

Review

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[Zhannur Myltykbayeva](#), [Binur Khabasovna Mussabayeva](#)*, [Yerdos Ongarbayev](#), [Yerzhan Imanbayev](#), [Dinara Mukhtaly](#)

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Review

Ultrasonic Technology for Hydrocarbon Raw Recovery and Processing

Zhannur Myltykbayeva ^{1,2}, Binur Mussabayeva ^{3,*}, Yerdos Ongarbayev ¹, Yerzhan Imanbayev ^{1,2} and Dinara Mukhtaly ^{1,2}

¹ Institute of Combustion Problems, Almaty 050010, Kazakhstan

² al-Farabi Kazakh National University, Almaty 050040, Kazakhstan

³ Astana International University, Astana 010017, Kazakhstan

* Correspondence: mussabayevabinur@gmail.com

These authors contributed to this work equally.

Abstract: A review discusses recent research findings spanning the last two decades concerning ultrasonic technologies applicable to the oil, gas, and coal sectors. Various experiments conducted in laboratories have demonstrated the efficacy, cost-effectiveness, and environmental friendliness of ultrasound in recovering and processing oil, bitumen, coal, and oil shale. Ultrasound enhances formation permeability, coal gas permeability, and oil viscosity, particularly when delivered in short, powerful pulses at medium frequencies. Combining ultrasound with traditional recovery methods has shown promising results, boosting recovery efficiency by up to 100%. At the same time, ultrasonic treatment reduces the use of traditional reagents, thereby reducing environmental pollution. Moreover, ultrasound treatment shows potential in tasks such as separating oil-water emulsions, desulfurization, dewaxing oil, coal enrichment, and extracting valuable metals from metal-bearing shales through hydrometallurgical leaching. However, widespread industrial implementation of ultrasonic technology necessitates further field and mathematical research.

Keywords: ultrasound; oil; bitumen; oil-bitumen rock; coal; oil shale

1. Introduction

The global demand for hydrocarbons is on a steady rise, prompting the need for the development and implementation of novel technologies aimed at enhancing hydrocarbon recovery and processing. The decline in production often stems from reduced reservoir pressure or reservoir damage. Ultrasonic technology emerges as a promising solution for increasing the permeability of porous media while minimizing environmental pollution, thereby boosting hydrocarbon recovery.

Ultrasonic treatment operates on the principle of acoustic cavitation [1]. As ultrasonic vibrations traverse through a liquid, particles experience cyclic compression and stretching aligned with the vibration frequency. During stretching phases, cavitation bubbles form within the liquid, typically filled with gas or steam. These bubbles can reach extreme conditions, with temperatures up to 1500°C and pressures of 150 MPa. Upon compression, the bubbles collapse, generating powerful shock waves. The combined energy of bubble collapse and ultrasonic waves can effectively disrupt the structure of various materials.

2. Ultrasound in Oil Recovery and Processing

Ultrasonic technologies are actively employed to enhance oil recovery efforts, with significant attention devoted to this in the USA, China, Russia, and Canada. These efforts primarily aim at reducing water content and eliminating pollutants from organic impurities in oil reservoirs. By utilizing ultrasound across varying frequencies, oil production rates can surge by 40-100%, contingent upon the specific characteristics of each oil well. This boost stems from improvements in oil viscosity and enhanced rock permeability, facilitated by the emergence of numerous microcracks and a reduction in pore blockage [2,3].

The application of ultrasonic irradiation generates heat, reducing oil viscosity by up to 86% and aiding in the breakup of emulsions [4].

A recent review delves into the latest advancements in ultrasonic oil processing technologies, offering a comprehensive examination of the underlying mechanisms. Among these mechanisms, cavitation plays a pivotal role. The shock waves resulting from bubble collapse disperse solid particles and disrupt chemical bonds, thereby enhancing emulsification and diffusion processes. Additionally, other mechanisms include heating, acoustic fluxes, and radiation effects [3].

Ultrasonic technology proves to be cost-effective in boosting oil well productivity. It achieves this by altering capillary and gravitational forces, thereby facilitating improved oil movement within reservoirs. These forces are influenced by mechanisms such as cavitation, coalescence, Bjerknes force, micro jets, peristaltic motion, sonocapillary effect, and acoustic flow, as highlighted by certain authors [5].

Cavitation is influenced by two main categories of parameters: acoustic parameters and media properties [6]. Acoustic parameters encompass factors like frequency, sound intensity, exposure duration, distance from the ultrasound source, operational mode, and field type. On the other hand, media properties include liquid viscosity, saturated vapor pressure, interfacial tension, dissolved gas content, and solid particle porosity.

Studies indicate that the efficacy of ultrasound treatment is maximized when employing periodic ultrasound with frequencies ranging between 20 to 30 kHz, maintaining sound intensity below critical levels, prolonging irradiation duration, and minimizing fluid consumption [7]. Higher frequencies, characterized by shorter wavelengths, have limited penetration in porous media. Extending ultrasonic exposure distance can be achieved by elevating ultrasound intensity, but excessive power may lead to well damage and accumulation of sand and debris particles [4].

Some research explores the combined impact of multiple frequencies during oil production. For instance, a comparison between single frequencies and simultaneous application of double frequencies (e.g., 28 kHz and 68 kHz) revealed a substantial enhancement in productivity from 13% to 95% when employing double frequencies [8].

In the latest review [9], a thorough analysis of available literature on laboratory experimentation and field trials of ultrasound technology is presented. Publications are classified based on research type, including theoretical, mathematical or computational modeling, laboratory studies, and field tests, either individually or in combination. However, it's noted that while there's an abundance of laboratory research, there's a dearth of mathematical modeling concerning ultrasound's effects in downhole zones, and there's a pressing need for more field tests to bridge this gap.

Based on laboratory studies, most researchers suggest that the increase in oil recovery is primarily influenced by the intensity rather than the frequency of ultrasonic treatment (Table 1).

Table 1. Data of some laboratory studies of ultrasonic effects on oil recovery.

Ultrasound frequency	Ultrasound intensity	Exposure time	The effect of exposure	Reference
40 kHz	150, 300, 500 W	3-90 min	Injection of water and surfactants using ultrasound improves oil recovery by 11% and 12%, respectively. With increased ultrasonic intensity, oil recovery improves from 61.1% (150 W) to 67.4% (500 W)	[10]
20 kHz	300 W	3-10 min	Ultrasound changes the morphology of the carbonate rock by forming microcracks. Sandstone particles	[11]

			exfoliated more strongly than dolomite particles.	
30 kHz	100 W	-	Improved mobility and oil percolation depending on the viscosity and pore geometry of the rock. The effect of ultrasound was stronger for light oils. The completeness of oil recovery was mainly influenced by the intensity of ultrasound and the sludge's	[12]
25-125 kHz	120-300 W	15-120 min	hydrophilicity (the maximum recovery level - 92% was achieved for hydrophilic sludge with an ultrasound intensity of 240 W).	[13]
18, 20, 25 kHz	1000 W	10-100 min	When using ultrasound and hydrogen peroxide together, the permeability increased to 40.90%.	[14]
15-28 kHz	-	-	Ultrasound with a frequency of 20 kHz caused the formation of microcracks in the cores. The viscosity of oil and the surface tension between oil and water have also decreased.	[15]
40 kHz	200 W	8 h	The oil recovery rate increased by 11.7%. The oil viscosity at 60 °C decreased by 32%, the content of resins and asphaltenes decreased by 49% and 37%, respectively.	[16]
42, 46 kHz	35-50 W	8 min	Ultrasonic irradiation reduced the number of asphaltene clusters in the oil. Ultrasound of 50 W and 46 kHz during 8 minutes reduced the viscosity of the heated oil to 40%, and of the cooled oil by 10%.	[17]
21.7; 41.9; 98.0; 123.0 kHz	0.5-0.7 W/sm²	5-35 min	The efficiency of oil recovery from sludge increases with processing time, increased intensity and decreased frequency of ultrasound.	[18]
50 kHz	10 kW/m²	0-200 h	Improved recovery of low-maturity shale oil was achieved by expanding the pores of the reservoir and increasing the mobility of oil. With an ultrasonic treatment duration of less than 150 hours, the diameter, surface and total	[19]

			pore volume increased slightly with increasing treatment time. With longer processing (200 h), these pore parameters increased significantly.	
50 kHz	30, 60, 100 W	2-18 min	The combined use of ultrasound and solvent (n-heptane) led to the greatest decrease of the viscosity of heavy asphaltene oil.	[20]
			The extraction of paraffin (as the heavier oil) and kerosene (as the lighter oil) from a 2D micro-model of a porous medium has been studied.	
40 kHz	150, 500 W/sm ²	15-60 min	Short-term and intermittent ultrasound can recover more oil compared to continuous ultrasound for a longer time. With an increase of ultrasound intensity, oil extraction increased. When using paraffin, extraction was 74%, and kerosene - 82% at 500 W/cm ² intensity with intermittent ultrasound.	[21]
-	80, 100, 120 W	1-3 min	Ultrasonic and thermal treatment of heavy oil samples leads to an decrease in viscosity by 20% and by 2.3 times for two oil samples. Thermal and ultrasonic treatment showed the same effect.	[22]
18, 24, 35 kHz	-	-	The viscosity of heavy oil samples decreases by 5.3-12.1%, average oil by 37%, and bio-oil by 2 times.	[23]
22 kHz	1000 W	80 min	Ultrasound increases the permeability of low-permeability cores to 80, 42, 87 and 81% and removes inorganic deposits.	[24]
20 kHz 40 kHz	60 W	0-99 min	The water-oil emulsions were treated with ultrasound, then surfactants or biosurfactants produced by aerobic microorganisms were added to them. Emulsions with biosurfactants were more stable, their injection increased oil recovery to 86.9%	[25]

Field tests on existing oil wells are crucial for further technological development. Detailed consideration of a few such tests in reviews [26,27] has demonstrated a significant boost in recovery coefficient through ultrasound treatment. The absence of reservoir contamination and the simplicity of ultrasonic technology underscore its promising prospects.

For instance, employing a borehole radiator for ultrasonic treatment led to a doubling of permeability in porous media at a frequency of 1 kHz and a fivefold increase at 2 kHz [28]. Another study [29] showcased a notable 11% increase in oil recovery through testing the acoustic effect at a 1 kHz frequency alongside reservoir pressure maintenance technology. Moreover, the persistent cavitation aftereffect lasting several months was observed. The acoustic impact during reagent injection facilitates deeper penetration into the formation, expanding coverage and consequently enhancing oil displacement [27].

In the primary processing of oil, ultrasound serves a vital role in demulsification, desulfurization, and dewaxing processes.

During the recovery of crude oil, stable water-oil emulsions frequently develop. Traditional separation methods involve the use of chemical demulsifiers to break these emulsions. However, ultrasound presents an alternative approach. Depending on the application method and the intensity of ultrasonic treatment, cavitation induced by ultrasound can have dual effects, stimulating both emulsification and demulsification processes. This phenomenon leads to the coagulation of droplets, facilitating the subsequent separation of water and crude oil [30,31].

Research highlighted in [32] demonstrates that low-frequency ultrasound is effective for separating emulsions with high viscosity, while high-frequency ultrasound is advantageous for emulsions with low dispersed phase content and small droplet sizes.

Ultrasound can be employed independently or as a complement to traditional methods for emulsion separation. Combining ultrasound with electrostatic separation, as noted in [33], notably reduces emulsion separation time. For instance, emulsion destruction was achieved through ultrasonic treatment with a 1.0 kW intensity alongside the addition of a 4-8% volume suspension of AlN nanopowder in acetone. This approach yielded a separation efficiency of up to 64% for helium-containing emulsions within 0.5-3 minutes, compared to conventional emulsions with up to 6% efficiency [34].

In [35] for the demulsification of crude oil, it is proposed to use an orthogonal two-frequency ultrasonic wave, which provides a higher rate of demulsification and dehydration of oil.

Research findings indicate that ultrasound-based emulsion separation can outperform other methods in terms of effectiveness and speed, even without the use of demulsifiers [36–38].

Substituting chemical demulsifiers with ultrasound can shorten settling periods, reduce demulsifier consumption, and significantly decrease soil and wastewater pollution. However, the relatively high cost of ultrasonic technology necessitates further refinement to minimize expenses and substitute chemical demulsifiers effectively.

In [39], the impact of ultrasound on oxidative desulfurization of crude oil was explored. Results indicate that increasing ultrasound power and catalyst quantity led to a threefold reduction in sulfur content within the initial 10 minutes of treatment. In another study [40], ultrasound treatment of oil at 60°C resulted in 56.5% sulfur removal, accompanied by an over 80% reduction in reaction time.

Combining ultrasound with UV irradiation enhances desulfurization efficiency compared to their separate use. This combined approach, when coupled with oxidizing agents and catalysts, creates optimal conditions for successful sulfur removal [41].

Ultrasound proves effective not only for sulfur removal from crude oil but also from various petroleum products like oils, gas oil, kerosene, and fuel oil [3,42].

In combating paraffin deposits, ultrasound emerges as a promising method, augmenting the effectiveness of existing approaches. Research by [43] showcases the enhanced efficiency achieved through combined ultrasound of different frequencies with chemical acid treatment, nearly doubling the cleaning efficacy compared to singular ultrasound or chemical treatments. Frequencies around 20-25 kHz were found most effective for removing paraffin plugs. Ultrasound exerts a multifaceted impact on paraffins, inducing heating, structural changes, molecular rupture, and the generation of free radicals [44].

Bitumen and oil separation from oil sand and sludge represent crucial processes in light of declining crude oil reserves [45]. Oil bitumen rocks (OBR) and oil sludge are heterogeneous mixtures

comprising oil, water, and soil particles, with OBR typically containing 3-20% bitumen, 80-87% sand and clay, and 3-6% water [46].

Conventional methods for bitumen separation from oil sand include water flushing, hot water extraction (HWBE), solvent extraction (SE), pyrolysis, reactive extraction (RE), and extraction using ionic liquids (IL) [47–52]. Ultrasonic processing technology offers an alternative, facilitating bitumen recovery in the presence of water.

Ultrasonic energy, spanning a wide frequency range, can serve as both primary and auxiliary methods for bitumen separation from oil sand, and for environmental purposes such as soil decontamination from petroleum products. The ultrasonic wave penetrates the bitumen, affecting the oil-solid interface. When cavitation bubbles collapse, they generate high temperature, pressure, shock waves, and micro jets, disrupting the bond between sand and bitumen [53]. Acoustic cavitation induces bitumen surface destruction, forming micro-holes that gradually expand, leading to complete bitumen layer removal. Sonochemical reactions further transform bitumen into organic compounds like resins and oils.

For example, organic component separation from OBR at the Imankara deposit (Kazakhstan) was achieved through ultrasonic treatment in the presence of solvents and the flocculant Uniflok. Extraction rates were found to depend on ultrasound intensity, solvent nature, and flocculant concentration [54].

The addition of alkali has been found to enhance the efficiency of ultrasonic bitumen separation from oil sand. Increasing pH levels result in decreased adhesion [55]. Additionally, alkali reacts with carboxylic acids in bitumen, forming surfactants in situ [56]. These surfactants reduce the interfacial tension of bitumen/water and increase the zeta potential of both bitumen droplets and silica particles, facilitating bitumen separation from solid surfaces [57]. Maintaining the desired pH value enables the reaction to proceed without the need for additional surfactants.

Mixing oil sand with aqueous solutions of sodium salts and treating the mixture with ultrasound (intensity of 400 W, frequency of 22 Hz, exposure time of 15 minutes, concentration of 0.5 M sodium silicate, and 1.1 M sodium carbonate) resulted in the separation of 94-96% of bitumen [58].

In [46], three phases of ultrasonic oil recovery are identified based on treatment time. Powerful ultrasound treatment for 1 to 2.8 hours separates the oil component of bitumen. Subsequently, in the 2.8 – 4 hour interval, asphaltenes are separated. Surfactants formed in situ from the neutralization reaction destroy open asphaltene micelles and form Hartley micelles. Continued ultrasound treatment for up to 6 hours leads to asphaltene disintegration.

Medium frequency and high-intensity ultrasound are commonly used for bitumen separation from oil sand (Table 2).

Table 2. Data on ultrasonic bitumen and oil separation from oil sand and oil sludge.

Country	Process Parameters	Obtained results	Reference
Kazakhstan	Solvents: benzol, kerosene, hexane, hexyl alcohol, diesel fuel and white spirit in ratios from 5:1 to 1:5 Flocculant: “Uniflok” (hydrolyzed polyacrylonitrile derivatives) Ultrasonic treatment	It has been established that the rate of separation of organic components depends not only on ultrasonic treatment, but also on the solvents used. When kerosene and white spirit are used as solvents, as well as at a concentration of flocculant 0.1%, the maximum separation of the organic part is achieved within 10 minutes.	[54]

	Process time: 2-3 min to 6 hours.		
	Solution: surfactant including SDBS, NAOL, NaLA	Multi-frequency ultrasound treatment results in faster oil separation than single-frequency ultrasound treatment. Optimal separation was achieved using three-frequency ultrasound at a temperature of 20-30 °C, a surfactant concentration of 1.5 g/l for 10-15 minutes.	[59]
China	Frequency: 28 kHz, dual-frequency combined ultrasounds (28/68), (28/80), (68/80), and tri-frequency combined ultrasounds (28/68/80)		
China	Frequency: 28 kHz Intensity: 200W The mass ratio of the agent (YSFL) and oil sand: 1:1 Temperature: 70°C Solution: Na ₂ SiO ₃	The oil product yield is 94.2% in 13 minutes. The optimal process temperature is 60°C. The optimal mass ratio agent:oil sand is 0.8:1.	[60]
Russia	Frequency: 22 kHz Intensity: 1000W Temperature: 30°C and 75°C. Solution pH: >7 Solution: Sodium silicate (Na ₂ O·SiO ₂), Na ₂ CO ₃ (sodium carbonate) and sodium hydroxide (NaOH).	94% bitumen is separated at 60°C during 8 minutes at concentration of Na ₂ SiO ₃ 6%.	[61]
Russia	Frequency: 28 kHz and 200 kHz. Intensity: 60-200 W Temperature: 30°C and 75°C.	It has been found that the high intensity of ultrasound separates more bitumen. Purification using an alkaline solution recommended only for mixtures with particle sizes of at least 10 µm.	[62]
Kazakhstan	Process time: 15 min Solution: alkaline medium of sodium silicate and sodium carbonate Frequency: 22 kHz Intensity: 400W Process time: 8-15 min	At the optimal concentration of the solution, Na ₂ SiO ₃ – 0,5 mol/l, Na ₂ CO ₃ – 1,1 mol/l, a high degree of bitumen separation was achieved 94-96%.	[58]

Russia	<p>Solution: Sodium silicate ($\text{Na}_2\text{O}\cdot\text{SiO}_2$), Na_2CO_3 (sodium carbonate) and sodium hydroxide (NaOH). Temperature: 300-350 K (27-77°C) Intensity: 100 W Frequency: 22 kHz</p>	<p>With a sufficiently high alkalinity (more than 3-5% by weight), the bitumen separation increases by about 95%. The rate of separation of bitumen from oil sands increases with increasing temperature.</p>	[56]
China	<p>Solution: surfactant SDBS Frequency: For single frequency: 28 kHz or 68 kHz, for dual- frequency: frequencies of 28 kHz and 68 kHz simultaneously Intensity: 75W Process time: 30 min</p>	<p>The dual-frequency ultrasound treatment technology increases the level of oil production from oil sands to 95%, reduces the temperature by 40 °C, the concentration of surfactants in solution by 60%, water consumption by 20%, and also reduces the process time by 66%.</p>	[8]
Canada	<p>Combined treatment by ultrasonic and freeze/thaw. Solution: bio-surfactant (rhamnolipid), NaCl Frequency 20 kHz Intensity: 66 W Process time: 10 min</p>	<p>Ultrasound treatment with an intensity of 66 W for 10 minutes, an oil sludge/water ratio of 1:2 and without the addition of bio-surfactant and salt, the degree of oil recovery was 80%. As a result of the combined treatment, oil recovery was 64.2%. Ultrasound helps to separate oil from solid particles, and freezing/thawing promotes the separation of water and oil.</p>	[63]
Canada	<p>Solution: 3% NaCl Frequency 20-40 kHz Intensity: 45, 84 W Process time: 160 min</p>	<p>As a result of the work, a high degree and speed of oil extraction from sandstone was noted at a higher ultrasound frequency and a shorter distance from the ultrasonic electrode.</p>	[64]
China	<p>Solution: Surfactant SDBS Frequency: 20, 28, 40 kHz Intensity: 540 W Process time: 160 min</p>	<p>It was found that at an ultrasound intensity of 4.89 W/cm², the number of oil droplets first increases and then decreases with increasing ultrasound intensity. At an ultrasound frequency of 20 kHz, the number of oil droplets varies from 250 to 300 mμ.</p>	[65]
China	<p>Extractants: petroleum ether, toluene</p>	<p>It has been found that with an increase in the intensity of ultrasound and processing</p>	[18]

	<p>Solution: surfactants SDBS and Triton X-100, Na₂SO₄·H₂O, NaOH Frequency: 21.7, 41.9, 98.0 and 123.0 kHz Intensity: 1 W/cm² Process time: 35 min LAS and AEO-9 were chosen as surfactants, and Na₂CO₃ and Na₂SiO₃ were chosen as dispersants. Frequency: 28 kHz Intensity: 500 W Process time: 10 min Temperature: 60°C Solution pH: 10 Modification reagents: Sx4056: petroleum sulfonate: sodium silicate = 1:4:10</p>	<p>time, the efficiency of separating oil from oil sludge increases.</p> <p>As a result of the experiment, the oil recovery from the oil sludge increased to 99.32%. The oil separated from the oil sludge contained 0.53% of solid particles.</p>	
China			[66]
China	<p>Frequency 35 kHz Intensity: up to 90 W Process time: 20 min Temperature: 60°C pH of the solution: 10</p>	<p>The oil sand with an organic content of 30.8% was pretreated with a modifying reagent under the influence of ultrasound, and then flotation extraction was performed. At a concentration of the modifying reagent of 10.0 g/l, an ultrasound frequency of 53 kHz, and a intensity of 75 W, the content of the organic part decreased to 0.66 %</p>	[67]
China	<p>Frequency 25, 50, 100 kHz Intensity: up to 300 W Process time: 120 min</p>	<p>The optimal conditions for separating oil from oil sludge are the frequency of 25 kHz, the ultrasound intensity of 0.33 W/cm² and the ratio of oil sludge:water is equal to 1:2. It has been established that the use of surfactant solution is necessary for the extraction of resinous asphaltene components from oil sludge when exposed to ultrasound</p>	[68]
Japan	<p>Frequency 28 kHz Temperature: 200°C Reagent: THF</p>	<p>88% of bitumen was separated from oil sands and 42% of sulfur was removed from bitumen.</p>	[69]
Japan	<p>Frequency: 28 kHz Intensity: 11 W Process time: 0-180 min</p>	<p>When using 3 wt% H₂O₂ and 60 minutes of irradiation, the degree of bitumen separation was 93%, and the degree of desulfurization was 86%.</p>	[70]

	Temperature: 450°C Reagents: hydrogen peroxide and THF Frequency: 28 kHz Intensity: 200 W	Bitumen is effectively separated from an alkaline solution using ultrasonic irradiation	
Japan	The temperature: 850°C pH=13 (concentrated alkali solution) gas CO ₂	with CO ₂ injection. Bitumen recovery rate of 70% at a CO ₂ injection rate of 20 ml/min.	[71]
	Jet cavitation	The mass of bitumen-free sand when using cavitating jets was greater than with non-	
Canada	The temperature: 5-55 °C. Process time: 10 min	cavitating jets. The cavitation effect for bitumen separation ranged from 40% to 50%.	[72]
	Jet cavitation Cavitation σ =0.37 - 0.46 Intensity: 69-93 W The temperature: 12-23 °C	Higher cavitation activity was observed when using a self-resonating nozzle. Cavitation jets can be used instead of hydraulic transport, thereby reducing the energy consumption of the bitumen separation process.	[73]
Canada	Process time: 3 hours Six cavitation nozzles with a diameter of 13-17 mm have been tested		
	Jet cavitation	At an inlet pressure of 12 MPa, a temperature of 35 °C, and a hydrodynamic	
China	Inlet pressure 6-14 MPa	cavitation time of 4 s, the oil recovery coefficient from oil sludge reached 82.3 %	[74]

Table 2 illustrates that ultrasonic bitumen separation from oil sand is more effective in an alkaline medium with the addition of surfactants.

Bitumen's viscosity is notably high (>500 Pa·s), preventing flow at ambient temperature [71]. Recent research [75] explored the effect of ultrasonic treatment on bituminous oil viscosity, revealing a 30% viscosity reduction and increased lighter component content after 3 minutes of ultrasound exposure.

3. Ultrasonic Treatment of Coal

Coal serves as a crucial energy source and a vital material for generating valuable products. Ultrasonic technology finds application in both coal mining and the retrieval of methane from coal seams.

In hydraulic fracturing of coal seams, ultrasound plays a pivotal role. As mining operations delve deeper, the methane content within the coal mines escalates. However, the coal seam's low permeability not only poses safety concerns for mining but also complicates methane extraction, an essential energy source [76].

The application of ultrasonic vibrations triggers the rupture of coal pores and facilitates crack propagation, consequently enhancing coal permeability. Prior to ultrasonic treatment, injecting water

into the coal seam becomes necessary. Ultrasonic waves induce pore expansion, with the effectiveness of this expansion directly proportional to the water content within the coal. Experimental tests on coal samples with varying moisture content - 2%, 4%, 6%, and 8% - were conducted, revealing a correlation between moisture content and pore expansion. Ultrasonic waves expedite moisture evaporation within the coal mass, thereby contributing to pore formation. Consequently, both the porosity and permeability of the coal mass increase during hydraulic fracturing [77]. The cavitation effect can further elevate coal permeability by 30-60% [78].

Ultrasonic treatment can modify the pore size of coal, expanding it from 1 nm to 100 nm. Research indicates that prolonged exposure to ultrasound results in larger pore volumes. For instance, when subjected to ultrasound at 25 kHz and 3-18 kW for 2 hours, the average pore diameters of tested coal increased by 5.05 - 61.81% [79]. A model experiment examining ultrasonic stimulation of coal revealed that the rates of pore expansion, alterations in porosity, and enhancements in coal permeability exhibit a linear relationship with the duration of hydraulic fracturing [80].

Water injected into coal seams may linger in the pores, potentially causing blockages [81]. To address this issue, scientists propose replacing pure water with a surfactant solution during injection. Surfactants enhance coal wettability, diminish capillary pressure within pores, consequently augmenting coal seam permeability [82].

In a study [83], experiments were conducted varying parameters such as ultrasound duration and power, liquid pressure applied to coal, and the impact of surfactant treatment (specifically sodium dodecyl sulfate). Findings demonstrate that ultrasonic stimulation significantly increases coal pore volume and specific surface area, while also roughening the inner surfaces of pores. Notably, the duration of ultrasonic excitation exerts a more pronounced effect on smaller pores. Liquid pressures below 4 MPa proved most effective for pore expansion. Treatment of coal with a 0.85% dodecyl sulfate solution resulted in the cleansing of primary small pores.

Ultrasonic treatment for half an hour improved the gas permeability of coal by 34.3 - 43.8%. With continuous ultrasonic stimulation, gas permeability initially increased rapidly, then gradually slowed down. After several cycles of stimulation, permeability levels stabilized. Research indicates that ultrasonic treatment induces multidimensional structural damage and expands interconnected crack networks, significantly enhancing methane production from coal seams [84].

In another study [85], a 3D reconstruction of ultrasonic excitation of coal based on computed tomography images was conducted. Ultrasound treatment with a power of 3 kW and 25 Hz for 2 hours led to a 75.44% to 111.8% increase in nitrogen sorption, a 12.15% to 20.81% rise in average pore diameter, and a 30.99% to 56.02% expansion in pore surface area. Additionally, mesopores with a size of 2-50 nm increased by 16.46% to 79.15%, and macropores increased by 2.38% to 14.82%. Crack volume and crack surface saw increases ranging from 8.11% to 11.81% and 13.92% to 21.63%, respectively. The proportion of connected cracks also rose by 12.78%. These findings underscore how ultrasound can significantly enhance the multiscale structure of coal pores and cracks, thereby boosting methane production from coal seams.

Ultrasonic waves generate heat within coal seams. In a related study [86], acoustic-thermal, mechanical, and hydrological models of ultrasonic heating were developed. Simulated data from the acoustic-thermal model aligned entirely with experimental findings. It was observed that lower frequencies and higher sound pressures resulted in more effective heat transfer from ultrasonic waves.

Researchers [87] suggest that the temperature increase in coal during ultrasonic exposure can be categorized into three stages: rapid increase, slow increase, and fluctuating increase. Temperatures can peak at a maximum of 263.9°C within 1 hour.

The combined application of ultrasound and CO₂ has yielded promising outcomes in augmenting methane production from coal seams. Ultrasound treatment enhances the proportion of oxygen in coal by increasing the presence of oxygen-containing functional groups while reducing the content of adsorbed methane. Moreover, CO₂ exhibits superior sorption capacity in coal, thereby amplifying the transport diffusion of methane [88].

In a study [89], the propagation velocity of ultrasound in coal rock was tested using a Tektronix ultrasonic device. It was observed that the velocities of longitudinal and shear waves escalate with increasing density. Additionally, the ultrasound speed in the rock is influenced by the composition and size of particles, with larger mineral particles correlating with greater longitudinal wave velocity.

Ultrasonic treatment has demonstrated efficacy in enriching low-grade coals. A review [90] outlines studies employing ultrasonic energy across various coal enrichment methods: physical, chemical, and physico-chemical techniques. Ultrasound was utilized for pretreatment or concurrently during coal operation.

In another study [91], coal underwent pretreatment before physical enrichment. Ultrasound treatment during separation in a hydrocyclone resulted in reduced ash content and increased calorific value compared to untreated coal. Furthermore, two-stage ultrasound treatment facilitated additional ash and sulfur removal [92].

Ultrasound also finds application in coal flotation. Cavitation induces the formation of point defects on the surface, leading to the fragmentation of coal particles in water and the separation of sludge and ash impurities. High-ash brown coal flotation using ultrasound (20 kHz) demonstrated significantly higher yields and selectivity compared to conventional flotation methods [93].

Ultrasonic treatment during chemical leaching processes reduces reagent consumption and processing time. The shock waves generated from cavitation induce surface cracks and fractures on coal, while shear forces direct the leaching agent towards the core of coal particles [90]. Consequently, studies have shown that ultrasonic leaching with mineral acids is notably more effective than conventional leaching methods [94].

In a study [95], researchers achieved maximum demineralization of coal samples through combined exposure to microwave and ultrasonic energy. Microwave oven treatment resulted in an ash yield of 51.28%, which increased to 66.34% after ultrasonic treatment. This combined approach effectively removed mineral phases such as quartz, kaolinite, and gypsum from the coal.

Ultrasonic treatment has also emerged as an effective method for coal desulfurization. Treatment of coal in an aqueous medium with hydrogen peroxide under ultrasonic conditions led to the removal of 87.52% of total sulfur from coal [96].

The intensification of O-alkylation of organic matter in brown coal through ultrasonic action was explored. Ultrasonic stimulation notably increased the yield of bitumoids by 15.7% compared to O-alkylation without ultrasound. Additionally, wax yield increased by 6.1%, and resin yield by 9.6%. The group composition of extracted bitumoids remained consistent in both cases. Under ultrasonic influence, the extractability of aromatic compounds doubled. Moreover, an increase in the proportion of saponified components was observed in resins [97].

4. Ultrasonic treatment of oil shale

Oil shales are composed of mineral and organic components, with the mineral part predominating, primarily comprising clay and calcareous minerals. The organic component, known as kerogen, consists of petrolens, humic substances, and bitumen. Oil shale serves as both a fuel source and a valuable technological raw material, utilized for extracting shale gas and shale oil. Processing oil shale yields various products such as oils, resins, and gasoline.

Ultrasound technology facilitates shale gas extraction from shale deposits. Experimental testing of shale samples revealed that ultrasound reduces adsorption and enhances desorption of shale gas. Researchers attribute this effect to supersonic waves intensifying gas molecule vibrations, thereby disrupting adsorption equilibrium. Increased ultrasound power augments permeability by inducing microcrack formation in shale [98].

For oil recovery from shale, a combination of organic solvents and ultrasound treatment at a frequency of 20 kHz and intensity ranging from 10 to 33.33 W was employed. Extraction efficiency reached 90% when tetrahydrofuran was utilized as the extractant alongside ultrasound intensity of 33 W [99].

Ultrasonic extraction of kerogen obtained through acid treatment of oil shale involves using an organic solvent, with the most effective being a 60:40 (wt%) mixture of CHCl_3 and CS_2 . The mass ratio

of demineralized oil shale to solvent is maintained at 1:20. Ultrasonic extraction can yield up to 15.6% of oil based on the demineralized oil shale. Optimal operating parameters include an ultrasonic frequency of 60 kHz, intensity of 200 W, temperature of 313 K, and extraction duration of 30 minutes. The extracted compounds predominantly comprise low molecular weight alicyclic hydrocarbons, constituting 68.3% of the total compound content [100].

Experimental assessments involving static and dynamic measurements of shale compaction at seismic and ultrasonic frequencies revealed varying sensitivity of shales to stress at these frequencies. Authors attribute this to concurrent changes in dispersion under applied stress. Moreover, it was observed that at ultrasonic frequencies, wet samples exhibit higher voltage sensitivity. Increased sensitivity of elastic properties to stress was noted parallel to the plane of occurrence [101].

Numerical modeling was conducted to analyze the responses of different shale occurrence structures to ultrasonic waves [102]. Wave field imagery indicated that higher occurrence density corresponded to lower ultrasound speeds. Setting occurrence angles from 0° to 90° at constant layering thickness and density values in the model revealed a decrease in wave velocity in a power function with increasing occurrence angle, while the attenuation coefficient exhibited a linear increase.

During mechanical tests, ultrasound velocity measurements revealed a substantial increase in ultrasonic attenuation both before and during fracture in brittle shale, with a comparatively smaller increase in plastic shale. Plastic shale, being softer and containing less cement, experiences less damage [103].

Triaxial compression tests conducted on shale samples with a horizontal bedding structure at various limiting pressures demonstrated that the applied limiting pressure influences strength, elastic parameters, P- and S-wave velocities, and fracture characteristics. Increasing pressure correlates with an increase in P-wave velocity, while the velocity of the S-wave initially rises and then declines due to crack damage. Compression results in the gradual consolidation of relatively soft pores, microcracks, and minerals, leading to the formation of a complex crack network [104].

Ultrasound examinations revealed that the acoustic velocity of shales increases with rising limiting pressure and decreases with increasing temperature and angle of occurrence [105].

Researchers [106] confirmed that as the angle of occurrence increases from 0° to 90°, the direction of ultrasonic wave propagation gradually shifts from parallel to the vertical direction of the layer. This change necessitates traversing more layers, resulting in a slowdown in wave propagation speed.

Nanocomposites incorporating single-walled carbon nanotubes (SWCNTs) for mechanical strength and hydrophobicity, along with polyvinylpyrrolidone (PVP) as a binder and filler, were employed to mitigate shale swelling and fluid loss from drilling mud. Ultrasonic treatment was utilized to achieve a uniform distribution of SWCNTs within a PVP matrix. The modified drilling mud containing the 5-SWCNTs/PVP composite exhibited the highest dispersion recovery (89.5%) and swelling rate (21.6%), along with a 23% reduction in fluid loss. The synthesized nanocomposite forms a protective layer on the shale surface, preventing water ingress and ensuring structural stability of the drilling mud [107].

In recent times, there has been a growing interest in utilizing ultrasound technologies for the enrichment and processing of metal-bearing shales. For instance, in [108], researchers investigated the impact of ultrasound of varying power levels during the flotation process of carbonaceous copper-containing shales. Flotation was conducted in the presence of a foaming agent (MIBC) and a collector (KEX). Microflotation results indicated a 40% increase in mass extraction with an ultrasound power of 20 W. However, the authors suggest that ultrasound treatment induces the formation of free radicals H and OH, which subsequently leads to the oxidation of particle surfaces.

Ultrasound has also found widespread application in hydrometallurgical leaching processes aimed at extracting valuable metals from raw materials. Ultrasound enhances extraction rates during leaching, while concurrently reducing leaching time, reagent consumption, and energy usage. Mechanisms of ultrasound leaching are continuously refined, with improvements observed in leaching kinetics, enhanced mass transfer and diffusion of leaching substances, and stimulated oxidative transformations of metals from insoluble to soluble states [109].

Comparative studies on ultrasonic versus conventional vanadium leaching from burnt V-shaped shale demonstrated notable benefits of ultrasound utilization. Ultrasound-enhanced leaching led to an increase in vanadium extraction from 87.86% to 92.93% and a remarkable 87.5% reduction in leaching time (from 240 minutes to 30 minutes) [110].

The combination of ultrasound and CaF_2 resulted in a significantly improved extraction of vanadium from shale (66.28%), surpassing the extraction rates achieved by ultrasound (26.97%) and CaF_2 (60.35%) used separately. This synergistic effect of ultrasound and CaF_2 is attributed to the formation of a more abundant structure of pores and cracks, which facilitates diffusion. Additionally, there was a notable decrease in the activation energy (E_a) required for the process, reduced from 62.03 to 27.61 kJ/mol, whereas using CaF_2 alone only lowered E_a to 50.70 kJ/mol [111].

The impact of Al, Fe, P, Si, and Na on the characteristics of ultrasonic deposition of vanadium from model solutions was also investigated. Results revealed that the negative influence on the kinetics of vanadium deposition diminishes in the following order: $\text{Al} > \text{Fe} > \text{P} > \text{Na}$. Silicon exhibited no discernible effect on vanadium deposition within the studied concentration ranges [112].

5. Conclusion

Recently, there has been a surge in interest in hydrocarbon production utilizing ultrasound, driven by the intensified recovery process, low cost, and energy efficiency it offers. Ultrasonic technology presents several advantages over traditional thermal and chemical extraction methods. Its adoption increases the recovery coefficient while reducing the cost of raw material extraction, all without causing environmental pollution.

Literature predominantly showcases research results on oil, bitumen, coal, and oil shale recovery using ultrasonic technology in laboratory settings. Additionally, there are findings on ultrasound's efficacy in primary oil treatment, enriching low-grade coal, and processing metal-bearing shale. Combining ultrasonic waves with traditional technologies significantly enhances raw material recovery rates.

Frequency, output intensity, and exposure time to ultrasound are identified as critical factors influencing process efficiency. However, their optimal values are contingent upon various conditions, necessitating further study. It is believed that short-term, powerful pulses of ultrasound at medium frequency yield superior results. Nevertheless, exceeding critical intensity and exposure time thresholds can sometimes produce adverse effects.

Employing dual-frequency and tri-frequency ultrasound has demonstrated better outcomes compared to single-frequency ultrasound. Some scholars suggest using orthogonal multi-frequency waves, as well as jet cavitation.

While almost all laboratory experiments have yielded positive results, it's acknowledged that laboratory conditions cannot entirely replicate reservoir conditions. Hence, there's a need to augment field tests alongside continuous equipment enhancements. Further improvement of ultrasonic technology is required, reducing its cost.

Consensus on the mechanism of ultrasound's stimulation of layers remains elusive. Therefore, a comprehensive study incorporating all potential factors -reservoir pressure and temperature, ultrasound characteristics, among others - is imperative, necessitating digital and mathematical analyses.

In addition, field tests will help to identify all the advantages and disadvantages of ultrasonic technology, as well as all aspects of the impact of ultrasonic recovery of hydrocarbon raw on the environment.

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