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Mini-Review

# Application of Cavitation in Oil Processing: An Overview of Mechanisms and Results of Treatment

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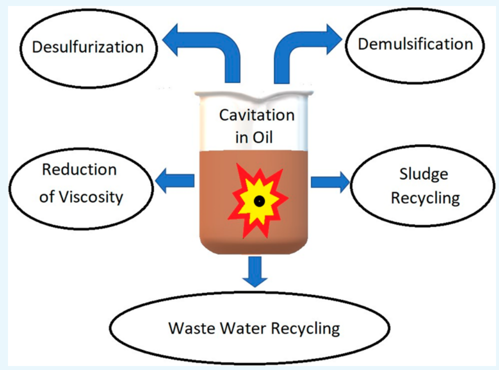
**ABSTRACT:** The integrated effect on homogeneous and heterophase liquids that can be used for technological purposes has drawn the attention of researchers in various sciences. Cavitation impact on oil is among the efficient methods of intensifying chemical−technological, hydromechanical, and mass-exchange processes and the destruction of substances. This work reviews in detail and analyzes the mechanisms of impact and application of cavitation in various processes in the petroleum industry, including the refining processes, that are associated with crude oil and petroleum waste, such as reduction of viscosity, demulsification, desulfurization, and improvement of quality of heavy oil and petroleum refinery products, including oil sludge and waste oil-containing water.




## ■ INTRODUCTION

Use of liquid fuel has forced mankind to process and use heavy and ultraheavy oil to produce special chemicals and dispose oil industry waste. Existing conventional processing technologies are unable to economically process ultraheavy oil stock without contaminating the environment. Technologies based on ultrasonic or hydrodynamic cavitation effects could be among the breakthrough technologies to address the challenges of oil production and refining.

Cavitation is the formation, growth, and collapse of bubbles filled with gas, vapor, or their mixture when pressure in the liquid drops to the saturated vapor pressure of the liquid. Irrespective of its nature, cavitation is a multicomponent process[1−5] accompanied by local increase of temperature and pressure inside the exploding bubble, turbulent mixing and micromixing by formation of microjets during bubble explosion, and thermal dissociation of water molecules forming hydroxyl radicals (Figure 1). In the case of hydrodynamic cavitation, the turbulent mixing of the processed volume of liquid is more intensive and accompanied by rapid mass transfer. The rapid bubble collapse occurs in an adiabatic state because the extremely short time of collapse denies heat exchange inside and outside the bubble. The totality of physical and chemical processes during cavitation changes the properties of processed liquids. The results of cavitation processing can conditionally be divided into the increase of oxidative reactions, the increase of dispersion of components of heterogeneous liquids (emulsions or suspensions), and variation of colloid stability.

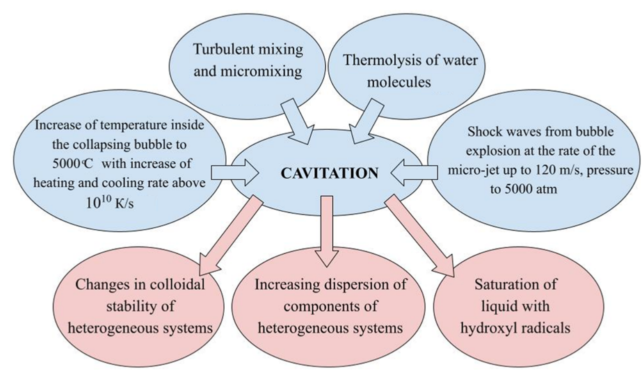



**Figure 1.** Processes in blue bubbles and phenomena in pink bubbles during cavitation.

Hydrodynamic cavitation is observed when a high pressure drop occurs inside the moving liquid, for example, passage through constriction such as a throttle valve or aperture. The hydrodynamic cavitation arises in various mechanical devices, such as a Venturi tube, nozzle, or rotor-stator units when the local pressure in the liquid drops to threshold value−liquid vapor pressure at an operational temperature. Then, when the

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liquid jet expands, the pressure recovers, resulting in the explosion of cavities (cavitation bubbles, voids). The acoustic cavitation is mainly initiated by piezoelectric transformers to generate sound of high amplitude. The frequency range of ultrasound used in sonochemistry is about 20 kHz to 10 MHz.[5] Ultrasound is a mechanical wave with pressure oscillations capable of propagating through gaseous, liquid, and solid media. Under ultrasonic irradiation, the medium is exposed to an expansion and contraction cycle under pressure. In the field of oscillating pressure when the bubble reaches an unstable size, it explodes to generate shock waves and microjets.

The integral cavitation effect on homogeneous and heterophase liquids, which can be used for technological purposes, has widespread application in various fields of human activities. Cavitation is considered a green technology because it avoids excessive use of toxic compounds by replacing them with environmentally safer solvents and, in some cases, avoids the use of chemical additives at all. Technological processes involving cavitation are specified by improved reaction conditions and selectivity, lack of toxic settlement, and reduced consumption of energy for chemical transformations.

Ultrasonic activation at room temperature makes if possible to esterify and transesterify brown grease—a mixture of oils, fats, solid substances, and detergents from food-industry waste captured in grease-removal tanks to produce biodiesel fuel in several minutes. Ultrasonic cavitation improves not only the efficiency but also the safety of the process compared to a conventional thermal activation method. These results offer challenges to develop efficient, inexpensive, and clean production of biodiesel.[6]

Ultrasound is a technology with great potential for the food industry. Extraction of polysaccharides of plant or animal origin by ultrasound increases the yield of the product and reduces extraction time and modifies their physical−chemical and biological properties. Physical processes caused by acoustic cavitation decrease the size of milk component particles, modify protein structures (casein, lactalbumin, and lactoglobulin), and increase activity of enzymes to improve the texture and increase their shelf life. The mechanical impact of the collapsing bubble on bacterial cells, formation of radicals, and activation of sonosensitizers caused by cavitation were recommended as antibacterial mechanisms alternative to thermal treatment. The benefits of ultrasound in the treatment of food products over conventional methods include more efficient mixing and micromixing, faster transfer of energy and mass, reduced temperature in the reactor, compact size of equipment, and faster reaction in extraction process control.[7]

For years, ultrasonic technologies have been used to improve the efficiency of mineral and coal flotation.[8] Longitudinal sonic waves increase the probability of collision of ultrafine particles with flotation-sized bubbles, impact the oxidation films on minerals, and make their surface less hydrophilic by increasing adhesion and reducing detachment. Carryover of clay or waste rock deteriorates the quality of ore concentrate which can be reduced by cavitation devices in mineral flotation processes.

To prepare coal−water fuels, which are a suspension of coal in water, it is common to use hydrodynamic cavitation; this affects the basic properties of liquid fuel (the size of particles of the disperse phase of the slurry, thermal−physical, rheological, and sedimentation properties) and provides for intense mass transfer and turbulent stirring. In ref 9, cavitation treatment of the coal−water slurry and its components was shown to reduce harmful emissions during its combustion. Time-stable coal−water mixtures produced by cavitation are attributed to a sophisticated mechanism of interaction of coal particles, modifying additives and humic acids, which are also a part of coal and the variation of pH of the disperse medium.

The method of cavitation treatment of suspensions, emulsions, and other liquids is successfully used in the following cases: to prepare cementing slurry and drilling fluids for drilling rig systems; to prepare concrete compositions with improved performance; to control radioactive scales in gas and oil wells; to dispose of radioactive waste of atomic power plants; to prepare nanoemulsions for use in pharmacology and medicine. Among the most amazing applications of cavitation effects is the sonochemical synthesis of nanoparticles. Short-time localized hot points of explosions of the cavitation bubbles at extremely high temperatures and pressures provide conditions to synthesize nanostructured metals, alloys, oxides, sulfides, carbides and carbon, polymers, and biomaterials.[10]

Even though the cavitation technologies, as evident, have widespread application in various industries, for the challenges of the petroleum industry, they have been used relatively recently. Currently, intense research is carried out to intensify individual technological processes in oil recovery to recover oil from oil-bearing sand, to demulsify oil emulsion at the stages of desalination, to reduce viscosity of crude oil, to oxidatively desulfurize and demetallize, and to improve the quality of crude oil for cracking[11] and decontaminating oil-containing waste.

Figure 2 shows diagrams produced by analytical instrument SciVal data of Scopus based on the number of publications dedicated to cavitation studies, including fundamental problems of single cavitation bubble motion and application of cavitation technologies in oil extraction and oil refining. As is evident, the subject of these publications is relevant in recent several years.

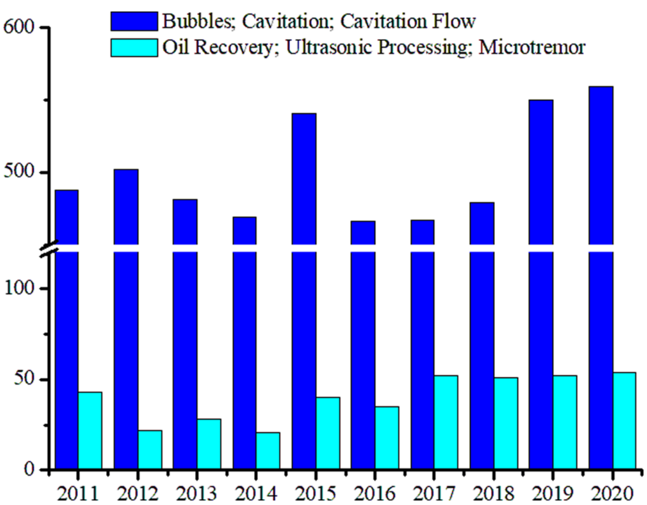


**Figure 2.** Number of publications by year: thematic cluster "bubbles; cavitation; cavitation flow" (blue) and "oil recovery; ultrasonic processing" (light blue).

The cavitation method is in agreement with principles of sustainable development of "green science" because it operates under soft conditions and is not associated with the production of hazardous chemical reagents. Complex multiple-parameter physical and chemical effects of cavitation make the mechanism of powerful ultrasound or intense hydrodynamic cavitation flow for different applications in the petroleum industry that are necessary to optimize operational parameters and improve efficiency difficult to understand. Major obstacles for the broad application of cavitation include scaling and energy efficiency. Although the laboratory equipment used in ultrasonic reactors is commercially available, large-scale equipment is still rare. The equipment for the hydrodynamic cavitation effect is practically unavailable for sale; to develop it is a challenge for independent solutions of individual research teams.[12]

This work analyzes the mechanisms of the cavitation effect on different oil liquids conditioned mostly by variation of frequency and intensity of ultrasound, treatment time, temperature of the process, and the nature of the medium processed. Here, we present a detailed review of applying cavitation in different processes of the petroleum industry, including oil refining processes, that are associated with crude oil and oil waste, such as reduction of viscosity, demulsification, desulfurization, and demetallization, and improvement of the quality of crude oil and petroleum refinery products.

## ■ REDUCTION OF CRUDE OIL VISCOSITY

Exploration of heavy crude oil and bitumen faces engineering problems at every stage from extraction (extraction from reservoir) to transportation and processing. Transport of heavy crude oil and bitumen by pipes to storage or oil refineries for processing is a difficult problem because of its high density and viscosity. In addition, deposition of asphaltenes and paraffins on the pipe walls hinders its operation and is among the major engineering challenges of beneficial use of crude heavy and ultraheavy oil.

There are a number of methods to reduce the density of petroleum products based on increased temperature (hot piping), addition of surfactants, and dilution with lighter oil compositions, gas condensate, or water. Diluted heavy oil can change the stability of asphaltenes, promoting their flocculation and deposition, which can also clog the pipes. To avoid failure of the equipment and transportation systems, it is necessary to understand the reasons and mechanisms of aggregation of flocculation of asphaltenes and crystallization and deposition of paraffins.

Heavy oil comprises a large fraction of asphaltenes, whose molecular weight is difficult to evaluate because of their self-aggregation and coagulation. The asphaltenes can be present in the oil in dissolved form but also can form a disperse system. In a colloidal disperse system of crude oil, the asphaltenes are in the form of micellar cores stabilized by adsorbed resins and are alkane-insoluble. Therefore, stable asphaltene colloid formation in the oil depends on the structure and component composition of disperse medium and the disperse phase of oil—the ratio of asphaltenes and resins, aromaticity, etc.

The authors of a previous study[13] found the viscosity of heavy oil to increase exponentially with asphaltene content: from trace amounts in the light oil to 20% in highly viscous oil, even though they are not components prevailing in the composition. It is also known that the size of asphaltene formation determines the rheological behavior of oil. Thus, prevention of serious agglomeration of asphaltenes is a key to reduce the viscosity of crude oil, especially of heavy and ultraheavy oil.

In crude heavy oil, cavitation effects are possible with transmission of ultrasound energy or hydrodynamic movement into the energy of the collapsing bubble. This process can promote transfer of large molecules of ultraheavy oil into molecules of light hydrocarbons of smaller size without additional heating of the processed system, as the cavitation process is accompanied by an increase of temperature. The efficiency of ultrasonic processing on various oils has been shown by many authors. In ref 14, the effect of ultrasonic hydrodynamic treatment of oil was studied, and its advantage over acoustic treatment was shown. Intense treatment of the medium flow caused an instantaneous (1−100 $\mu$s) pressure drop with instantaneous emission of gas in the drastic pressure drop zone. Pressure pulsations arising in the constrained zone of the flow at the nozzle exit and interacting with the obstacle cause a discontinuity in the processed oil (Figure 3).

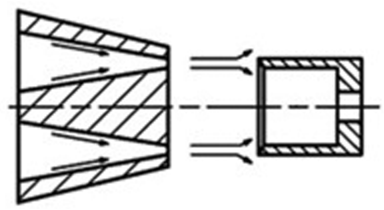

Figure 3. Diagram of the hydrodynamic radiator in an ultrasonic hydrodynamic treatment unit. Reprinted with permission from ref 14. Copyright 2017 Elsevier.

Moreoever, the pass over of the medium movement mode from supersonic to subsonic flow makes the pressure surge (8−50 MPa at the reactor inlet, 0.05−0.09 MPA in the reactor to 3.5−8 MPa at the reactor exist). In the efficient zone of the pressure surge, the gas-vapor bubbles collapse to mechanically impact the liquid.

This treatment results in the destruction of micellar connections and partial cracking of high-molecule compounds to increase the yield of light fraction in oil refining. Actually the authors observed that the fraction composition changed and the oil viscosity reduced by more than 30%. Combined use of chemical reactant (30% butyl acetate, 60% toluene, 10% xylene) reduced the viscosity by 72%. The authors note that the time between the treatment and monitoring of viscosity is irrelevant, and the difference between the viscosity index is less than 1%. However, another study[15] showed considerable reversibility of viscosity change caused by ultrasonic exposure, and it is important to measure the viscosity within several seconds after treatment.

Reversibility of viscosity after exposure of oil to irradiation is associated with thermal effects of ultrasonic irradiation. In ref 16, the relationship between parameters of ultrasonic treatment (irradiation time, output power, frequency), viscosity, and thermal behavior of crude oil with high asphaltene content was established. The optimal irradiation time at which the viscosity of cooled irradiated product is reduced to minimal values is shown to decrease due to an increase of power and/or frequency of ultrasonic irradiation. Reduction of viscosity caused by ultrasonic irradiation is connected to induced emission of heat, cavitation in the liquid, and changes in oil composition and molecular structure, including destruction of asphaltenes and heavy molecules into lighter ones. Qualitative evaluation of the effect of thermal destruction on viscosity of oil illustrates the results of a simple increase of temperature and ultrasound from the viewpoint of viscosity and amount of residual oil at the end of pyrolysis and oxidation stages. Even


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though the values of viscosity at equal temperatures in these processes are comparable, the ultrasound results in a constant decrease of viscosity (more than by 10%) and does not return to the values before the treatment (Figure 4, experimental data

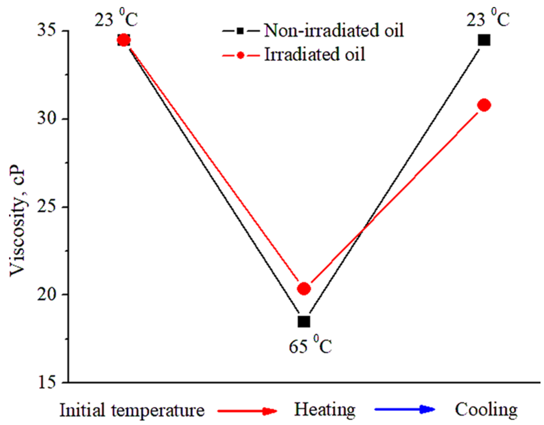


**Figure 4.** Comparison of initial viscosity of oil, viscosity of the oil sample exposed to heating in a kiln to 65 °C, and the viscosity of the ultrasonically treated oil immediately after stopping the irradiation and when the oil was cooled to the ambient temperature of 23 °C.

are taken from ref 16). Thermogravimetric measurements prove that the ultrasonic irradiation decreases the heavy components of oil by distillation and thermal cracking mechanisms, reducing the total amount of asphaltenes. Analogous results were produced in ref 17 for crude oil with an initial asphaltene content of 1.76 wt %.

The treatment time has been found to be the governing parameter in reduced oil viscosity, and the optimal treatment time increases with asphaltene content;[18] this is in agreement with the calculated data.[19] On the basis of experiments,[20] it can be argued that ultrasonic irradiation can, within optimal time, reduce asphaltene content in crude oil; after that, with an increase of time, the small molecules and free radicals reintegrate to form large oil molecules to increase its viscosity.[21] Within this optimal irradiation time, the decomposition rate of asphaltenes is equal to the rate of asphaltene formation by the mechanism of free radicals generated by ultrasonic cavitation.[12]

To fix and reinforce the reduction of oil viscosity, the treated oil can be added to various reactants. To estimate the expedience of the addition of a reactant after or during ultrasonic treatment and conversion of heavy asphaltenes and resins requires additional experimental studies.

## ■ DEMULSIFICATION OF OIL EMULSION

The presence of asphaltenes in oil not only determines the rheological properties of liquid but also affects the processes of demulsification (dehydration, desalting) of heavy oil. Within the framework of this section, we consider the formation of an emulsion as a negative factor affecting the properties of heavy and ultraheavy oil during its production and the wear of equipment during transportation and distillation and do not touch upon the increase of oil production by emulsification.

In traditional development of oil fields, water is most frequently injected in the presence of surfactants. The produced crude oil is the emulsion of "water-in-oil" type, in which the water droplets are dispersed in the oil, and "oil-in-water" type and multiple emulsions. The presence of surfactants in the oil emulsion and the presence of chlorine, sodium, calcium, and magnesium salts in demulsified water, asphaltenes, and resins make the emulsion stable for several hours or days. Therefore, stability of the emulsion during crude oil production entails challenges in further demulsification, desalting, and dehydration.

The demulsification methods used under industrial and laboratory conditions include physical, chemical, and biological demulsification. The demulsification process chain can be constructed as follows: aggregation of water (or oil) droplets and flocculation, creaming or sedimentation with stratification to be followed by coalescence and/or Ostwald ripening. The stability of the emulsion is governed by the strength of interfacial tension (water−oil boundary), and the differences in crude oil composition, presence, and component ratio of asphaltenes and resins, in particular, promote variability in the processes of emulsification and demulsification.

Stability of oil or water droplets can be explained by the presence of repelling electric charges on its surface. This stability is initiated by the formation of interfacial films encapsulating the droplets of oil or water, while destabilization or destruction of emulsions is directly connected with elimination of this interfacial film. The stability of an emulsion can be evaluated by taking into account the interaction forces between the droplets: coagulation of particles is described by Deryagin−Landau−Fairway−Overbeck theory, to be more specific, by the sum of energies of van der Waals attraction and electrostatic repulsion arising because of the presence of a double electric layer on the surface of the droplet.[22] When the repulsion forces are dominating, the system is in a stable state. On the contrary, when the interaction (attraction) force is increased by addition of an emulsifier or application of a physical field, the droplets flocculate and emulsions destabilize. The feasibility of producing stable or unstable emulsions can be precisely estimated by zeta-potential measurements.

To rationally manage resources and reduce environment pollution, energy consumption and waste flow during demulsification and dehydration must be reduced. Ultrasonic treatment energy avoids the use of chemical reactants and de-emulsifiers; however, the synergistic effect of their combined use can demonstrate an increased stratification effect.

The effect of ultrasonic waves on suspended particles, droplets, and bubbles has been thoroughly studied. As stated previously, the emulsion is destroyed as a result of creaming, coagulation, and coalescence followed by sedimentation (separation) processes. With the demulsification method with ultrasound, the droplets coalesce in the standing wave of the acoustic field generated between the transducer and reflector when the distance between them is a multiple of the half-wavelength. When water droplets in the oil get into the pressure nodes of the standing wave field, they agglomerate (aggregate) into strips to increase the probability of collision and coalescence of droplets. Because of the difference of density and compressibility of oil and water, the droplets of water in oil move toward pressure nodes of the standing wave (Figure 5) and the droplets of oil in water move toward the antinodes.[23,24] In addition, several droplets can be exposed to interparticle forces. When the droplets move either to the node or to the antinode of the standing wave, forces emerge, acting for short distances, called "secondary acoustic forces" or "Bjerkness forces", caused by sound scattering by neighboring droplets. These forces tend to attract the droplets within the plane.


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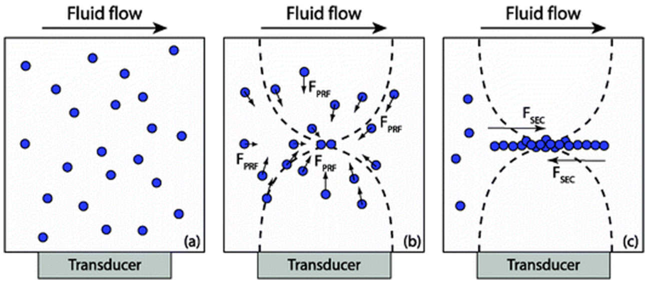


**Figure 5.** Typical configuration of water droplets in oil where a transducer emits sound in a direction perpendicular to the flow (a). Resonator at half-wavelength ($\lambda/2$) brings the droplets in focus on the nodal plane in the center of the unit (b). As soon as the droplets collect in the node, the secondary acoustic forces attract them together (c). Republished with permission from ref 24. Copyright 2012 Royal Society of Chemistry, with permission conveyed through Copyright Clearance Center, Inc.

First among the acoustic parameters affecting efficiency of demulsification are frequency, intensity of sound, and irradiation time. The lower frequency results in higher efficiency of the demulsification of crude oil. In ref 25, the water yield is shown to increase when the initial concentration of water in the emulsion is 15%, with use of ultrasonic horn at frequency 20 kHz and a power range from 80 to 1000 W and exposure time of 2 min. At higher initial water concentrations of 20 and 25%, the separation is less efficient, as well as when the irradiation time is increased to 5 min. It is noted that the higher the salt content in the crude oil, the more efficient the ultrasonic fields in separating water emulsion droplets from the crude oil and desalting the crude oil samples (Figure 6).

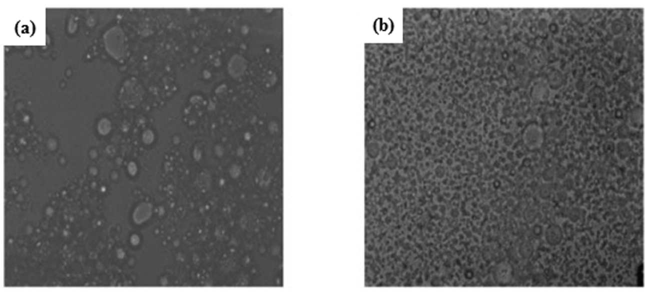


**Figure 6.** Physical characteristics of water droplets in oil without application of ultrasonic waves (a) and with application of ultrasonic waves (b). Reprinted with permission from ref 25. Copyright 2020 Elsevier.

Efficiency of demulsification at different frequencies is shown in ref 26. Powerful ultrasound (20−100 kHz) can transfer into the medium high specific density of energy and cause strong mechanical oscillations. In this case, the droplets of different sizes oscillate at different speeds and collide with each other to promote destruction of the interfacial boundary and coalescence of the droplets (Figure 7). Hence, the low-frequency ultrasound can separate the droplets from the carrying (disperse) phase, which is connected by mechanical oscillations. In high-frequency acoustic fields, the primary acoustic force makes the dispersed droplets unite into strips. However, the interfacial boundary cannot be destroyed and prevents coalescence of the droplets, reducing the efficiency of demulsification.

High-frequency ultrasound helps avoid strong mechanical effects of acoustic cavitation at low frequencies. As shown in ref 27, when a suitable frequency (>1 MHz) is chosen, the mechanical effects of cavitation can be restricted by chemical effects represented by dissociation of water. This technological difficulty of controlling bubbles in the turbulent flow restricts using hydrodynamic cavitation treatment for demulsification applications. The most known efficient demulsification of crude oil up to 65% without use of demulsifers was achieved in the frequency range of 25−45 kHz in 15 min.[28]

Demulsification in the MHz range can be achieved by use of two independent transformers operating in resonance.[29] Transverse arrangement of piezoelectric transducers to the direction of flow monitors the resonance frequency to produce a standing wave in the emulsion, even when composition and temperature of emulsion changes in a short irradiation time.

The effect of standing wave field combined with demulsifier, including factors affecting dehydration under the effect of ultrasound (power of ultrasound, operational temperature, demulsifier, and voltage in the desalting tank), demonstrates better results as compared to each method individually.[12,30]

## OIL SLUDGE TREATMENT

Demand for petroleum products is permanently increasing. Residue after crude oil distillation adversely affects systems of the oil refinery and environment because of its high viscosity and asphaltene content. Processing of oil sludge not only resolves the problem of adverse contamination but also can be a source of lubricants, fuels, etc.

The oil industry at the stages of production, transportation, storage, and processing is specified by production of oil sludge. The sources of oil sludge are bottoms of crude oil tanks, oil emulsion, contaminated effluents, oil-contaminated soil, and settling ponds. Worldwide production of oil-bearing sludge is more than 60 million tons.[31] Each ton of produced crude oil is thought to have up to 2 kg of oil sludge.[32]

Oil sludge is a complex mixture of oil sediments containing different amounts of petroleum products (oil as it is) up to

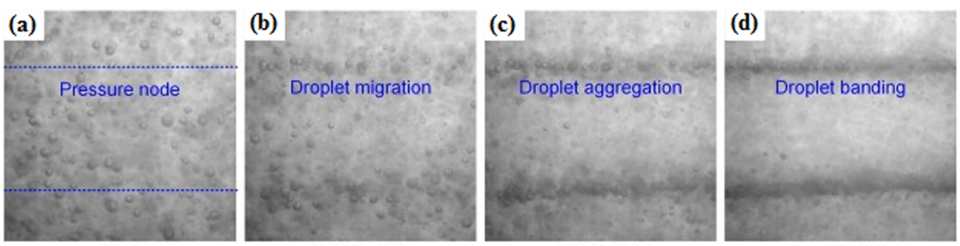


**Figure 7.** Aggregation of droplets with strip formation in high-frequency (126.4 kHz) ultrasonic waves in time: initial moment $t$ (a), after 14.54 s (b), after 29.68 s (c), and after 37.25 s (d). Reprinted with permission from ref 26. Copyright 2020 Elsevier.


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30%, from 30 to 40% of water, and solid inclusions (sand, soil, mineral components, heavy metals). Chemical composition of oil sludge is not standard and depends mostly on the composition of initial crude oil. The critical reasons of oil sludge formation can be changes in external conditions (temperature, pressure, humidity), cooling, evaporation of light factions, mixing with incompatible materials, and addition of water-forming emulsions. Toxicity, carcinogenicity, and mutagenicity of hydrocarbon compounds make them the most hazardous types of waste in the oil industry. The high viscosity of oil sludge and sophisticated mechanism of interaction with water, soil, and atmosphere, makes oil or its production waste spill remediation in the world's oceans or on land a great challenge.

Reduction of oil sludge amount can conditionally be divided into three states: reduction of sediment formation by technologies impacting oil at the stage of its production or processing, extraction of oil from oil sludge, and disposal of nonextractable oil sludge. Studies show that the profit from oil extracted from oil sediment exceeds the cleaning expenditures.[33] However, physical−chemical characteristics of oil-bearing sludge, produced quantities, availability, and feasibility of using the equipment are important parameters to define the technologies to treat oil sludge formed at a chosen oil refinery or deposit or burial site.

To characterize oil-containing sediment (sludge) requires evaluation of such quantitative parameters as pH, content of solid matter, phosphorus, nitrogen, carbon, sulfur, metals (As, Pb, Cd, Co, Cu, Cr, Ni, Zn, V, Hg), and polycyclic aromatic hydrocarbons (PAHs) and quantity of oil hydrocarbons, benzene, toluene, ethylbenzene, and xylenes. These parameters are most important; they should be correlated with specifics of each processing technology. Most of these components are difficult to process because of their strong molecular bonds, high molecular weight, hydrophobicity, and low solubility in water. The oil-containing sludges containing high concentration of sulfur, Cr, Pb, Hg, and PAH cannot be treated by thermal methods, such as combustion, combined treatment in clinkering kilns, microwave liquefaction, or destructive distillation.[34]

Treatment of oil sludge is the most preferable version in the oil industry as it makes the production potential more complete. Moreover, processing of the oil-containing residue can reduce the volume of hazardous waste, prevent contamination, and reduce use of nonrenewable energy sources. The known extraction methods are by dilutant, centrifugation, addition of surfactants, freezing/melting, pyrolysis of sediment, microwave irradiation, electrokinetic exposure, and creaming flotation.

High efficiency and minimal impact on the environment from ultrasonic technology are important as it is widely used in oil processing. Reduction of viscosity when treated with low power density is caused by disaggregation of the colloidal system. Processing with high power density can cause both disruption of the chemical bond and disaggregation of the colloidal system.[35]

In oil sludge processing, ultrasonic waves are used to change the physical properties and condition of the oil-containing sediment, containing solid particles of different sizes. The effect of cavitation and mechanical vibration, caused by acoustic irradiation, removes droplets of crude oil initially fixed to the surface of solid particles by disrupting hydrogen bonds between oil and solid particles to desorb the oil. This decreases the amount of crude oil on the surface of solid particles[36] (Figure 8).

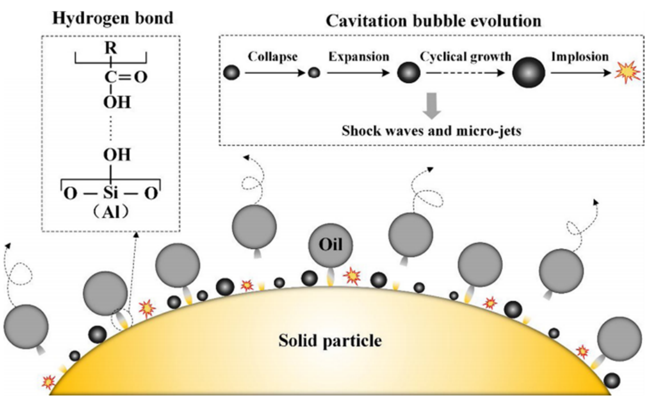


**Figure 8.** Mechanism of disintegration of oil-containing sludge by ultrasound. Reprinted with permission from ref 36. Copyright 2020 Elsevier.

Impulse waves of sound pressure make the water droplets and solid particles in sludge vibrate to destabilize it. Ultrasound can penetrate each phase of oil-containing sludge and completely disintegrate it. Under continuous irradiation by ultrasonic waves, the viscosity of water−oil emulsions continuously decreases. Small droplets in the emulsion mixture increase their motion, collide, and coalesce; in this manner, the water phase and oil separate. When oil sludge disintegrates into smaller parts, the efficient area between the cavitation bubbles and emulsion increases, and this makes removal of oil from solid surfaces deeper. The effect of cavitation bubbles on removal of oil from the oil-containing sludge includes not only mechanical disintegration but also oxidative degradation.

The ultrasonic waves create and uniformly distribute explosions of cavitation bubbles in liquid medium. The energy released can reach and penetrate the pores, closed holes, and areas generally inaccessible for other cleaning methods. This can substantially simplify further disposal of oil sludge.

Efficient use of ultrasound to separate water−oil sludge emulsion depends on several factors (described in the demulsification section), including frequency of the sound, intensity, treatment time, temperature properties of sludge, additives, and salts or other impurities. In ref 37, the power of ultrasound was shown to be the most important factor in treatment; its increase in totality with the least content of asphaltene oil extraction from the oil sludge amounted to 92%. Some model studies show that the light oil components (PAH, light hydrocarbons, kerosene, gasoline) can be relatively easily removed from solid substances, whereas heavy hydrocarbons (asphaltenes) remain fixed to solid surfaces.[38] Additional mixing of emulsion during acoustic impact also increases the amount of separated oil. Combined use of ultrasound and thermochemical treatment made extraction of more than 99% of oil under ultrasonic treatment parameters of 28 kHz, 15 min, 400 W, and 60 °C possible; an increase of treatment time to 400 min did not further increase oil recovery.[39] Complex use of acoustic impact with surfactants decreases the average size of solid particles in oil sludge; on the whole, this is useful to extract oil but heavily depends on the treatment time and can increase the probability of recombination of oil and solid matter with time.[40]


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Ultrasonic irradiation is a processing method that makes it possible to treat oil-containing sludges in a relatively short time. High efficiency of oil recovery and lack of secondary contamination notwithstanding, ultrasonic irradiation to recover oil from sludge is most frequently reported for laboratory systems and small volumes of treated media. To use a large tank for ultrasonic treatment can be more prospective from the viewpoint of processing large amounts of oil containing sludge, but low intensity of ultrasound can reduce its performance; implementation of this method is associated with special tanks or structures.[41] The high cost of equipment and maintenance also prevent commercial use of this technology.

## OIL DESULFURIZATION

Organic compounds of sulfur are difficult (most commonly impossible) to separate from crude oil and its derivatives, such as gasoline and diesel fuel, which account for a high share in total production of oil refineries. These compounds include sulfides, thiols, thiophenes, substituted benzo- and dibenzo-thiophenes, benzonaphthothiophenes, and numerous other more complex molecules.

Organic sulfur compounds during combustion in fuel form $SO_x$ compounds. They react in the atmosphere to form $H_2SO_4$, generating acid rain. Furthermore, $SO_2$ is associated with adverse respiratory effects in humans. Moreover, the content of pollutants (sulfur, nitrogen, oxygen, and metals) adversely affects equipment, catalysts, and the quality of finished product.

High environmental protection standards restrict sulfur content in fuel, demanding deep desulfurization of both fuel and petroleum products. The conventional method of removing sulfur from oil includes hydrotreatment entailing capital-intensive investments into hydrodesulfurization equipment at high pressure and high temperature. Furthermore, persistent aromatic sulfur compounds (e.g., 4,6-dimethyldibenzothiophene) cannot be removed by desulfurization because of their low reactivity. Oxidative desulfurization by ultrasound (UAOD) forms useful alternatives to conventional methods and makes deeper desulfurization under less aggressive conditions of the process possible with operating temperatures of 40−100 °C and pressures of 1−2 atm.[42]

The effect of ultrasound on desulfurization efficiency is technically associated with its chemical and physical mechanism. The chemical mechanism of ultrasonic treatment involves acceleration of the reaction by formation of radicals due to short-time collapse of cavitation bubbles, whereas the physical mechanism is formation of thin oil-in-water emulsion or water-in-oil emulsion, which increases mass transfer by increasing the inertial field between the oil and the oxidizing phase. In the oxidative desulfurization process, the ultrasonic cavitation operates by forming microturbulence, which increases the oxidation reaction between the hydrocarbons and $H_2O_2$, forming or added into the water.

Studies investigating oxidative desulfurization with use of ultrasound are aimed to select optimal, rational, and efficient operating parameters of the process to increase extraction of sulfur compounds. In ref 43, conversion of sulfur amounted to 98% at a temperature of 52 °C; the ultrasonic treatment time was 15 min, and ultrasound power was 70 W. Design of experimental techniques made it possible to determine the optimal UAOD parameter values for gas−oil volume of the oxidant, mass of the catalyst, and phase transfer agent and amplitude of ultrasonic waves for maximum conversion of sulfur at 95.92%. UAOD employing ionic liquids at room temperature (the organic salts which form liquid phase at temperatures below 100 °C) as a catalyst for phase transfer and extractive solvent achieved 99.9% desulfurization in diesel fuel samples exposed to 10 min long ultrasonic impact.[44] It should be noted that to make the UAOD process most efficient, the combination of oxidant, catalyst, and phase transfer agent should be selected for each oil fuel and its specific sulfur compounds. Ultrasonic treatment helps desulfurize oil, so oil and petroleum products can be expected to demetalize.

The complexity of scaling ultrasonic cavitation to a commercial volume is by restricting the volume of the ultrasound source. Hydrodynamic cavitation can form an alternative to ultrasonic (acoustic) cavitation. Hydrodynamic movement of liquid through a cavitation device creates cavitation over the entire volume of treated liquid and, consequently, can be efficiently used in large-scale deep and complete desulfurization operation.

## TREATMENT OF OIL-CONTAINING WASTEWATER

The amount of used oil increases with industrial development; the engineering solutions are, however, imperfect, and large quantities of oil get into water and pollute it. Moreover, the tertiary production processes, such as alkaline water flooding, polymer water flooding, and flooding with alkaline surfactants, form large amounts of oil-containing wastewater (stratal) that is difficult to process compared to conventional wastewater. To treat oil-containing wastewater, the oil industry (oil refining, oil storage, transport, and petroleum industry) has developed various methods, such as flotation, membrane filtration, electrochemical methods, centrifugation, and chemical oxidation.

Ultrasonic impact on oil-containing wastewater treatment processes is usually used with other methods to improve oil removal or compensate for their shortcomings. Ultrafiltration is efficient to treat complex oil-containing wastewater, as it does not need additions of chemical reactants. This reduces the cost of treatment and improves the quality of produced permeate. Ultrafiltration, however, has its own restrictions, resulting in reduction of permeate flow with time. Adsorption and accumulation of oil and particles on the membrane surface contaminate it and reduce service life of the membrane because of frequent chemical and physical cleaning. Ultrasound is among the most efficient methods of cleaning of ultrafiltration membranes.[45] Low irradiation frequency has been shown to be able to decelerate deposit formation, and higher frequency can improve removal of organic substances. On the other hand, cleaning using ultrasonic cavitation makes it possible to clean while filtration is still going on. There is no need to stop the filtration process or to pass over the pulsing mode, as this can reduce the cost of membrane cleaning. Therefore, combination of ultrasound with membrane ultrafiltration can reduce the rate of membrane contamination with high flow through the membrane and lower frequency.

In ref 46, the authors studied the effect of ultrasound in insignificant volumes of chemical reagents for flotation of oil-containing water to intensify the treatment process. After ultrasonic treatment, the flaky particles reduce their size and increase their number, and the capability to form conglomerates decreases. Experimental data speak in favor of increasing the number of coagulation kernels, this results in an improved degree of cleaning of water contaminated with petroleum


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products with similar consumption of the reactant. Solutions of alumosilicic flocculant coagulant contain both aluminum salts and active silicic acid, providing for coagulation and flocculation activities of the solutions. The authors of ref 47 showed a maximum degree of cleaning oil-contaminated water at a temperature of 6 °C and an ultrasound impact time of 60 s, with commercial flocculant "Praestol" 853 (2 mg/L) to 99.2%. Combined use of ultrasound and chemical or electrical flocculation makes the organic substances agglomerate and separate in water. Droplets of oil in wastewater feature high negative zeta-potential and high electrostatic repulsion among themselves, resulting in a stable disperse system (as noted in the demulsification section), and cationic flocculants play the role of an adsorption bridge and neutralize the charge on the surface of oil droplets.

Improved oxidation methods reinforced with ultrasound can be used to decompose organic matter in water: OH radicals promote a high rate of accelerated oxidation reaction (degradation rate of about $10^6$–$10^9$ l $mol^{-1}$ $s^{-1}$), reacting with organic molecules of contaminants.[48] It is common knowledge that, during cavitation, adiabatic collapse of microscopic bubbles takes place, and this creates localized high pressure and high temperature for reaction behavior. $H_2O$ thermally dissociates to form various highly active particles, such as radicals •OH, •OOH, •H, $H_2O_2$, and $O_2^-$. These circumstances promote oxidation reaction and recovery of the contaminant molecules, resulting in complete degradation.

Sonophotolysis is a combined improved oxidation method in which ultrasound and ultraviolet (UV) waves are simultaneously used to irradiate wastewater.[49] Treatment of wastewater by sonophotolysis forms highly active •OH radicals during themolysis of water molecules inside the cavitation microbubble (eqs 1–3):

$$H_2O + (\text{irradiation with ultrasound}) \rightarrow H\bullet + \bullet OH(\text{thermolysis}) \quad (1)$$

$$H\bullet + H\bullet \rightarrow H_2 \quad (2)$$

$$H\bullet + O_2 \rightarrow HO_2\bullet \quad (3)$$

and by decomposition of $H_2O_2$ under UV effect (eq 4):

$$H_2O_2 = h\nu(<254)(\text{irradiation with ultraviolet}) \rightarrow \bullet OH + \bullet OH \quad (4)$$

Hydrogen peroxide also forms during implosive collapse of the cavitation bubble or reacts with contaminant to destroy it or decomposes into the •OH radical under the effect of UV irradiation. Excess •OH radicals recombine to produce on site hydrogen peroxide, which further decomposes under UV light to form free radicals (eqs 5–7):

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (5)$$

$$H\bullet + HO_2\bullet \rightarrow H_2O_2 \quad (6)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (7)$$

These oxidizing radicals attack organic contaminants to decompose them to their intermediate products (eq 8):

$$\bullet OH + \text{pollutants} + \text{intermediate products} + CO_2 + H_2O \quad (8)$$

Excess concentration of $H_2O_2$ also results in the capture of radicals in the medium (eqs 9–11):

$$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet \quad (9)$$

$$H\bullet + H_2O_2 \rightarrow H_2 + HO_2\bullet \quad (10)$$

$$\bullet OH + HO_2\bullet \rightarrow H_2O + O_2 \quad (11)$$

Thermal decomposition and mineralization of intermediate products takes place at the gas–liquid interface of the bubbles. Hence, the ultrasound combined with UV light can provide for a synergistic effect in the degradation/mineralization of persistent organic contaminants by evaporation and thermal and photolytic dissociation of hydrogen peroxide caused by the sonoluminescence light emitted by short-living cavitation bubbles. Ultrasonic waves create microturbulence and intense mixing in the medium by shock waves. These physical properties of cavitation also accelerate the hydroxylation (oxidation) reaction and increase decomposition of intermediate products of UV radiation and reduce toxicity of contaminants.

The presence of dissolved oxygen in liquid medium can also intensify additional chemical reactions to form additional oxidizing radicals (eq 12):

$$\bullet OH + O_2 \rightarrow HO_2\bullet + O\bullet \quad (12)$$

Therefore, combinations of ultrasound and ultraviolet waves demonstrate their ability to provide for considerable synergistic effect.

Hybrid technologies including cavitation treatment are of much interest among research communities working on environmental remediation because sonohybridization methods are capable of destroying persistent organic contaminants. For instance, the combined use of hydrodynamic cavitation and the Fenton reaction improve the process of dewatering waste from activated sludge.[50]

## ■ CONCLUSION

Cavitation caused by ultrasonic waves or variation of hydrodynamic states draws has drawn the attention of the oil industry for the development of environmentally benign technology. Decreasing efficiency of crude oil production, the high cost of energy for oil transportation, and processing and increasing the scale of the environment pollution by oil waste has stimulated researchers to continuously search for alternative solutions. This promotes the investigation and implementation of cavitation treatment as a promising technology in various processes of the oil business in all countries associated with oil production in the past 30 years.

The reduction of viscosity of ultraheavy oil is one of the most promising directions of using wave technologies in oil industry—destruction of micelles and partial cracking of high molecular compounds increases the yield of light fractions in oil distillation without additional heating. Hydrodynamic cavitation is more efficient than acoustic methods due to the intensity of flow processing and the powerful mechanical impact on liquid. However, the technological difficulty of controlling bubbles in the turbulent flow restricts the application of hydrodynamic cavitation treatment for demulsification tasks. Ultrasonic demulsification equipment should provide for the possibility of varying acoustic parameters and stable output power to create the standing wave field. Combined use of ultrasound with a demulsifier to dehydrate the oil emulsion, including oil-containing waste, demonstrates better results than those for each method separately.



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The ultrasonic effect is commonly used in cleaning of waste or stratal oil-containing water in combination with other methods to improve oil removal or compensate their shortcomings. Persistent organic contaminants have been found to be sensitive to hybrid technologies including ultrasonic treatment; this has a positive effect on environmental remediation. In a general case, the trend is to use low irradiation frequency and high power with cavitation treatment for a short duration of seldom more than 1 h. To scale laboratory results, it is preferable to use equipment with several piezoelectric sources operating at certain frequencies. Oxidative processes used to treat waste and stratal water and in oxidative desulfurization by ultrasound play key role. High temperature (about 5000 °C) and high pressure (up to 5000 atm) within the scale of a microbubble along with slightly varying basic temperature and pressure of the liquid (at the environment level) efficiently help the oxidizing processes.

The cavitation technology is a technology relatively young for the petroleum industry; this calls for an investigation of its effects rather at the experimental stage of refining different oil compositions (particularly heavy and ultraheavy with high asphaltene content) and petroleum refinery products; this requires more time for numeric studies and cavitation aggregate simulation. Finally, achievement of stable output yield of oil production and oil refining and strict control of all parameters under the cavitation effect will allow mankind to prolong the efficient use of fossil energy.

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### Notes

The authors declare no competing financial interest.

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