent, ionic liquid as well as adsorbents [12]. Recent studies have claimed that among conventional treatment technologies, cavitation-based technologies overcome the main drawbacks that can be faced during using HDS or ODS treatment methods. During the cavitation phenomenon, the cavitation bubbles oscillate and keep growing until it reaches a varying size. Subsequently, the violent collapse of as-generated bubbles and their sudden implosion result in extreme pressure and temperature [14,15]. Each cavity can be considered as a micro-reactor where high temperature (5000–10000 K) and pressure (500–1000 atm) initiate the physico-chemical transformations of chemical compounds [1]. During cavitation phenomena induced by hydrodynamic or acoustic cavitation (acoustic cavitation), the release of energy from the bubble implosion is accompanied by the emission of weak light known as “luminescence” phenomenon [16,17]. This feature was used in the present experiments to generate additional radicals to create an alternative oxidation system for the desulfurization of fuel samples. Both hydrodynamic cavitation and acoustic cavitation have been utilized for the treatment of sulfur-containing fuels. The complete desulfurization of model fuel containing 300 ppm of thiophene in n-octane is reported within the treatment time of 120 min using a hydrodynamic cavitation system with a vortex diode as cavitation device [18]. The complete desulfurization was also reported for model fuel containing 300 ppm dibenzothiophene (DBT) in hexadecane using an ultrasonic bath with the frequency of 42 kHz and input power of 185 W. The 100% desulfurization was achieved when acoustic cavitation and solid catalyst of 30% Fe/SBA-15 and 30%Fe/Zr-SBA-15 were combined. During the cavitation process, sulfur compounds get oxidized to sulfoxides and sulfones, which are highly polar compounds and can be extracted from organic phase by liquid–liquid extraction (LLE) using polar solvents such as acetonitrile [19], dimethyl formamide (DMF) [20], methanol [21], etc. .

In the present study, different combined oxidation systems were used to achieve high desulfurization rates of non-hydrotreated naphtha as model sulfur-containing fuel with an initial concentration of 1619 ppm. Sole acoustic cavitation processes under different frequencies such as 40 kHz (sonoprobe), 120 kHz (transducer), 80 kHz (sonoprobe), and 200 kHz (transducer) were conducted separately and in combination (40& 120 kHz; 80& 200 kHz). The obtained data were used to attain the optimized operating conditions at which higher desulfurization (%) could be achieved. After the optimization, different oxidative agents including air, ozone, hydrogen peroxide, acetic acid, acetone, acetone: water in defined ratios of (1:1), (2:1), (1:2) as well as UV light were combined with acoustic cavitation. This research constitutes in a relatively new method, which is using the acetone merely as an oxidant and inducing the formation of peracetic acid system from acetone: water (defined ratios of 1:1, 2:1, and 1:2) combined with acoustic cavitation and photolysis. The novelty of these experiments consists of the fact that the liquid oxidant of acetone: water can be used as an alternative system to the peracetic acid or performic acid system which is studied so far as a very successful oxidation system. This aspect was supported by the ability of acoustic cavitation and photolysis to dissociate acetone and water into their proper radicals, which are further recombined to form organic acid, notably formic or acetic acid [1]. No study, to the best of our knowledge, has considered the utilization of the hybrid process of acoustic cavitation and photolysis of acetone and acetone: water mixture for the desulfurization of sulfur-containing fuel of naphtha.

Table 1

Pseudo-first order kinetic parameters for a different group of processes assisted by dual-frequency acoustic cavitation in the presence of selected oxidants.

Treatment processes	Time (min)	k (min^{-1})	R^2	(%) Desulfurization
AC_{High-F} (H_2O_2/r_{ox} 5.0)	180	0.0051	0.9912	63.68 ± 1.79
AC_{High-F} (CH_3COOH/r_{ox} 5.0)	180	0.0063	0.9869	47.36 ± 0.78
AC_{High-F} ($CH_3COOH/ H_2O_2/r_{ox}$ 5.0)	30	0.1337	0.9993	100 ± 1.41
AC_{High-F} (Acetone/ 5% v/v)	180	0.0030	0.9812	43.39 ± 1.00
AC_{Low-F} (Acetone/ 5% v/v)	180	0.0015	0.9845	24.74 ± 1.32
AC_{High-F} (Acetone/ 10% v/v)	180	0.0045	0.9723	50.12 ± 0.93
AC_{Low-F} (Acetone/ 10% v/v)	180	0.0021	0.9805	32.01 ± 1.42
AC_{High-F} (UV + Acetone/ 10% v/v)	60	0.0042	0.9769	45.70 ± 1.03
AC_{High-F} (UV + CH_3COCH_3: H_2O (1:1))	60	0.0374	0.9746	40.38 ± 0.68
AC_{High-F} (UV + CH_3COCH_3: H_2O (2:1))	60	0.0010	0.9994	42.24 ± 0.93
AC_{High-F} (UV + CH_3COCH_3: H_2O (1:2))	60	0.0236	0.9888	42.04 ± 0.32
AC_{High-F} (Ozone/ 0.5 dm^3/min)	180	0.0096	0.9829	65.55 ± 1.40
AC_{Low-F} (Ozone/ 0.5 dm^3/min)	180	0.0089	0.9882	60.68 ± 0.55
AC_{High-F} (Air/ 0.5 dm^3/min)	180	0.0051	0.9844	42.41 ± 0.92
AC_{Low-F} (Air/ 0.5 dm^3/min)	180	0.0042	0.9801	39.60 ± 0.92

2. Materials and methods

2.1. Chemicals

The following reagents were used for conducting experiments: Hydrogen peroxide 30% (POCH S.A., Poland), acetic acid with purity of 99.5–99.9% (POCH S.A., Poland), acetone (pure for analysis, POCH S.A., Poland). Standards used for the determination of sulfur compounds via gas chromatography – flame photometric detector (GC-FPD) were as follows: Thiophene, 2-ethylthiophene, carbon disulfide, dimethyl sulfide, diethyl disulfide, dipropyl sulfide, di-*tert*-butyl disulfide, 1,3-propanedithiol, 1,2-ethanedithiol, 1-pentanethiol, and 1,4-butanedithiol. They were purchased from Sigma-Aldrich (USA). Other materials including 3-methylthiophene, 2-methylthiophene, 2-propanthiol, 1,3-propanedithiol, 3-methyl-1-butanethiol, 1-decanethiol, thiophenol and thioanisole were obtained from Fluka and dibutyl sulfide was purchased from Acros. Ozonation was performed using a Tytan 32 ozone generator (Erem, Poland) at a rate of 4.59 g O_3 h^{-1}. Naphtha samples (untreated fraction from atmospheric distillation) with a concentration of 1619 ppm were obtained from Grupa LOTOS.

2.2. Acoustic cavitation set up

Two same acoustic cavitation reactors (Model: M206-402; Beijing Yongda Ultrasonic CO., LTD) with a volume of 4 dm^3 were employed in the experiments. Each sonoreactor is equipped with a sonoprobe and set of transducers. The first sonoreactor is equipped with a sonoprobe (frequency: 40 kHz; power: 300 W) and transducers (frequency: 120 kHz; power: 300 W). The second sonoreactor is comprised of sonoprobe with frequency of 80 kHz and transducers with frequency of 200 kHz applying the same power of 300 W. The reactor is rectangular in shape with the height of 280 mm and width of 140 mm.

Optionally, the sonoreactor can be connected to a 3-dm^3 chamber equipped with a UV lamp (UV HQ 250Z; Hg lamp, UV-Technik, Germany) with the power of 250 W and specific lamp power of 56 W/cm. Fig. 1a describes the schematic design of the acoustic cavitation reactor combined with a UV chamber. Naphtha sample was introduced to the system through the inlet port A. A peristaltic pump (Watson Marlow 503, USA) was used to circulate the naphtha between the sonoreactor and UV chamber through outlet port 4 and inlet port B. Samples were collected through outlet port 3. Inlet port 2 equipped with a frit was applied to purge ozone or air into the system and inlet port 1 was used to pump liquid oxidants into the system. A cooling system was connected to the sonoreactor via inlet port 5 and outlet port 6. Acoustic cavitation was performed by sonoprobe (80 kHz) and transducers (200 kHz). Second configuration of the system includes a sonoreactor connected with a Tytan 32 ozone generator (380 W) for the generation of ozone gas at a dosing rate of 4.59 g O_3/h. Fig. 1b describes the schematic design of acoustic cavitation equipped with an ozone generator. Ozone was purged into the system through the inlet port 2. At the top of the reactor, a condenser coupled with the thermostat (HAAKE K20) was connected to outlet port B. A mechanical stirrer with input power of 6 W is used to uniformly mix and distribute the naphtha-contained solution and oxidants inside the sonoreactor.

2.3. Experimental procedure

Samples containing 1619 mg naphtha/dm^3 with volume of 3.8 dm^3 were introduced to the acoustic cavitation reactor. Blank experiments

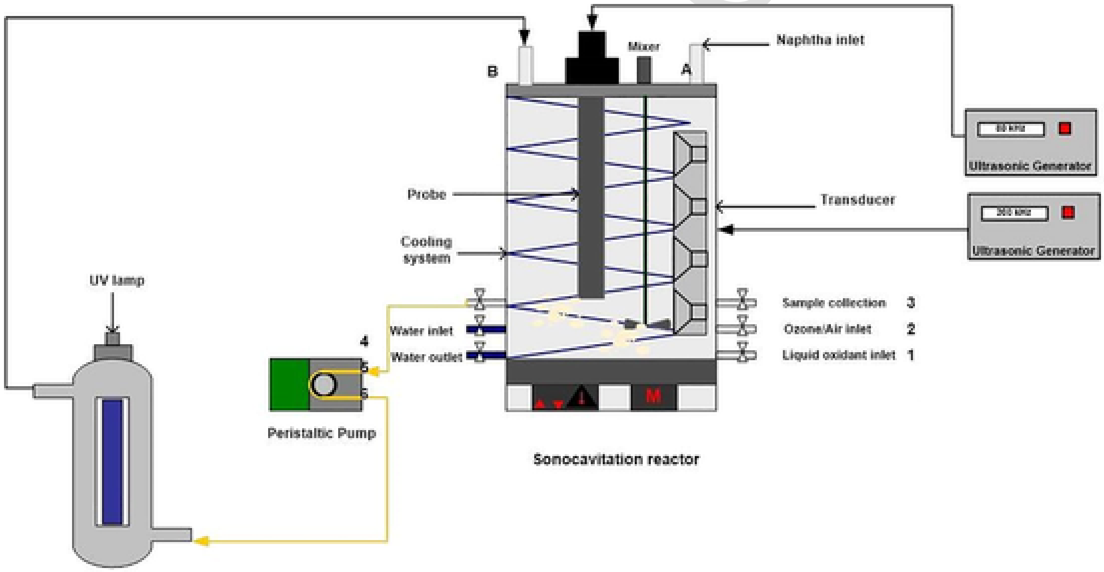

Fig. 1a. Acoustic cavitation reactor scheme for the desulfurization process of naphtha aided by UV irradiation.

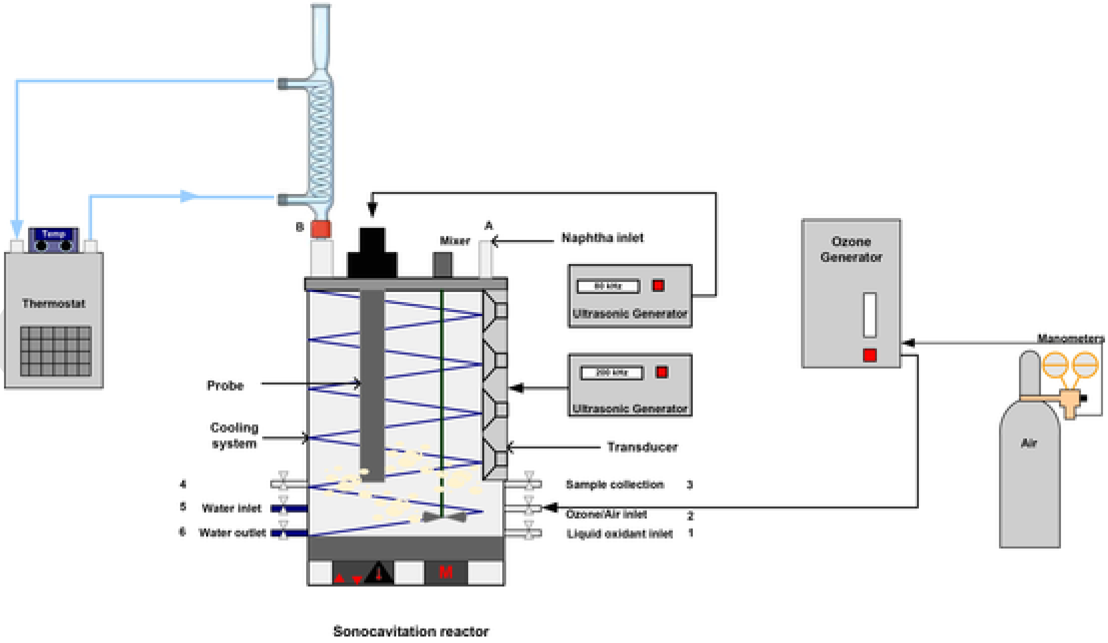

Fig. 1b. Acoustic cavitation reactor scheme for the desulfurization process of naphtha aided by ozonation.

including mechanical stirring without acoustic cavitation were performed for 180 min. Blank experiments are referred as ‘Sole’ processes throughout the text. They were used to check the possibility of any loss of sulfur compounds due to adsorption or evaporation.

Acoustic cavitation processes with different frequencies consisting of sonoprobes and transducers were performed to optimize the operating conditions for the desulfurization of naphtha. Sole and acoustic cavitation processes with different oxidants were performed for the desulfurization of naphtha within the treatment time of 180 min and operating temperature of 20 °C ± 2. The samples were collected at different time intervals including 15, 30, 60, 120 and 180 min. Acoustic cavitation processes were performed using high frequency sonoreactor with dual frequency system of sonoprobe (80 kHz) and transducer (200 kHz) which it is shortly described as $AC_{High\text{-}F}$. At the same reaction time, low frequency acoustic cavitation processes shortly described as $AC_{Low\text{-}F}$ were performed using the dual frequency system of sonoprobe (40 kHz) and transducer (120 kHz). Acoustic cavitation processes of AC $_{High\text{-}F}$ and AC $_{Low\text{-}F}$ were combined with selected reactants such as H_2O_2 (molar ratio oxidant to pollutant (r_{ox}) 0.5; 1.0; 5.0), CH_3COOH (r_{ox} 0.5; 1.0; 5.0), CH_3COOH/ H_2O_2 (r_{ox} 0.5; 1.0; 5.0), CH_3COCH_3 (5 % v/v; 10% v/v) and acetone: water (10% v/v) in defined ratios of (1:1); (2:1) and (1:2) as well as air and ozone (0.5 dm^3/min). Liquid oxidants like hydrogen peroxide and acetic acid were used at the concentration of 30% w/w. The dose of ozone was 0.459 g/h.

The first experiment was blank experiment applying only mechanical stirring for the desulfurization of naphtha within 180 min. In the second blank experiment, the air was purged into the sonoreactor, and samples were collected at regular time intervals within 180 min. The blank experiment applying air purging revealed an insignificant desulfurization efficiency of 6.72 %. This value was considered in the calculation of process efficiency to correct the real effectiveness of the acoustic cavitation process combined with air and ozone. The desulfurization efficiency was calculated via the following formula:

$$Desulfurizationefficiency\,(\%) = \frac{(C_0 - C_f)}{C_0} \times 100 \qquad (1)$$

where C_0 is initial concentration of selected sulphur compound and C_f is final concentration of sulfur compound. Total sulfur content was calculated on the basis of all peaks of sulfur compounds integrated on the chromatogram.

2.4. Analytical procedure

The concentration of sulfur compounds was measured using an Autosystem XL gas chromatograph equipped with an autosampler, split/splitless injector, and a flame photometric detector (FPD) (Perkin Elmer, USA). Separation conditions: a DB-1 column (60 m × 0.32 mm × 1.0 µm, BGB-1 Switzerland) was used in this study. Helium as the carrier gas was set to a volumetric flow rate of 2.0 cm^3/min. The temperature of heated zones: injection port temperature: 300 °C, detector temperature: 320 °C, temperature program: 50 °C (hold for 1 min), ramped at 15 °C min^{-1} to 150 °C (5 min), ramped at 10 °C min^{-1} to 300 °C (5 min), the total time of analysis was 32.67 min. A 10^{-3} cm^3 of naphtha sample was injected in split mode (1:5). The flowrates in the detector were: hydrogen: 75 cm^3/min, air 90 cm^3/min.

To identify the peaks on the naphtha chromatograms, sulfur compounds standards were analyzed, and their retention time values were determined. Identified sulfur compounds and corresponding retention time values are given in Table S1. Due to the non-polar character of the applied stationary phase, sulfur compounds are eluted according to their boiling point. Thus, standards of sulfur compounds were grouped based on their boiling point values. This allowed us to determine the retention time range up to thiophene, benzothiophene, and higher molecular weight sulfur compounds.

Identification of by-products was carried out by gas chromatography-mass spectrometry (GC–MS) using a QP2010SE GC–MS made by Shimadzu, Japan. DHA Restek column with total length of 100 m, thickness of 0.50 µm, and diameter of 0.25 mm was used. The temperature of heated zones: column oven temperature: initial 35 °C ramped 1 °C/min to final temperature 190 °C, injection temperature: 310 °C, ion source temperature: 260 °C, interface temperature: 310 °C. Samples were injected in split mode, with a split ratio of 150.0. The total time of analyses was 155 min. Same operating parameters (including the GC column) were used for GC analysis with flame ionization reactor (FID) to inspect changes of naphtha composition in relation to hydrocarbons as main components of naphtha. A GC-FID instrument model Clarus 580 made by Perkin Elmer, USA was used.

The presence of organic acids was confirmed using high-performance liquid chromatography HPLC (Merck-Hitachi, Germany) coupled with a UV array diode detector (DAD; Model 7455). A Zorbax Extend C-18 column with total length of 150 mm, diameter of 4.6 mm, packed with 3.5 µm particles (Agilent Technologies, USA) was utilized to perform the analysis. Identification of organic acids was carried out using RP-HPLC, which consists of acetonitrile: water (pH 3) in gradient conditions: ACN: water, 0: 100 isocratic for 3.0 min, next ramp to ACN: water, 100:0 in 14.0 min (ACN: water, 100: 0), isocratic 0,1 min. The flow rate of mobile phase was 1 cm^3/ min. Additional information on by-products identification by GC–MS and organic acid identification using RP-HPLC can be found in the supplementary file (Table S2).

3. Results and discussion

3.1. Optimization of acoustic cavitation conditions

Optimization of operating conditions is very important to identify the effectiveness of the selected treatment method. To evaluate the process effectiveness, a GC-FPD method was used for the detection of only sulfur-containing compounds. Identification database was performed on the basis of retention time values of standards (Table S1). GC-FPD system ensures an equimolar response to sulfur, which makes possible the quantitation of individual sulfur compounds as well as total sulfur content in naphtha-contained samples. In this paper total sulfur content was determined by adding together concentrations of each sulfur compound detected on the chromatogram. Sensitivity of FPD and applied temperature program assure that all VSC present in naphtha were quantified. Transformations of the identified sulfur compounds are further discussed in the next sections. Cavitation intensity is highly abundant in the close distance to the ultrasound source [22,23]. Low-frequency sonoreactors favor physical effects like polymer decomposition, cell disruption, solid–liquid extraction, while high-frequency sonoreactors emphasize the chemical effect in the process of wastewater treatment and chemical synthesis [24]. Four different ultrasonic frequencies and two dual-frequency systems were investigated during the desulfurization of naphtha. The irradiation frequencies were studied for the sole use of ultrasonic probes (40 kHz and 80 kHz) and the sole use of transducers (120 kHz and 200 kHz). The combined dual-frequency treatment system consisted of a low-frequency sonoreactor equipped with ultrasonic probe and transducer $AC_{Low\text{-}F}$ (40 and 120 kHz) and high-frequency sonoreactor $AC_{High\text{-}F}$ (80 and 200 kHz). Dual-frequency sonoreactors demonstrated higher desulfurization efficiency (%) compared to the use of single–frequency sonoreactors. The desulfurization efficiency (%) for the high dual-frequency ($AC_{High\text{-}F}$) system of sonoprobe-transducer (80 and 200 kHz) was 31.95% which was higher than the desulfurization efficiency (%) of low dual-frequency system (40 and 120 kHz) with desulfurization efficiency of 25.15% (Table S3). According to the desulfurization results, it can be concluded that high dual-frequency system of $AC_{High\text{-}F}$ provides more favourable conditions for desulfurization than $AC_{Low\text{-}F,}$ as high-frequency sonoreactors emphasize the chemical effect in the process of wastewater treatment and chemical synthesis [24]. The desulfurization efficiency of single-frequency systems within the reaction time of 180 min was linearly increased from low-frequency to high-frequency systems based on the following order: $AC_{40\ kHz}$ (20.21%), $AC_{80\ kHz}$ (21.04%), $AC_{120\ kHz}$ (23.56%) and $AC_{200\ kHz}$ (26.84%) **(**Table S3**)**. Implementation of dual-frequency sonoreactor using an ultrasonic probe and ultrasonic transducers results in the uniform distribution pattern of liquid inside the reactor since the acoustic cavitation wave will push the liquid downwards-upwards continuously. In this manner, the irradiation frequency covers all the region of treated media which leads to the bigger number of cavitation bubbles [25]. Application of dual frequency system causes better mixing of two different liquids with different densities i.e., mixture of organic phase and aqueous oxidants [25]. Higher effectiveness for two dual-frequency systems of $AC_{High\text{-}F}$ and $AC_{Low\text{-}F}$ is ascribed to fine distribution of liquid in the cavitation area and continuous interaction of as-generated bubbles due to the increased bubble volume fractions [26]. Dual frequency configuration used double power comparing to single frequency processes. In this case it would be discursive if the obtained higher effectiveness follows from high energy input or synergy of double frequency system. Preliminary studies revealed that prolongation of treatment didn't provide much higher desulfurization for each system. Thus, observed increase of desulfurization follows from synergistic effect of these combined frequencies. Acoustic cavitation intensity proved once again the effectiveness of dual frequency systems. The value of acoustic cavitation intensity for $AC_{High\text{-}F}$ and $AC_{Low\text{-}F}$ was 1.53 W/cm^2, while the value for the single-frequency systems was calculated to be 0.76 W/cm^2 **(**Table S3**)**.

3.2. *Role of hydrogen peroxide and acoustic cavitation*

Hydrogen peroxide has been widely used as a powerful and efficient oxidant for the decomposition and removal of organic pollutants from aqueous media [6,30]. The oxidation potential of hydrogen peroxide is related to the solution pH where the highest oxidation potential belongs to acidic conditions i.e., 1.8 V at pH = 0 and 0.87 V at pH = 14 [27].

In the present study, the role of H_2O_2 (30%) in combination with a dual high-frequency reactor (80 & 200 kHz; $AC_{\ High\text{-}F}$) for the desulfurization of naphtha was investigated. The oxidative effect of H_2O_2 was evaluated for the different r_{ox} values (0.5, 1.0, 5.0). The formed system has a biphasic (non-miscible) character. Due to density differences, the H_2O_2 was injected on the top of the reactor (through a perforated pipe providing a dispersion of the liquid in a form of small droplets) and allowed to fall in the naphtha phase assisted by mechanical stirring. As vigorous microcirculation was provided by ultrasonic transducers, this mechanical stirring had only auxiliary role in this scale of treatment. However, in case of process scale up, mechanical stirring should be used. A peristaltic pump was connected to the bottom of the reactor and provided circulation of the aqueous – oxidant-rich phase – from the bottom to the top of the reactor. Oxidation of the sulfur compounds takes place at the interface of the droplets of oxidant solution as well as inside of the aqueous phase where S-compounds are constantly partially extracted from the naphtha. Finally, products of oxidation – in the form of sulfoxides and sulfones – are effectively extracted to the aqueous phase. The remaining hydrophilic products generated during the oxidation of S-compounds were further removed by water washing after the treatment stage. Using sole H_2O_2, the desulfurization efficiencies (%) of 29.48, 11.29 and 44.43% were obtained at H_2O_2 to S-compounds ratios (r_{ox}) of 0.5, 1.0 and 5.0, respectively. While, under acoustic cavitation, the enhanced desulfurization efficiencies of 59.35%, 53.10%, and 63.68 % were obtained at the same oxidant to S-compound ratios (r_{ox}) of 0.5, 1.0 and 5.0, respectively. It was observed that as the loading of H_2O_2 was increased from 0.5 to 1.0, the desulfurization efficiency (%) was declined which can be explained by the scavenging effect of excess amounts of H_2O_2 towards $^{\bullet}OH$ radicals.

Under the cavitation conditions, hydrogen peroxide can be dissociated into hydroxyl radicals ($^{\bullet}OH$) identified as one of the main radical species with a oxidation–reduction potential of 2.8 V responsible for the oxidation of S-compounds into sulfoxides and sulfones which are further extracted and removed from organic phase [28]. As-generated radicals attack the pollutant molecules and the remaining radicals interact with hydrogen peroxide to form hydroperoxyl radicals ($^{\bullet}OOH$) and water [19,29].

After decomposition of hydrogen peroxide into $^{\bullet}OH$ and $^{\bullet}OOH$ radicals, the predominant species which will define the route of the reaction mechanism is hydroxyl radical due to the bigger number of generated reactive radical species. The amount of H_2O_2 in the organic phase treatment determines the oxidation potential and efficiency of treatment system for the removal of S-compounds from the aquatic medium. Sinhmar et al. (2020) observed and reported that the desulfurization of model diesel using ultrasonic flow cell and longitudinal bath was raised as the loading of H_2O_2 was increased from 10 cm^3/dm^3 (37.35%) to 30 cm^3/ dm^3 (55.92%) [31]. Moreover, increasing H_2O_2 to 40 cm^3/dm^3 caused a reduction in the desulfurization efficiency (%) because the excess amounts of H_2O_2 may act as $^{\bullet}OH$ scavenger.

To check the effect of cavitation in the desulfurization, naphtha treatment by sole H_2O_2 (r_{ox}; 0.5, 1.0, 5.0) was studied - only mixing of the organic phase and liquid oxidant was performed – without acoustic cavitation. The comparison revealed the main role of cavitation phenomenon in the oxidant activation. Under acoustic cavitation, the desulfurization efficiency (%)increased from 29.48% to 59.35%, 11.29% to 53.10% and 44.43% to 63.68% at H_2O_2 to S-compounds ratios (r_{ox}) of 0.5, 1.0 and 5.0, respectively. Acoustic cavitation process of $AC_{\ High\text{-}F}$ (H_2O_2/r_{ox}: 5.0) was evaluated to be the most effective method with a synergistic coefficient (calculated based on rate constant values) of 1.88, followed then by $AC_{\ High\text{-}F}$ (H_2O_2/r_{ox} 0.5) with a synergistic coefficient of 1.21. This leads to a conclusion that for processes with smaller r_{ox} the predominant factor is cavitation and for processes with higher r_{ox} the predominant factor is the loading of liquid oxidant.

Analysis of results presented on Fig. 2, reveals that from the detected compounds it was observed that thiophene, di-tert butyl disulfide and 1-pentanethiol achieved higher desulfurization rate. In case of thiophene derivatives, unsubstituted thiophene is the most susceptible for degradation. It follows from lack of steric barriers for radical species to attack sulfur atom. In other studied groups it is hard to find such dependencies. It is known, that in case of disulfides much higher rate constant values for reaction with hydroxyl radicals in comparison to thiols and sulfides were reported in literature. It follows from different mechanism, as in case of disulfides hydroxyl radicals tends to attack directly the weak S-S bond. In case of sulfides a slower two main pathways can take place – formation of S-–OH adduct or H-abstraction on secondary alkanes [32,33]. In case of thiols, these compounds under oxidative conditions can undergo conversion to disulphides. Such effects can overlay on main reaction pathway, making the results difficult for detailed analysis, when trying to provide some general rules of sulfur compounds degradability under studied conditions. Among different sulfur compounds, the highest desulfurization efficiency (%) of 65.05% was achieved for di-tert butyl disulfide **(**Fig. 2**b)**. The lowest desulfurization efficiency of 14.27% was observed for 1,3-propanedithiol **(**Fig. 2**c)**. The desulfurization efficiencies of 63.06%, 58.68%, 40.56%, 30.97% and 30.53% were obtained for thiophene, diethyl sulphide, 1-pentanethiol, 1,4-butanedithiol, and benzyl thiol, respectively **(**Fig. 2**c)**. The reported values correspond to $AC_{\ High\text{-}F}$ (H_2O_2/R_{ox} 5.0).

The results confirmed the significant desulfurization of thiophene and di-tert butyl disulfide compared to the other two compounds.

3.3. *Determination of role of acetic acid in desulfurization of naphtha*

To elucidate the role of acetic acid (30% w/w) in the aqueous phase of peracetic acid, acoustic cavitation experiments in the presence of

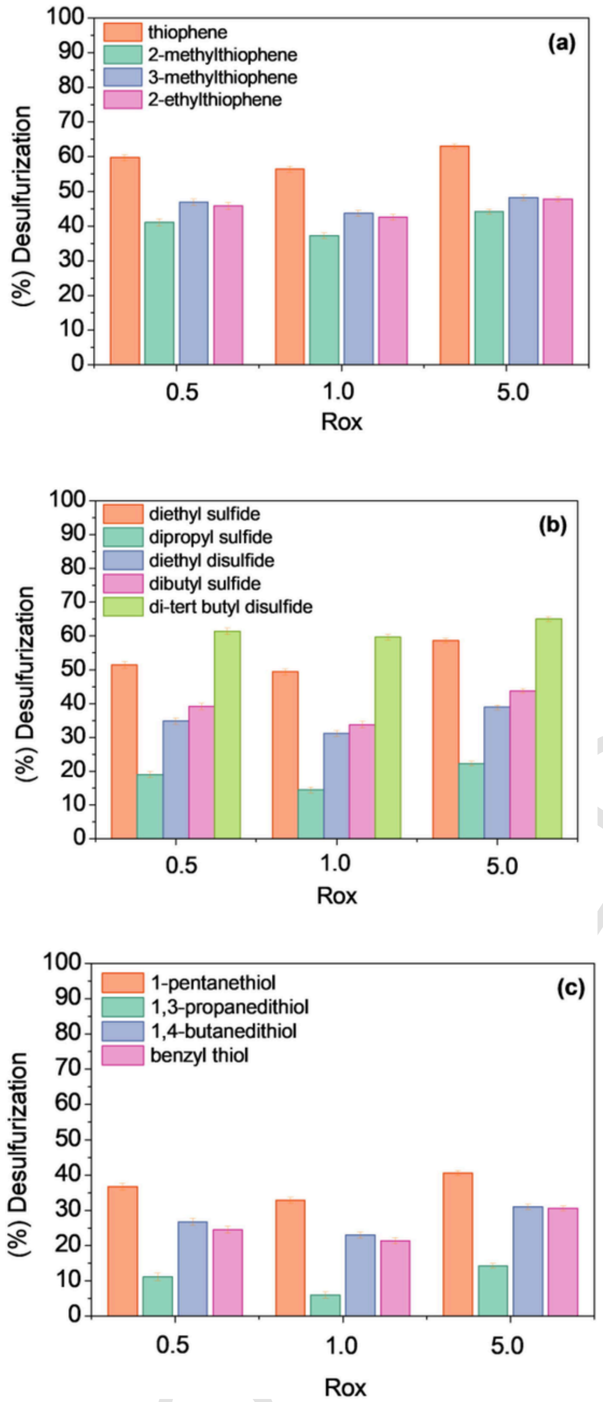

Fig. 2. Desulfurization of different S-compounds (thiophenic (Fig. 2a), sulphide (Fig. 2b), and thiols (Fig. 2c)) via acoustic cavitation process of AC $_{\text{High-F}}$ with different r_{ox} of 0.5, 1.0, and 5.0, utilizing AC $_{\text{High-F}}$ based on r_{ox} of 5.0 (Fig. 2d) under operating temperature of 20 ± 2 °C and reaction time of 180 min.

acetic acid as a single oxidant were performed. The experiments were conducted in the high-frequency sonoreactor (AC $_{\text{High-F}}$) at three different molar ratios (r_{ox}) of 0.5, 1.0, and 5.0.

In the absence of acoustic cavitation, the highest desulfurization (%) of 18.67% was obtained for the sole process of CH_3COOH/r_{ox} 5.0, followed then by the sole process of CH_3COOH/r_{ox} 0.5 (9.17%). The lowest desulfurization efficiency (%) of 6.0% was obtained for the sole process of CH_3COOH/r_{ox} 1.0. In the case of the combined process of acoustic cavitation/acetic acid using AC $_{\text{High-F}}$, the desulfurization efficiency of 35.54, 40.87, and 47.36% were obtained for r_{ox} values of 0.5, 1.0 and 5.0, respectively.

The most effective process in terms of desulfurization was AC $_{\text{High-F}}$ (CH_3COOH/r_{ox} 5.0). Using AC $_{\text{High-F}}$ (CH_3COOH/r_{ox} 5.0), the highest desulfurization efficiency was achieved for sulfides group (79.56%) **(**Fig. 3**b)** in comparison with the other groups of sulfur compounds such as substituted thiophenes (67.71%) **(**Fig. 3**a)** and substituted thiols (44.80%) **(**Fig. 3**c)**. For sulfide group, the lowest desulfurization efficiency was obtained for dibutyl sulfide (42.69%); while, in the case of thiophenes, the lowest desulfurization efficiency (%) of 48.34% was ob-

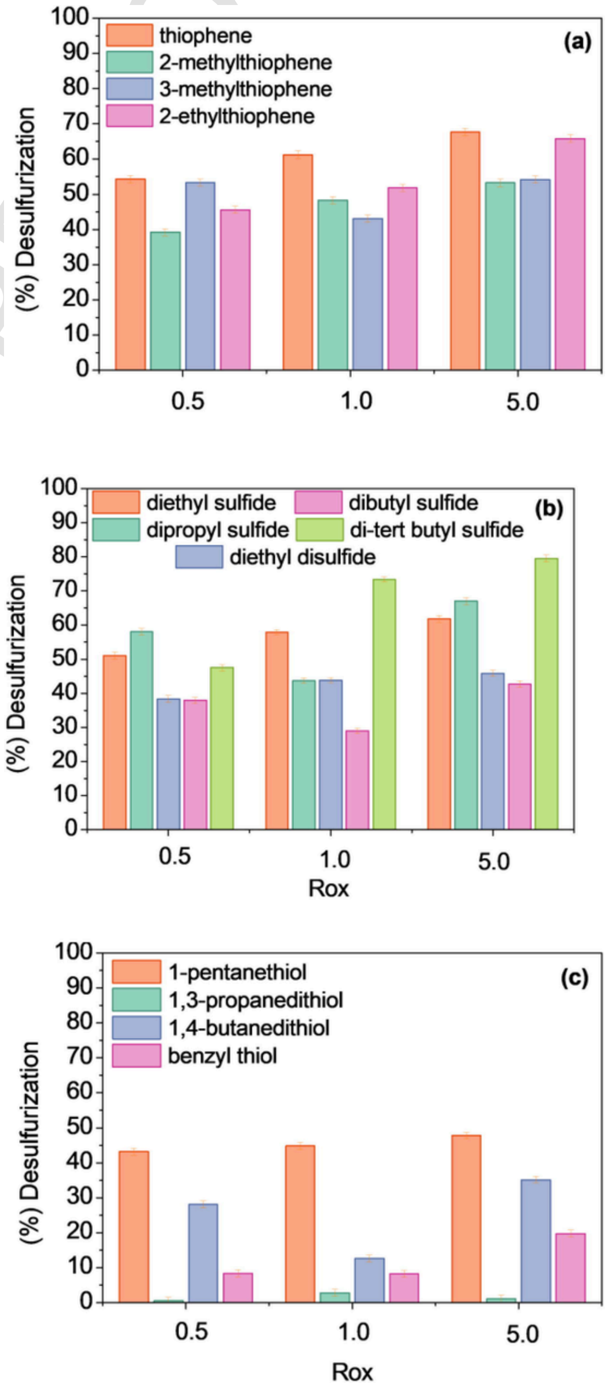

Fig. 3. Desulfurization of S-compounds (thiophenic compounds (Fig. 3a), sulfide compounds (Fig. 3b), and thiol compounds (Fig. 3c)) using AC $_{\text{High-F}}$ (CH_3COOH/ r_{ox} 0.5; 1.0; 5.0), at operating temperature of 20 °C and reaction time of 180 min.

tained for 2-methylthiophene. For thiols, negligible desulfurization efficiency of 1.10% was attained for 1,3-propanedithiol.

The desulfurization of di tert butyl disulfide was 73.40% and 47.53%, thiophene was 61.23% and 54.28%, dipropyl sulfide was 65.84% and 58.02% and 1-pentanethiol was 43.12% and 43.20% for AC $_{High\text{-}F}$ (CH_3COOH/r_{ox} 1.0) and AC $_{High\text{-}F}$ (CH_3COOH/r_{ox} 0.5) processes, respectively. The lowest desulfurization efficiency of 0.50% was obtained for 1,3-propanedithiol at r_{ox} of 0.50. The desulfurization of 1,3-propanedithiol at r_{ox} of 0.50 was also negligible (2.70%).

In addition, the combination of acoustic cavitation with acetic acid was synergetic. The maximum synergistic coefficient was 2.33 obtained for AC $_{High\text{-}F}$ (CH_3COOH/r_{ox} 5.0). At r_{ox} values of 0.5 and 1.0, synergistic coefficients were 1.50 and 1.27 using the same treatment process of AC $_{High\text{-}F}$, respectively.

3.4. Role of peracetic acid in the desulfurization of naphtha

Attempts on combined application of hydrogen peroxide and acoustic cavitation for treatment of some fuels were reported in few papers, including systems such as H_2O_2/UV, H_2O_2/O_3 and catalysts [34], inorganic acids [35], organic acids, and Fenton's reagent Fe^{2+}/H_2O_2 [21].

In the present study, acetic acid was combined with acoustic cavitation (AC) and H_2O_2 for the desulfurization of sulfur compounds in the naphtha. Among various carboxylic acids, formic acid is unstable and corrosive and propionic acid with longer carbon chain has a lower solubility in H_2O_2; thus, they were not appropriate for the treatment process. Acetic acid is considered as the best choice to achieve more than 95% desulfurization [36].

Peracetic acid was applied as an oxidant in the desulfurization of naphtha by the acoustic cavitation (Eq.7). Acetic acid (30% w/w) was added to H_2O_2 (30% w/w) in the defined ratio of 2:1 (CH_3COOH: H_2O_2). The role of peracetic acid was investigated for three molar ratios (r_{ox}) of 0.5, 1.0, and 5.0. The solution pH dropped to 2.0. In this approach, it can be stated that acetic acid plays a dual role of oxidant and pH corrector, accelerating the desulfurization of the organic phase. Accordingly, the desulfurization efficiencies of sole processes were as follows: $CH_3COOH/\ H_2O_2/\ r_{ox}$ 0.5: 16.75%, $CH_3COOH/\ H_2O_2/\ r_{ox}$ 1.0: 27.29%, and $CH_3COOH/\ H_2O_2/\ r_{ox}$ 5.0: 37.36%. Higher amount of available oxidants introduced into the fuel provides generation of radical species which can be directly initiated from the dissociation of H_2O_2 forming hydroxyl radicals $^{\bullet}OH$. Furthermore, the dissociation of as-generated peracetic acid results in the formation of acetyl ($CH_3CO^{\bullet}$) and peroxyl ($HOO^{\bullet}$) radicals which will further contribute to the oxidation of sulfur compounds [19]. Therefore, there is a sufficient amount of oxidant and reactive radicals for the desulfurization of sulfur compounds at higher r_{ox} values. For lower r_{ox} values, the desulfurization reaction requires higher reaction time to firstly recombine and enter into the regeneration cycle of acetic acid and after that, the formation and dissociation of peracetic acid will contribute to the formation of reactive radicals such as $CH_3CO^{\bullet}$ and $HOO^{\bullet}$ [38]. The oxidation route of peracetic acid is described by the following equations [39,40]:

$$CH_3COOH + H_2O_2 \xrightarrow{)))} CH_3COOOH + H_2O \tag{2}$$

$$CH_3COOOH \xrightarrow{)))} CH_3CO^{\bullet} + HOO^{\bullet} \tag{3}$$

$$H_2O_2 \xrightarrow{)))} HO^{\bullet} + HO^{\bullet} \tag{4}$$

$$H_2O_2 \xrightarrow{)))} HO^{\bullet} + HO^{\bullet} \tag{5}$$

$$H_2O_2 + HO^{\bullet} \xrightarrow{)))} HOO^{\bullet} + H_2O \tag{6}$$

$$\text{S - compound} + HOO^{\bullet} \xrightarrow{)))} \text{Sulfoxide/Intermediates} + HO^{\bullet} \tag{7}$$

$$\text{Sulfoxide} + HOO^{\bullet} \xrightarrow{)))} \text{Sulfone/Intermediates} + HO^{\bullet} \tag{8}$$

$$CH_3CO^{\bullet} + HO^{\bullet} \xrightarrow{)))} CH_3COOH \tag{9}$$

Dual-frequency acoustic cavitation was used in this reaction system of peracetic acid and naphtha. A complete desulfurization efficiency of 100% was achieved for the process of AC $_{High\text{-}F}$ ($CH_3COOH/H_2O_2/r_{ox}$ 5.0) within 30 min.

More and Gogate [37] reported a desulfurization efficiency of 57% within 60 min using a coupled system of ultrasound (1050 W) and peracetic acid (10% loading). It revealed a significant improvement as $CH_3COOH/\ H_2O_2$ system was reported to provide only 24% desulfurization. This study was performed using acoustic cavitation system working under frequency of 28 kHz and ultrasonic power of 200 W. Comparatively, in another study, desulfurization efficiency of 29.4% was attained for the sole process of $CH_3COOH/\ H_2O_2$, while the desulfurization efficiency of 43.1% was obtained for the combined process of US/CH_3COOH/H_2O_2 [30].

The effectiveness of the combined process of high dual-frequency acoustic cavitation/peracetic acid was confirmed by a high synergistic index of 7.55. Two remaining processes of AC $_{High\text{-}F}$ ($CH_3COOH/H_2O_2/r_{ox}$ 1.0) and AC $_{High\text{-}F}$ ($CH_3COOH/H_2O_2/r_{ox}$ 0.5) had the synergistic coefficients of 3.77 and 5.41 corresponding to the desulfurization efficiencies of 93.07 and 95.10% during the reaction time of 180 min, respectively. The combined process of acoustic cavitation/peracetic acid/H_2O_2 at r_{ox} of 1.0 was less effective than the combined process at r_{ox} of 0.5. Results of this set of experiments are presented in Table S4. The obtained results indicated catalytic properties of the treatment system at r_{ox} of 0.5, i.e. The obtained desulfurization efficiency highly exceeded the expected values (based on r_{ox}). Therefore, the optimum value for the combined process of acoustic cavitation/peracetic acid was more than r_{ox} 1.0 (i.e., 5.0). The decreased desulfurization efficiency and synergy index at r_{ox} 1.0 can be explained by the scavenging of $^{\bullet}OOH$ radicals by H_2O_2 molecules. Equal ratio of hydrogen peroxide to acetic acid (1:1) is not preferred since as-generated $^{\bullet}OOH$ will be scavenged by H_2O_2 molecules before they get displaced into the organic phase via interfacial area [40]. This problem was not observed at r_{ox} of 0.5 and r_{ox} of 5.0 because of the fact that the reaction of hydrogen peroxide is faster than the formation of peracetic acid leading to the generation of limited number of radical species. Increased formation of peracetic acid results in the increased desulfurization due to high evaporation of peracetic acid into the cavitation bubbles [40]. It can be concluded that H_2O_2 concentration is a limiting factor. This fact is also supported by the results obtained for the coupled process of acoustic cavitation/H_2O_2 at different r_{ox} of 0.5, 1.0, and 5.0 (see section 3.2) where the lowest desulfurization was obtained in the presence of H_2O_2 at r_{ox} of 1.0. This adverse effect was not observed during the application of CH_3COOH alone (r_{ox} 0.5, 1.0 and 5.0). Comparing acoustic cavitation/peracetic system to the one based on hydrogen peroxide it can be concluded that it is less selective in respect to studied groups of sulfur compounds. It follows mostly from higher abundance of reactive radical species. In case of excess of oxidant (rox 5) a total degradation is observed.

The desulfurization efficiency of 100% was obtained for three groups of S-compounds including thiophenic compounds (Fig. 4**a)**, substituted sulfides (Fig. 4**b)**, and thiols (Fig. 4**c)** using AC$_{High\text{-}F}$ ($CH_3COOH/\ H_2O_2\ r_{ox}$ 5.0) process. Even though complete desulfurization of S-compounds in naphtha composition was achieved using AC $_{High\text{-}F}$ ($CH_3COOH/H_2O_2/r_{ox}$ 5.0), a sulfonated intermediate by-products were emerged and identified after the reaction time of 30 min. Analysis of samples after treatment via GC–MS analysis confirmed the presence of an additional peak (*m/z* 142). A comparison of the acquired mass spectra with the GC–MS library revealed that identified peak may belong to 2-thiophene acetic acid or 3-thiophene acetic acid. Suspected intermediate by-products may be yielded by the reaction of 2-methylthiophene or 3-methylthiophene present in the sample in the

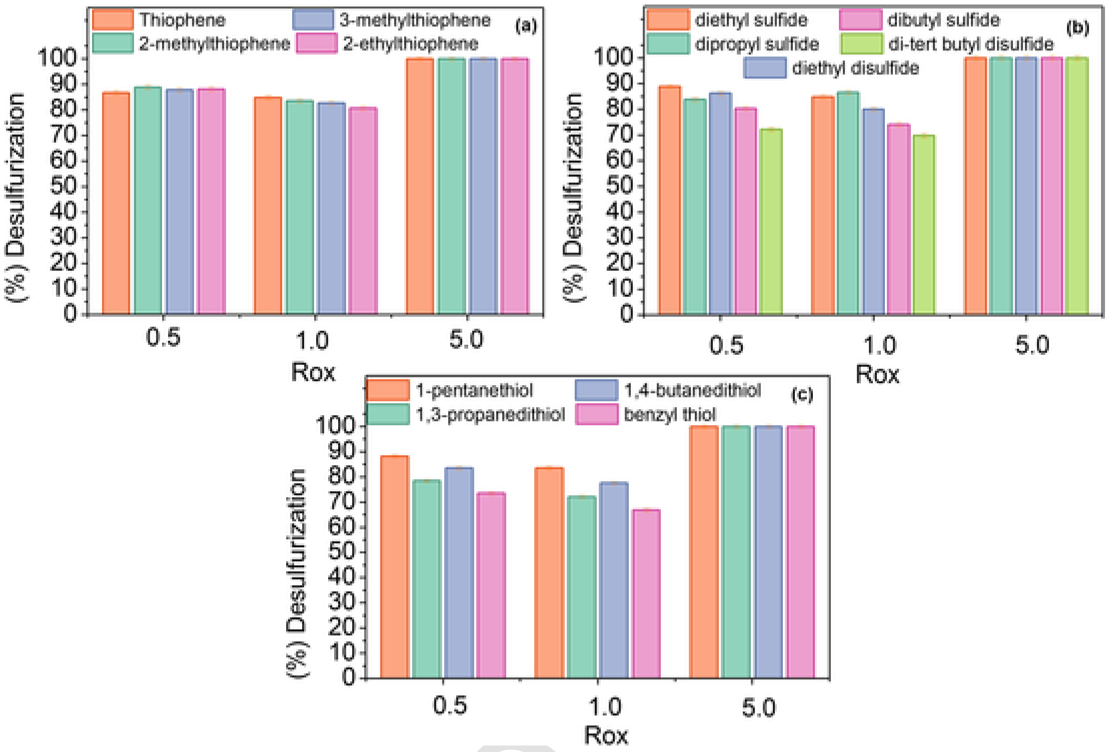

Fig. 4. Desulfurization of S-compounds by means of AC $_{\text{High-F}}$ (CH_3COOH/H_2O_2 r_{ox} 0.5; 1.0; 5.0) within 180 min at 20 ± 2 °C (thiophenic compounds (a), sulfide compounds (b) and thiols (c)).

presence of both hydroxyl and acetyl radicals ($CH_3CO^\bullet$). Further oxidation of 2-methylthiophene by hydroxyl radical will form 2-carboxaldehyde thiophene (*m/z* 112) [41]. The generation of above-mentioned by-products confirmed proposed pathway of naphtha decomposition. These intermediates compounds can be removed from naphtha by water washing after oxidation. This part of study revealed the main role of $^\bullet OH$, $CH_3CO^\bullet$ and $^\bullet OOH$ in the oxidation of S-compounds in the naphtha. A desulfurization efficiency of 100% was attained using AC $_{\text{High-F}}$ (80 and 200 kHz) and peracetic acid (r_{ox} 5.0) for all identified S-compounds within the reaction time of 30 min.

3.5. *Desulfurization of naphtha using combined process of acoustic cavitation/UV irradiation*

Photolysis via UV irradiation combined with acoustic cavitation has been widely used for wastewater treatment. The combined process of cavitation/UV produces $^\bullet OH$ radicals in the aqueous phase due to the photolysis of H_2O by UV irradiation, enhancing the decomposition of pollutant molecules in the wastewater. Different types of refractory organic pollutants like pharmaceutical contaminants [42], petroleum spill contaminants [43], industry effluents [44] have been successfully degraded in wastewater by photolytic assisted cavitation methods. The photolysis coupled with cavitation and other types of oxidants such as H_2O_2, acetic acid, peracetic acid and TiO_2 has been also investigated for the desulfurization of different types of hydrocarbon streams, like model fuels simulating diesel, kerosene, and naphtha [45,46]. The combination of UV with oxidants like H_2O_2 and acetic acid causes the homolytic cleavage of O-O bond which results in the formation of reactive radicals like $^\bullet OH$, $^\bullet OOH$ and $CH_3CO^\bullet$ [46]. Since the naphtha sample contains thiophenic compounds, sulfides, and mercaptans, the results will be interpreted based on the nature of such compounds. The UV photolysis causes the S-S bond cleavage, rather than C-S cleavage for disulfide compounds. In the case of monosulfides and mercaptans, the C-S bond will be attacked and cleaved by as-generated radicals before the cleavage of S-H bond [47]. The schematic flow-diagram of the sonoreactor aided by UV irradiation is depicted in Fig. 1a.

During photolytic processes of naphtha combined with acoustic cavitation, the highest desulfurization was obtained for the dual high-frequency reactor of AC$_{\text{High-F}}$ aided by UV with desulfurization efficiency of 50.69% within 180 min. The sole process, which consists of only mechanical stirring of liquid fuel in the absence of acoustic cavitation, yielded only desulfurization efficiency of 5.95%.

Based on the results of a similar study, a combination of UV and ultrasound without additives resulted in the desulfurization efficiency of 10.9% for the model fuel, which was higher than the US alone (8.7%) and UV alone (3.4%) [45].

On the basis of the obtained results, it can be inferred that high dual-frequency acoustic cavitation AC $_{\text{High-F}}$ aided by UV was more effective than the low dual-frequency acoustic cavitation AC $_{\text{Low-F}}$ (UV) with corresponding synergetic coefficients of 1.51 and 0.87, respectively. Using AC $_{\text{High-F}}$/UV, the highest desulfurization was achieved for 2-methylthiophene (84.09%), thiophene (59.26%), and diethyl sulfide (57.74%), respectively. The process was not effective for desulfurization of 1,3-propanedithiol with an efficiency of 4.16% using AC $_{\text{High-F}}$ aided by UV. In case of AC $_{\text{Low-F}}$/UV, concentration of this compound increased (by 6.18 %) after treatment – it reveals that this compound is a by-product of treatment of other sulfur compounds present in naphtha. This observation is important for further studies as dithiols concentration should be monitored during treatment as potential secondary sulfur pollutants.

3.6. *UV/acetone process coupled with acoustic cavitation for desulfurization*

Photolysis of acetone produces acetyl radicals $CH_3CO^\bullet$ and methyl radicals $CH_3^\bullet$ via two pathways. Since acetone molecule will absorb a photon in the UV range of 200 to 300 nm, an electron will be transferred from oxygen n-orbital to π* orbital leading to dissociative radical forms of acetone [48]:

$$CH_3COCH_3 + h\upsilon \xrightarrow{)))} CH_3CO^{\bullet} + CH_3^{\bullet} \quad (10)$$

Under UV irradiation of acetone: water (1:1), hydroxyl radicals $^{\bullet}OH$ are produced from homolytic cleavage of H_2O as represented in the following equation:

$$H_2O + h\upsilon \xrightarrow{)))} H^{\bullet} + HO^{\bullet} \quad (11)$$

There are two ways that hydroxyl radicals can react with acetone. Firstly, hydroxyl radicals can recombine with acetone to produce the hydrated form of pyruvic aldehyde which undergoes a chain reaction to produce pyruvic acid and later acetic acid. Pyruvic acid can react with hydroxyl radicals to produce acetic acid, which proved to be a very effective oxidant in the oxidation of S-compounds [49]. The second way consists of the formation of organic acids like acetic acid and formic acid which are proved to be very successful oxidants in the desulfurization of sulfur compounds based on the following equations [48,50]:

$$CH_3CO^{\bullet} + HO^{\bullet} \overset{)))}{\leftrightarrows} CH_3COOH \quad (12)$$

$$CH_3CO^{\bullet} + H^{\bullet} \xrightarrow{)))} CH_3^{\bullet} + HCO^{\bullet} \quad (13)$$

$$HO^{\bullet} + HCO^{\bullet} \overset{)))}{\leftrightarrows} HCOOH \quad (14)$$

After dissociation of acetone into acetyl and methyl radicals, acetyl radicals can react with hydroxyl radicals $HO^{\bullet}$ to form acetic acid. Hydrogen radicals $H^{\bullet}$ will interact with acetyl radicals to form methyl radicals and formyl radicals. Formyl radicals can further react with hydroxide radicals to produce formic acid. As-generated radicals like hydroxyl radicals, acetyl radical and formyl radicals can directly attack sulfur species to form oxygenated sulfur compounds. Remaining reactive radicals will re-enter the regeneration cycle to produce respective organic acids, until the aqueous oxidant is completely consumed.

As results, the combination of high dual frequency system AC $_{\text{High-F}}$ (80 and 200 kHz) and 10% v/v loading of acetone under UV irradiation revealed a desulfurization efficiency of 45.70% in 180 min **(**Table S5**).** Considering the desulfurization efficiency of each sulfur compound present in the naphtha sample, it was observed that thiophenic and sulfide compounds exhibited a higher affinity to be oxidized by acetyl radicals. The desulfurization of diethyl sulfide, 2-methylthiophene and 1-pentanethiol was found to be 65.70, 62.69, and 55.22%, respectively **(**Fig. 5**a)**. Additionally, three groups of experiments with an added source of hydrogen and hydroxyl radicals coupled with acetone and acoustic cavitation were investigated. In this approach, H_2O was chosen as source of hydroxyl and hydrogen radicals in the defined ratios of acetone: water (1:1; 2:1; 1:2) **(see Eq.** (17)**)**. After photodissociation of hydrocarbons and S-compounds, acetyl radicals $CH_3CO^{\bullet}$ which are generated from acetone molecule may react with S-compounds to form polar by-products which are directly extracted by the aqueous phase circulating in the treatment system. The highest desulfurization was observed for disulfides and mercaptans. According to the obtained data, the complete desulfurization of di-tert butyl disulfide, dibutyl sulfide, benzylthiol, and 1,3-propanedithiol was achieved. The lowest desulfurization efficiency corresponded to thiophenic derivatives, pentanethiol, diethyl disulfide and dipropyl sulfide **(**Fig. 5**b).** In case of sulphides, longer hydrocarbon chain makes the reaction with relatively bigger – in respect to hydroxyl radical – acetyl radical easier. This observation relates also to thiophenic derivatives which were effectively degraded by hydroxyl radical based processes, while in this case lower effectiveness was obtained.

A detailed evaluation for the photolysis of acetone assisted by acoustic cavitation was carried out with and without water addition. Fig. 6 exhibits a total desulfurization efficiency of 50–60% for thiophenic, sulfide and thiol compounds when UV/acetone (10% v/v) aided by acoustic cavitation was utilized. Addition of water in the biphasic process of acetone: water (1:1; 2:1; 1:2) did not favor the oxidation of thiophenic compounds leading to desulfurization efficiency of < 20% **(**Fig. 6**a)**. The same tendency was also observed for diethyl sulfide, dipropyl sulfide, diethyl disulfide, 1-pentanethiol and 1,3-propanedithiol compounds **(**Fig. 6**a, b and c)**. The present findings confirmed that UV/acetone/water aided by acoustic cavitation is merely a selective treatment method regarding desulfurization of specific S-compounds including dibutyl sulfide, di-tert butyl disulfide, 1,4-butanedithiol and benzyl thiol since desulfurization efficiency of 100% was achieved for such compounds during treatment time of 180 min. Comparative data showed that UV/acetone aided by acoustic cavitation (AC $_{\text{High-F}}$ (UV + CH_3COCH_3 (10% v/v)) can be considered as a comprehensive method for the desulfurization of all groups of sulfur compounds including thiophenes, sulfides and thiols (mercaptans) compounds. On the other hand, the photolysis of biphasic system of fuel-acetone: water (AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (2:1)) is a restricted method which favors the complete desulfurization of specific sulphur compounds **(**Fig. 6**b and c)**.

Moreover, it can be concluded that addition of water to reaction system strongly increases the degradation of dibutyl sulphide, ditertbutyl disulphide as well as benzylthiol and dithiols. These compounds were much persistent to degradation for AC/H_2O_2 system. Thus, a target process for selected sulfur compounds could be based on presence of water as important parameter of treatment system. Addition of water provided an extractive environment for formed more polar by-products. They were continuously removed from the fuel. Thus, formed radical species reacted only with the remained compounds. On the other hand acoustic cavitation formed in aqueous phase produced additional amounts of radical species, which could react with extracted compounds as well as – in some part – react with pollutants on the water-organic phase interface. Opposite effect was observed for thiophene derivatives. Addition of water negatively affects their degradation. It is clear that formed aqueous phase removes most of acetone, i.e. source of radicals, from the fuel and secondly under ultrasonic irradiation increases the turbidity lowering the UV light absorption. A detailed study on selectivity of studied systems in respect to each group of sulfur compounds and their homologs, demands more data and a focused research, which will be performed in the near future.

When excess acetone loading (CH_3COCH_3: H_2O (2:1)) in the biphasic system was used, the desulfurization of all S-compounds was slightly higher in comparison with other two biphasic systems of CH_3COCH_3: H_2O (1:1) and CH_3COCH_3: H_2O (1:2) **(**Fig. 7**b and c)**. Thus, the content of acetone was the limiting factor for the desulfurization using AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (2:1)) process. Additional studies were performed to verify the formation of organic acids in post-process medium. For this, the presence of organic acid in the aqueous phase (formic acid; HPLC retention time (Rt) 1.5 min) was assessed by using HPLC analysis for both acoustic cavitation and UV-assisted acoustic cavitation. Moreover, benzoic acid (Rt 3.0 min) was also identified as another by-product. The presence of benzoic acid indicated advanced oxidation of benzyl thiol to corresponding aromatic compound. Identified by-products in organic and aqueous phase are listed in the supplementary file **(**Table S2**)**. The desulfurization efficiency values of 40.38, 42.24 and 42.04% were obtained for AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (1:1)), AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (2:1)), and AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (1:2)) processes, which are comparable to the desulfurization efficiency (47.36%) obtained for the combined process of acoustic cavitation/acetic acid (AC $_{\text{High-F}}$ (CH_3COOH/ r_{ox} 5.0)) **(**Table S5**)**. It can be concluded that acetone: water mixture (CH_3COCH_3: H_2O) combined with UV and acoustic cavitation can be used as an alternative source of organic acid (formic acid) to produce reactive radicals such as acetyl $CH_3CO^{\bullet}$, formyl $HCO^{\bullet}$, hydroxyl $^{\bullet}OH$ and $CH^{\bullet}_3$ radicals.

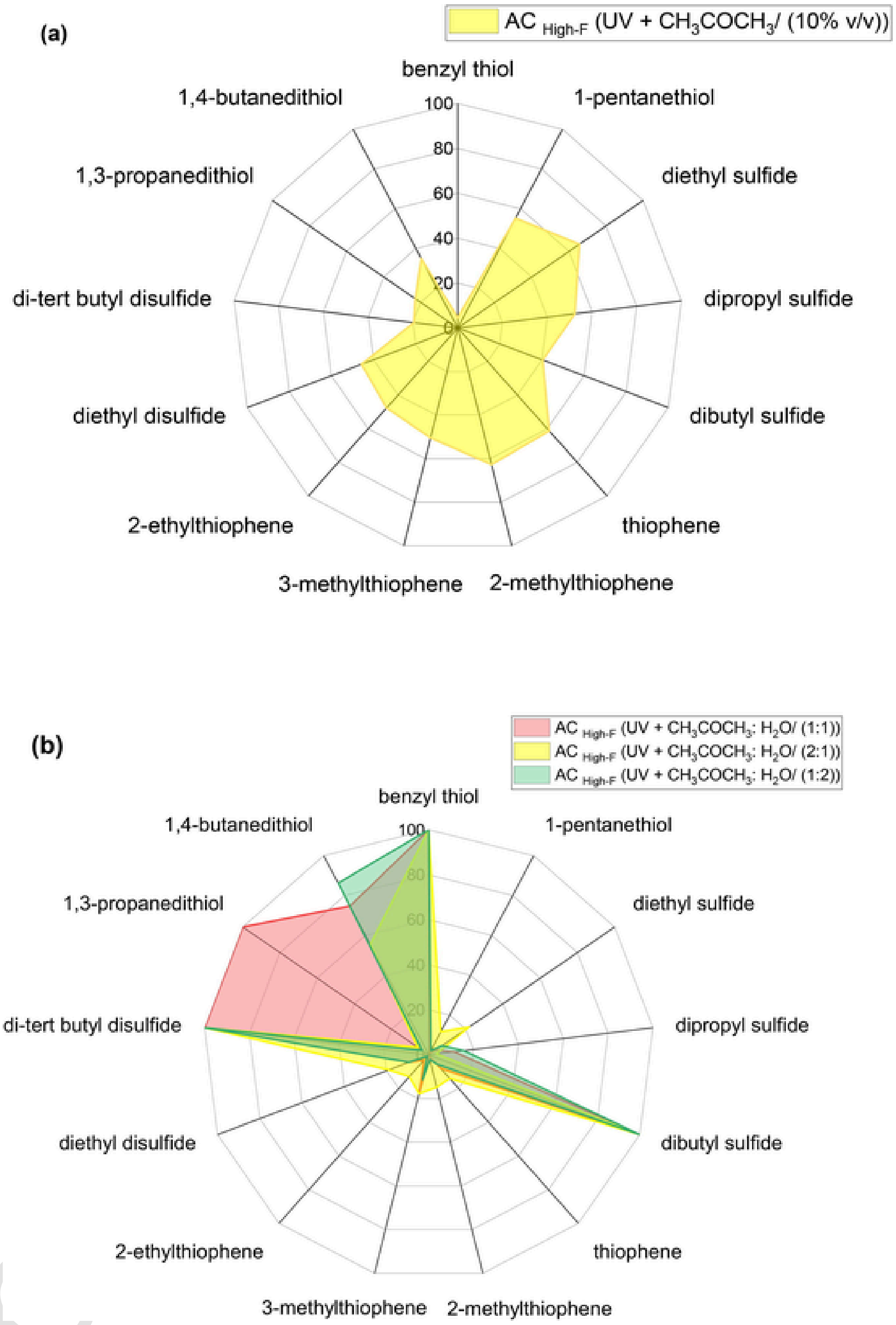

Fig. 5. Radial charts for desulfurization of sulphur compounds present in naphtha samples using different combined processes [AC $_{\text{High-F}}$ UV + Acetone/(10% v/v) (Fig. 6**a**), AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (1:1)), AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (2:1), and AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (1:2) (Fig. 6**b**)] within treatment time of 180 min and operating temperature of 20 ± 2 °C.

3.7. Aeration-assisted acoustic cavitation for desulfurization of S-compounds

The effect of aeration on the desulfurization efficiency of naphtha was studied using two dual-frequency processes. For this purpose, the flow rate of air into the reactor was fixed to 0.5 L/min and the whole process was operated in treatment time of 180 min.. The removal of volatile sulfur compounds was found to be negligible when aeration alone was implemented (desulfurization efficiency of 6%), while the enhanced desulfurization efficiencies of 39.60 and 42.41% were obtained for AC $_{\text{Low-F}}$ (Air/0.5 dm^3/min) and AC $_{\text{High-F}}$ (Air/0.5 dm^3/min) processes, respectively (Table S5).

It is well known that the presence of dissolved gases in the sonicated liquid enhances the cavitation effect [1]. Continuous aeration of the liquid phase results in saturation of the liquid media with dissolved gases, thus maximizing the cavitational effect. The reaction of thiophene in the presence of oxygen consists of the hydrogen abstraction pathway and addition/elimination pathway [51].

The synergy coefficients of the combined process (acoustic cavitation/aeration) demonstrated the effectiveness of this approach for the

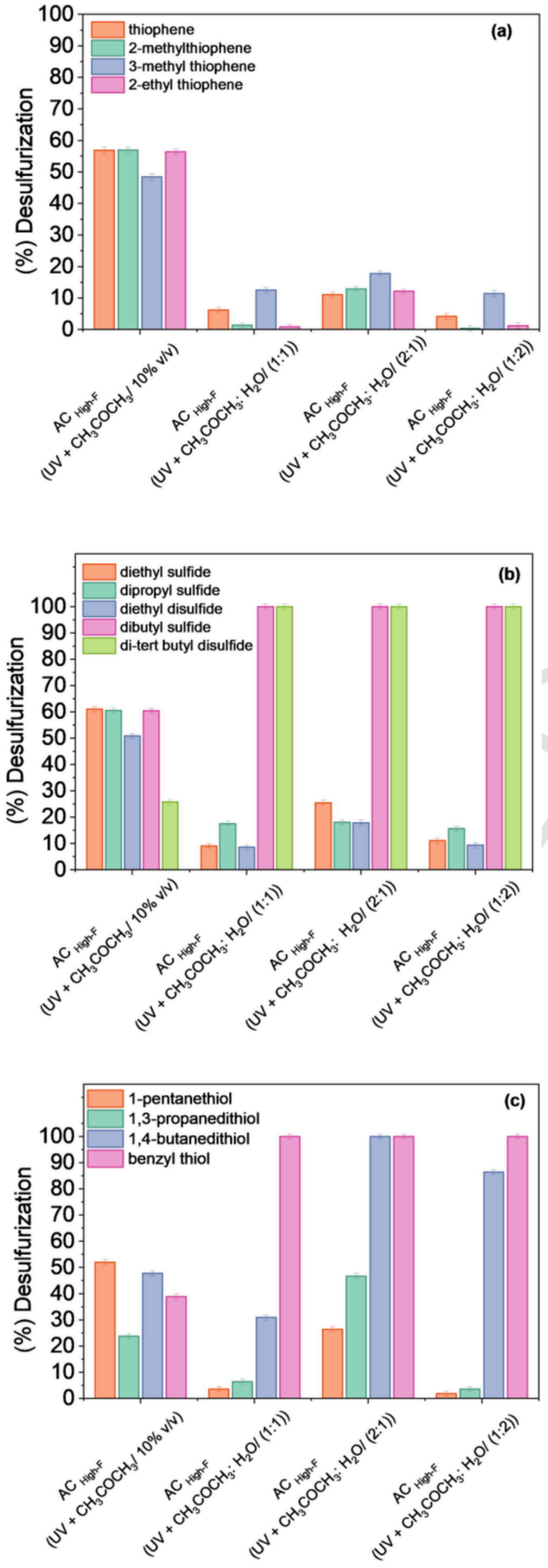

Fig. 6. Desulfurization of sulfur compounds (thiophenic compounds **(a)**. sulphides **(b)**, and thiols (mercaptans) **(c)**) using combined processes of AC $_{\text{High-F}}$ (UV + Acetone/ (10% v/v)), AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (1:1)), AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (2:1)) and AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (1:2)), using AC $_{\text{High-F}}$ (UV + CH_3COCH_3: H_2O (2:1)) process within treatment time of 180 min at 20 ± 2 °C.

desulfurization of non-hydrotreated naphtha. The synergy coefficient values were 1.13 and 1.05 for AC $_{\text{High-F}}$ (Air/0.5 dm^3/min) and AC $_{\text{Low-F}}$ (Air/0.5 dm^3/min) processes, respectively.

The acoustic cavitation processes of AC $_{\text{High-F}}$ (Air/0.5 dm^3/min) and AC $_{\text{Low-F}}$ (Air/0.5 dm^3/min) showed higher efficiency for the oxidation of sulfides than thiophenic compounds. In the case of AC $_{\text{High-F}}$ (Air/ 0.5 dm^3/min), the desulfurization efficiencies (%) of dipropyl sulphide, diethyl sulphide, 2-methylthiophene and thiophene were 74.30%, 57.20%, 55.67% and 54.21%, respectively **(**Table S5**,** Fig. 7**a)**.

3.8. Ozonation coupled with dual-frequency acoustic cavitation for desulfurization of naphtha

Ozone as a strong oxidant with oxidation potential of 2.08 V is widely used for treatment of wastewaters containing organic pollutants [27]. The reaction of ozone with contaminants consists of direct attack via ozone molecules (acidic pH) and radical attack through •OH radicals (basic pH). Direct attack via ozone molecules occurs through electrophilic, nucleophilic and dipolar addition [52]. Ozone exhibit a selective nature which means that it will first react with unsaturated bonds of C = C, C = N and C = N. Decomposition of ozone under cavitation conditions is described in the following reactions as a function of solution pH [53,54]:

$$O_3 + S - compounds \xrightarrow{)))} \text{sulfoxides/ sulfones (no - pH correction)} \quad (15)$$

$$O_3 \xrightarrow{)))} O_2 + O^{\bullet} \text{ (no pH correction)} \quad (16)$$

$$O_3 + 2H^+ + 2e^- \xrightarrow{)))} O_2 + H_2O \text{ (acid pH)} \quad (17)$$

$$O_3 + OH^- + 2e^- \xrightarrow{)))} O_3^{\bullet-} + HO^{\bullet} \text{ (basic pH)} \quad (18)$$

$$O_3^{\bullet-} \rightarrow O^{\bullet-} + O_2 \quad (19)$$

$$O^{\bullet-} + H^+ \xrightarrow{)))} HO^{\bullet} \text{ (basic pH)} \quad (20)$$

The reaction of ozone with a different group of sulfur compounds like thiophene and their derivatives, sulfides, and mercaptans (thiols) were studied. For this, ozone (0.5 dm^3/min) was combined with two dual-frequency systems of AC $_{\text{High-F}}$ and AC $_{\text{Low-F}}$. Higher desulfurization was obtained for AC $_{\text{High-F}}$ (Ozone/ (0.5 dm^3/min)) with desulfurization efficiency of 65.55% in 180 min **(**Table S6**)**. Using sole ozonation, insignificant desulfurization efficiency of 16.09% was obtained. The synergistic coefficient was evaluated to be 1.71, proving thus good effectiveness between combined methods. Regarding the desulfurization of each S-compound, the highest desulfurization was obtained for 2-methylthiophene (85.86%) and the lowest was 40.05% obtained for dipropyl sulfide **(**Fig. 7**b)**. When ozone is injected into the naphtha samples, a direct attack on double bonds of thiophene generate CO_2, SO_2, O_2, and C_3H_4 [55]. The direct attack of ozone on double bonds is known as the Criegee mechanism [56]. In the case of the disulfide compounds, S-S bond scission occur together with monosulfides and thiols C-S and S-H bond cleavage which leads to the formation of additional oxidation by-products like alcohols, carboxylic acids, aldehydes [47]. The same mechanism takes place in the presence of ozone and air containing oxygen. Ozone attacks the double bond between aromatic carbons of benzothiophene and dibenzothiophene to yield o-mercaptobenzaldehyde and possibly thiophene sulfone [57].

The application of lower frequency cavitation system led to a desulfurization efficiency of 60.68% in 180 min. In this case, the desulfurization efficiency values for 1-pentanethiol, diethyl sulphide, and 2-

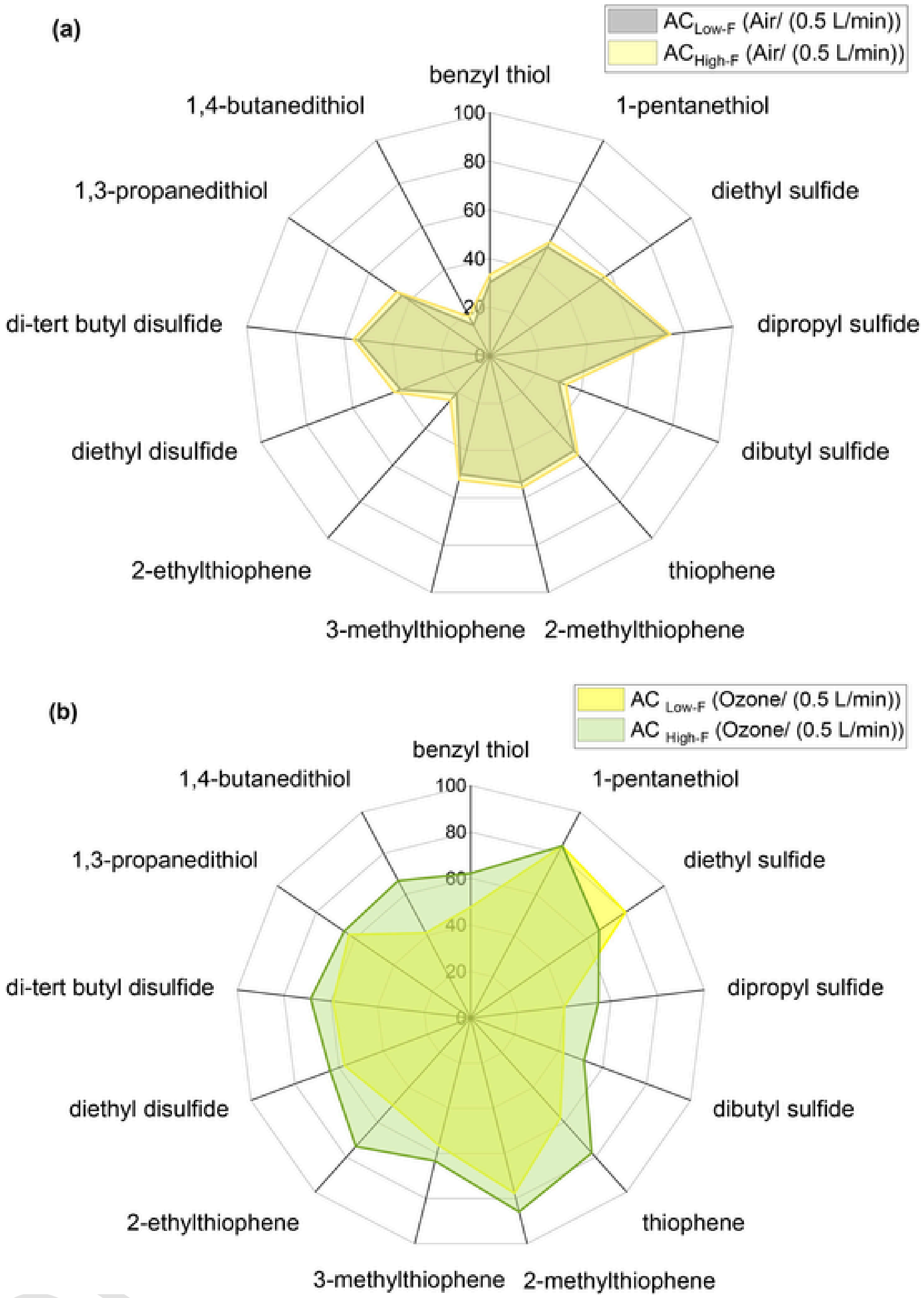

Fig. 7. Radial charts of desulfurization of S-compounds using AC_{High-F} and AC_{Low-F} in the presence of 0.5 dm^3 air/min air **(a)** and AC $_{High-F}$ and AC_{Low-F} in the presence of 0.5 dm^3 ozone /min **(b)** within treatment time of 180 min and operating temperature of 20 ± 2 °C.

methylthiophene were 83.55, 79.95 and 77.59%, respectively. The lowest desulfurization efficiency was achieved for 1,4-butanedithiol (41.31%). Synergistic coefficient of 1.74 proved the effectiveness of AC $_{Low-F}$ (Ozone/ 0.5 dm^3/min)). It has been reported that the highest reaction yields (degradation of S-compounds) were achieved when ozonation processes were performed under pH corrections of aqueous phase where oxidants are introduced [58]. Even though no pH correction was done in the current study, the desulfurization results demonstrated that the combination of acoustic cavitation and ozone is a promising method for the desulfurization of naphtha. Due to the diffusion resistance of ozone molecules in the liquid phase, stand-alone processes of ozone gave less desulfurization compared to the combination of ozone and acoustic cavitation. To increase the interfacial area between the molecules of ozone and the organic phase, small bubble diameter enhance mass transfer of ozone, and small bubble diameter can be generated employing acoustic cavitation [59]. Since microcavities display high inner pressure and high interfacial areas they assist in the gas transfer into the liquid phase. Combination of AC $_{High-F}$ (Ozone/0.5 dm^3/min) and AC $_{Low-F}$ (Ozone/0.5 dm^3/min), defined as ultrasonic homogeneous catalytic ozonation, was an efficient method for the desulfurization.

Summarizing this hybrid treatment process, application of high dual frequency acoustic cavitation and ozone (0.5 dm^3/min) resulted in desulfurization efficiency of greater than 80% for 1-pentanethiol, diethyl sulfide, thiophene and 2-methylthiophene. The lowest desulfurization efficiency of about 20% was attained for 1,4- butanedithiol, dipropyl sulfide and dibutyl sulfide aided by only air.

3.9. Kinetics of desulfurization reaction

The kinetic of desulfurization of naphtha was determined to specify the reaction rate constants of the sulfur compounds transformation via various treatment processes combined with acoustic cavitation. In the present study, the rate constant was calculated using a typical pseudo-first order equation as described below [61]:

$$\ln \frac{C_0}{C_f} = -kt \tag{21}$$

where C_f (mg/dm^3) is the total sulfur concentration of the non-hydrotreated naphtha after treatment, C_0 (mg/dm^3) is the initial total sulfur concentration, t is the treatment time (min), and k is the calculated reaction rate constant (min^{-1}).

For the acoustic cavitation combined with hydrogen peroxide, acetic acid and their mixture, the obtained values of coefficient of determination (R^2) were found to be 0.9912, 0.9869, and 0.9993, respectively; thus, the obtained data followed the first order kinetic model (Fig. 8**a**). Additional kinetic plots are provided in supplementary material. The highest reaction rate constant was calculated for $CH_3COOH/H_2O_2/$ r_{ox} 5.0 treatment system with a value of 0.1337 min^{-1}, and it was found to be 26-fold higher than the reaction rate constant of AC $_{High-F}$ ($H_2O_2/$ r_{ox} 5.0) with a value of 0.0051 min^{-1} and 21-fold higher than that of AC $_{High-F}$ ($CH_3COOH/$ r_{ox} 5.0) with a value of 0.0063 min^{-1}.

The desulfurization of different liquid fuels was previously reported by other researchers to follow the first-order kinetics. Dai et al.,[30] reported that increasing power of ultrasonic system from 50 W to 100 W improved the rate constant from 0.063 to 0.2378 dm^3/mol^{-1} min^{-1} on the basis of first-order kinetic model. Sinhmar et al., revealed that the desulfurization of dimethyl disulfide followed the first-order reaction with the maximum rate constant of 2.9×10^{-3} min^{-1}[60].

The intensified reaction rate constant demonstrated that the oxidative desulfurization reaction is highly synergistic when acetic acid and hydrogen peroxide are combined to form a peroxyacetic system and the effective desulfurization takes place within 30 min. Since the pH of aqueous media drops to 2, the equilibrium will shift to the formation of peroxyacetic acid which will be faster dissociated into acetyl ($CH_3CO^\bullet$) and perhydroxyl ($HOO^\bullet$) radicals. After the formation of peroxyacetic acid, the speed of dissociation will be favored towards the regeneration of acetic acid which extends the time of S-compounds oxidation. In the case of two other oxidants, the rate constant changes by 1.24 and there is no big difference in the obtained desulfurization (%) for both processes. It can be stated that the reactions are steady and after dissociation of oxidants into their respective radicals, some of these radicals go to oxidize S-compounds, and some need to enter the regeneration cycle of oxidants like H_2O_2 and CH_3COOH until the amount of them is consumed.

Furthermore, UV irradiation revealed to be a useful additional factor for desulfurization enhancement in the case of acetone-based combined system (Fig. 8**b**)**.** The reaction rate constants were significant for the combined processes with defined ratios of acetone: water (1:1) (0.0374 min^{-1}) and (1:2) (0.0236 min^{-1}). This result can be explained due to the fast dissociation of acetone as a result of AC/UV irradiation within 60 min, at which higher reaction rate values were achieved. A lower reaction rate constant of 0.0010 min^{-1} was calculated for the process with acetone: water ratio of 2:1. The reason stands for the excess amount of acetone which continues to dissociate. Therefore, the reaction can be considered slower and steady. Additionally, higher rate constant values were observed for defined ratio of acetone: water (1:1) and (1:2). This finding implies that the reaction merely takes place in the aqueous phase, where the generation of reactive radicals occurs faster. Since disulfides and mercaptans get faster oxidized compared to thiophenic compounds, they will be faster extracted to water phase and oxidized by as-generated radicals.

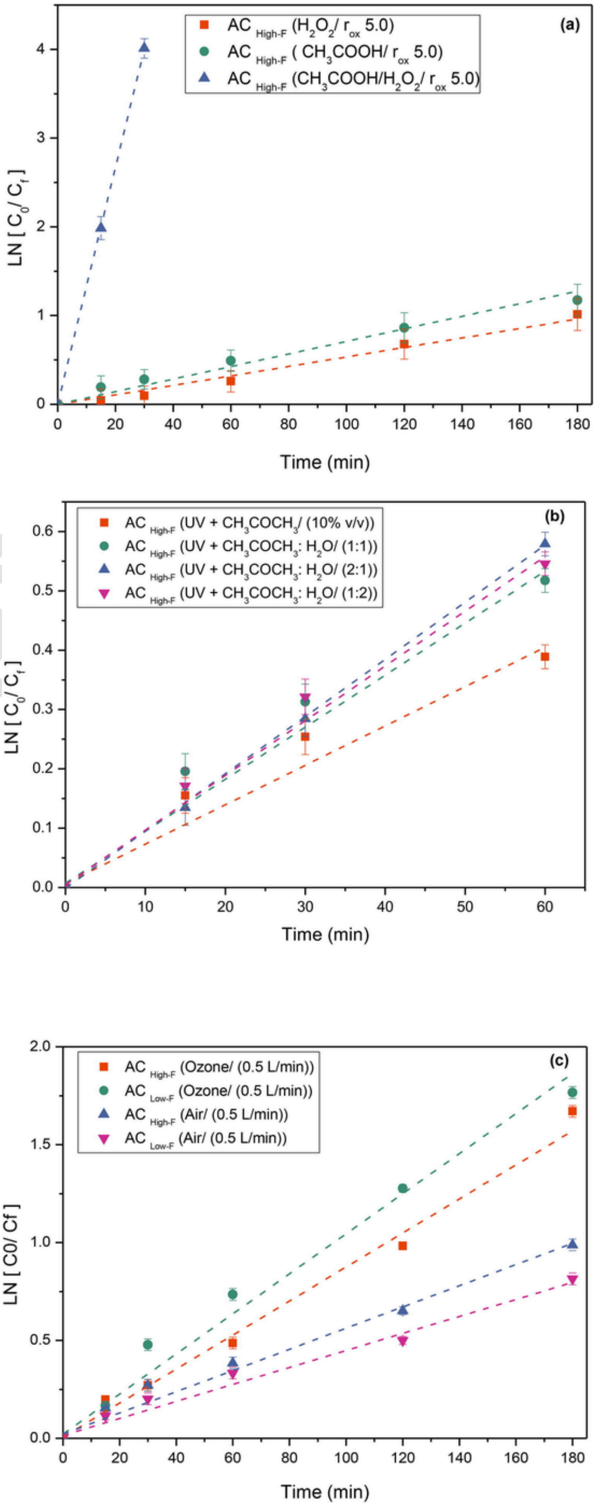

Fig. 8. Plot of pseudo-first order kinetic for high dual-frequency system AC $_{High-F}$ in the presence of $H_2O_2/$ r_{ox} 5.0, $CH_3COOH/$ r_{ox} 5.0, and $CH_3COOH/H_2O_2/$ r_{ox} 5.0 within 180 min at operating temperature of 20 ± 2 °C **(a)**, plot of pseudo-first order kinetic for high dual frequency system AC $_{High-F}$ in the presence of UV + Acetone/ (10% v/v), UV + CH_3COCH_3:H_2O/ (1:1), UV + CH_3COCH_3:H_2O/ (2:1) and UV + CH_3COCH_3:H_2O/ (1:2) 10% v/v aqueous oxidant, within 60 min at 20 ± 2 °C **(b)**, and plot of first order kinetic for high dual frequency system AC $_{High-F}$ and low dual frequency system AC $_{Low-F}$ applying ozone and air with a constant flow rate of 0.5 dm^3/min **(c)**(treatment time of 180 min and operating temperature of 20 ± 2 °C).

Table 2

Cost of acoustic cavitation processes aided by different oxidants within treatment time of 180 min.

No.	Treatment process	Time (min)	Oxidant Cost [USD]	Energy Consumption* [kJ]	Cost of Energy [USD]	Average desulfurization for identified S-compounds (%)	Total Cost [USD/m^3]
1	AC (40 kHz)	180	–	3240	0.1476	20.21 ± 1.16	38.84
2	AC (80 kHz)	180	–	3240	0.1476	21.04 ± 1.68	38.84
3	AC (120 kHz)	180	–	3240	0.1476	23.56 ± 0.87	38.84
4	AC (200 kHz)	180	–	3240	0.1476	26.84 ± 1.65	38.84
5	$AC_{Low\text{-}F}$ (40&120)	180	–	6480	0.2952	25.15 ± 1.45	77.68
6	$AC_{High\text{-}F}$ (80&200 kHz)	180	–	6480	0.2952	31.95 ± 0.48	77.68
7	AC $_{High\text{-}F}$ (H_2O_2/r_{ox} 5.0)	180	0.91	6480	0.2952	**63.68 ± 1.79**	**78.59**
8	$AC_{High\text{-}F}$ (CH_3COOH/r_{ox} 5.0)	180	0.24	6480	0.2952	47.36 ± 0.78	77.90
9	$AC_{High\text{-}F}$ (CH_3COOH/ H_2O_2/r_{ox} 5.0)	30	2.08	1080	0.0492	**100 ± 1.41**	**15.03**
10	$AC_{High\text{-}F}$ (UV + Acetone/ 10% v/v)	180	2.95	9180	0.4182	**57.34 ± 1.99**	**64.45**
11	AC $_{High\text{-}F}$ (UV + CH_3COCH_3: H_2O (1:1))	60	1.47	3060	0.1394	40.38 ± 0.68	21.97
12	AC $_{High\text{-}F}$ (UV + CH_3COCH_3: H_2O (2:1))	60	2.06	3060	0.1394	42.24 ± 0.93	22.56
13	AC $_{High\text{-}F}$ (UV + CH_3COCH_3: H_2O (1:2))	60	0.88	3060	0.1394	42.04 ± 0.32	21.38
14	$AC_{High\text{-}F}$ (Ozone/ 0.5 dm^3/min)	180	–	10 584	0.4821	**65.55 ± 1.40**	**126.80**
15	$AC_{Low\text{-}F}$ (Ozone/ 0.5 dm^3/min)	180	–	10 584	0.4821	**60.68 ± 0.55**	**126.80**
16	$AC_{High\text{-}F}$ (Air/ 0.5 dm^3/min)	180	–	6544.8	0.2981	42.41 ± 0.92	78.46
17	$AC_{Low\text{-}F}$ (Air/ 0.5 dm^3/min)	180	–	6544.8	0.2981	39.60 ± 0.92	78.46

*Energy consumption for specific period of time – given in corresponding column of this table.

The last group that was studied in terms of its kinetic and reaction rate constant was acoustic cavitation in the presence of air and ozone for two different dual-frequency systems (Fig. 8**c**). The fastest reaction in this group was found to be AC $_{High\text{-}F}$ (Ozone/0.5 dm^3/min), with a reaction rate constant of 0.0096 min^{-1} and corresponding desulfurization efficiency of 65.55% within the reaction time of 180 min. The reaction rate constants of three combined processes of AC $_{Low\text{-}F}$ (Ozone/ 0.5 dm^3/min), AC $_{High\text{-}F}$ (Air/0.5 dm^3/min) and AC $_{Low\text{-}F}$ (Air/ 0.5 dm^3/min) were found to be 0.0089, 0.0051 and 0.0042 min^{-1}, respectively. Overall, acoustic cavitation is effective in the processing of the organic phase, due to the increased naphtha – oxidant interfacial area via emulsification, which is significant in the oil phase liquid which contains gas-filled bubbles and cavitation bubbles [30]; however, based on the results, high dual-frequency acoustic cavitation had higher reaction rate constant than that of low dual-frequency. A comparison of studied processes in aspect of kinetics is given in table 1.

3.10. Economic assessment

An economic evaluation on the studied process was performed considering treatment time, cost of oxidants, and cost of energy. The cost of electricity for industrial customers in Poland in 2020 was 0.150 US dollars (USD) per 1 kWh (3600 kJ). The cost of treatment was first estimated for 3.8 dm^3 of naphtha and then recalculated for 1 m^3 liquid fuel treatment. In the case of UV-aided processes, the cost of treatment was calculated for 6.8 dm^3 volume since the UV chamber is attached to the acoustic cavitation reactor.

In this analysis only processes that provide minimum 50% desulfurization were included. The most expensive processes are based on ozonation – with treatment costs exceeding 100 USD/ m^3 (Table 2**, No. 14 and 15)**. The high cost of treatment is attributed to the ozone generator (380 W) combined with the acoustic cavitation reactor with a power of 600 W as well as long reaction time required to obtain acceptable desulfurization efficiency. According to the calculations, UV-aided treatment processes imposed moderate costs (slightly above 60 USD/m^3) in comparison with the ozone-aided treatment processes.

The combined application of acetic acid and hydrogen peroxide $AC_{High\text{-}F}$ (CH_3COOH/ H_2O_2/ r_{ox} 5.0) was considered to be the most economical process with a treatment cost of 15.03 USD/m^3. In addition, the combined process of CH_3COOH/ H_2O_2/ r_{ox} 5.0 was the most efficient process with desulfurization efficiency of 100% within the reaction time of 30 min (Table 2**, No. 9)**. Since complete desulfurization was obtained for the treatment process of $AC_{High\text{-}F}$ (CH_3COOH/ H_2O_2/ r_{ox} 5.0), an additional parameter known as E_{EO} (electrical energy per order) was also calculated. Electrical energy per order is a parameter to calculate the amount of energy required to decrease the concentration of pollutant by one order of magnitude (90% reduction) in unit volume and is described as E_{EO} (kWh/m^3) [62]. Accordingly, E_{EO} for $AC_{High\text{-}F}$ (CH_3COOH/ H_2O_2/ r_{ox} 5.0) was found to be 100.17 kWh/m^3. Obtained results indicated cost-effectiveness of the desulfurization of naphtha using $AC_{High\text{-}F}$ (CH3COOH/ H2O2/ rox 5.0) process under ambient conditions within short reaction time.

Desulfurization by developed processes allows to maintain primary hydrocarbon composition of naphtha. In this case a target oxidation is focused on sulfur compounds, while hydrocarbons remain in primary form. This aspect was studied both by GC-FID and GC–MS techniques. No changes in naphtha hydrocarbons composition was found for studied variations of processes. Examples of overlaid chromatograms are provided in **Fig. S8-S11**.

4. Conclusions

In the present study, desulfurization of naphtha using dual-frequency acoustic cavitation combined with different advanced oxidation systems was investigated. Results showed that high dual-frequency system favoured the desulfurization compared to the low dual-frequency system. External sources of radical species such as hydrogen peroxide, acetic acid, ozone, and acetone were applied as well their mixture and UV light irradiation. According to the results, the addition of aforementioned oxidizing agents improved the desulfurization efficiency of naphtha under dual-frequency acoustic cavitation. Among them, the mixture of acetic acid/hydrogen peroxide named peracetic acid led to the complete desulfurization of naphtha within a short reaction time. In this regard, the oxidant to sulfur compounds molar ratio was determinative; thus, optimization of oxidant dose is required to attain the highest desulfurization efficiency of naphtha fuel. For instance, the content of acetone was the limiting factor for the desulfurization using high dual-frequency combined with UV/CH_3COCH_3/H_2O process. The addition of water to the combined process of acoustic cavitation/acetone/UV resulted in the oxidation of specific sulfur compounds such as thiophenic compounds, while it was not efficient for the desulfurization of other sulfur compounds. All combined processes followed the pseudo first-order kinetic model with high correlation coefficients. The utilization of the combined process of acoustic cavitation/acetone/UV/water not only led to the complete desulfurization but also improved cost-efficiency of the treatment process with the highest synergy coefficient in comparison with the other combined processes. The acoustic cavitation combined with ozonation was the most expensive process due to the electric power consumption. The $AC_{\text{High-F}}$ (peracetic acid, CH3COOH/H2O2/rox 5.0) is superior in desulfurization of all considered sulfur compounds without discrimination. Overall, the combination of various oxidizing agents and their mixture with acoustic cavitation at an appropriate oxidant to sulfur compounds molar ratio can be considered as cost-effective and promising approaches for the removal of sulfur compounds from fuels. Despite of effective desulfurization, studied treatment methods revealed to maintain primary composition of hydrocarbons in naphtha, assuring conversion of only the target – sulfur containing pollutants. Selection of preferred treatment method should relay on the demands in respect to used fuel. For instance in case of aviation fuels the main concern relates to lowering the thiols content due to their acidic (corrosive) character. For this purpose acoustic cavitation systems with ozone or CH_3COOH/H_2O_2 seems to be a good selection. To obtain overall lowering of sulfur content of fuels, acoustic cavitation/acetone/water or acoustic cavitation/peracetic acid approaches are the most economic one with treatment cost of 15–23$/$m^3$.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2022.135354.

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