Review

Supercritical Fluid Application in the Oil and Gas Industry: A Comprehensive Review

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Abstract: The unique properties of supercritical fluid technology have found wide application in various industry sectors. Supercritical fluids allow for the obtainment of new types of products with special characteristics, or development and design of technological processes that are cost-effective and friendly to the environment. One of the promising areas where supercritical fluids, especially carbon dioxide, can be used is the oil industry. In this regard, the present review article summarizes the results of theoretical and experimental studies of the use of supercritical fluids in the oil and gas industry for supercritical extraction in the course of oil refining, increasing oil recovery in the production of heavy oil, hydraulic fracturing, as well as processing and disposal of oil sludge and asphaltenes. At the end of the present review, the issue of the impact of supercritical fluid on the corrosion of oil and gas equipment is considered. It is found that supercritical fluid technologies are very promising for the oil industry, but supercritical fluids also have disadvantages, such as expansion or incompatibility with materials (for example, rubber).

Keywords: supercritical fluid; enhanced oil recovery; carbon dioxide; supercritical extraction; oil recovery; oil sludge; hydraulic fracturing; asphaltenes; equipment corrosion
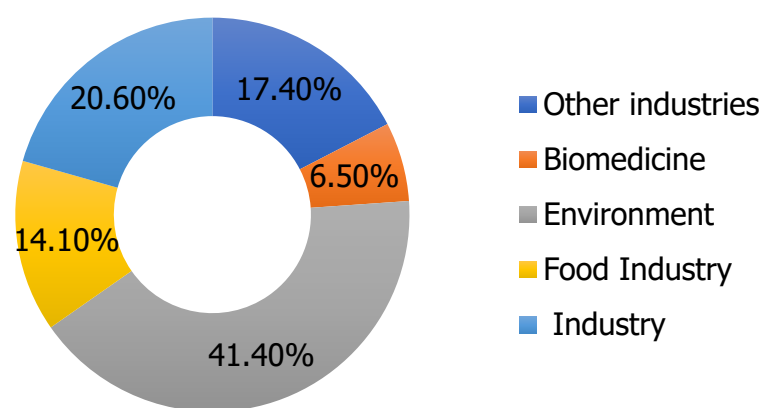
1. Introduction

There is an urgent need of mankind for liquid fuel forces to process and use heavy and super-heavy oil, produce special chemicals, and dispose of waste from the oil industry. Existing conventional refining technologies cannot ensure the economic processing of super heavy oil reserves without polluting the environment. Technologies based on the use of supercritical fluids could become one of the breakthrough technologies in oil production and refining. Supercritical fluid (SCF) is a state of matter in which the difference between the liquid and gas phases disappears [1–7]. Many physical properties of SCF (density, viscosity, and diffusion rate) are intermediate between the properties of a liquid and a gas.

Supercritical fluids as solvents are characterized by the following main advantages:

(1) possessing the properties of gases at high pressures (low viscosity, high diffusion coefficient) and liquids (high solubility),
(2) high mass transfer rate due to low viscosity and high diffusion coefficient; combining negligible interfacial tension with low viscosity and high diffusion coefficient, allowing supercritical fluids to penetrate porous media more easily, as compared with ordinary liquids,
(3) the high sensitivity of the solvent capacity of SCF to changes in pressure or temperature, and
(4) easy separation of SCF and dissolved substances during pressure relief.

The ability of the SCF to dissolve substances is widely used in the industry.

Due to its unique properties, SCF is used in the production and processing of polymers, in the food industry, pharmaceuticals, and medicine, for the production of new types of materials and biodiesel, for the processing of biomaterials, the purification of materials, and the regeneration of sorbents. According to estimates [8,9], in world practice, SCF has the broadest scope of application in solving environmental problems (Figure 1). This industry sector is characterized by the production of liquid motor fuels (mainly bioethanol and biodiesel), based on biological raw materials [9]. In comparison with the classical methods of producing motor fuels from biological raw materials, the use of SCF as a solvent allowed for a reduction in the reaction time, exclusion of the technological process of additional purification of the resulting product, as well as the use of heavy vegetable oils as feedstock, and an increase in the yield of methyl esters [9,10]. However, supercritical fluids also have disadvantages, such as expansion or incompatibility with materials (for example, rubber).

Figure 1. Diagram of the application of the SCF-based technologies in various industry sectors.

Supercritical fluids are used for supercritical extraction, drying, supercritical liquid chromatography, in the production of nano- and microparticles, pharmaceutical co-crystals, improvement of the geothermal system, refrigeration facilities, and in the synthesis of organic, inorganic, and organometallic substances.

Works are underway to create Generation IV nuclear reactors based on supercritical water cooling, and to use supercritical carbon dioxide for solar energy systems.

Even though the technologies based on the supercritical state of matter have found very broad application in various branches of human activity, they are just beginning to be introduced on an industrial scale in the oil and gas industry [11–14]. Figure 2 displays information retrieved from the SciVal database on the number of publications over the past 10 years devoted to the application of SCF-based technologies in the oil and gas industry for the topics and clusters: "Supercritical Carbon Dioxide; Fracturing Fluids; Thickeners". As demonstrated, the average number of publications on this topic in the world is about 30 articles.

Figure 2. Annual number of publications by SCF thematic cluster.

The tag cloud most commonly found in these publications, retrieved from the SciVal database, is presented in Figure 3. A review and analysis of the publications demonstrate that the possibility of using supercritical technologies to enhance individual technological processes of oil recovery is currently being actively studied. These studies also cover hydraulic fracturing [14–17], extraction of hard-to-recover oil reserves, high-viscosity oils [10,11,18], extraction of hydrocarbon compounds [19,20], and processing and neutralization of oil sludge [21].

Figure 3. Tag cloud demonstrating the use of SCF in the oil and gas industry problems.

Detailed reviews of using SCF in various industries can be found in [22–26]. However, currently, there are no detailed reviews on the use of SCF in the oil industry. Nevertheless, in our opinion, the use of SCF in the oil industry is the most promising. Therefore, the present article is devoted to the review of the application of SCF in various processes of the oil industry related to oil production, oil refining processes, and the disposal of oil waste.

2. Supercritical Extraction

At present, the supercritical fluid extraction (SFE) method is widely used for the production of coffee, hops, and essential and fatty oils from plant materials. According to the authors of [19,20], the supercritical fluid extraction method is the most promising for oil refining and the petrochemical industry. In the petrochemical industry, the supercritical fluid extraction method has a commercial appeal in catalytic hydrogenation, hydroformylation reaction, olefin metathesis, polymer synthesis, and oxidation reaction in the SCF medium.

The main component of catalytic hydrogenation is hydrogen, which is an explosive substance, especially in the environment of volatile organic compounds. Due to this circumstance, in this reaction, classical organic solvents are replaced as far as feasible with supercritical CO_2 [27–29]. Also, in the petrochemical industry, SCF-based technologies are used to reduce the amount of unwanted aromatic hydrocarbons in the hydrogenation of diesel fractions in the SCF medium, which allows for increasing the content of paraffins in these fractions [30,31]. Besides, these technologies are employed in the processes of liquid-phase catalytic hydrogenation of alkenes to produce chemical and petrochemical products [32–34].

It is proposed to use supercritical CO_2 as a reaction medium in catalytic hydroformylation, which allows for easy separation of the product and the catalyst by changing the density [35–38].

An environmentally friendly and economically feasible way to create complex carbon structures is the olefin metathesis reaction. In this reaction, supercritical CO_2 is used, especially in combination with heterogeneous catalysts based on Ru- and Mo-carbene complexes or salts of several transition metals [39].

Many scientific papers and reviews discuss the use of SCF in polymer synthesis [40–42]. The article [43] discusses the latest achievements in the field of polymer synthesis using SC-CO_2. SCF-based technologies can be applied in polymer chemistry for micronizing polymer particles and forming effective powder polymer coatings, disposing of plastic waste, and implementing continuous foaming technology using micro- and super-micro cells.

Since the solubility of oxygen in supercritical carbon dioxide is approximately ten times higher than that in the traditional organic solvents, much attention is also paid to the possibility of implementing oxidizing reactions of various substrates in the presence of oxygen and supercritical CO_2. The selective heterogeneous-catalytic oxidation of various organic substrates in SC-CO_2 is studied in [34]. Conducting oxidation reactions using CO_2 as a solvent is a promising strategy for creating more environmentally friendly chemical processes [44–46]. One example of oxidation in the SCF medium is the production of terephthalic acid [47,48]. Supercritical water can be successfully used in the treatment of wastewater containing organic pollutants, as well as in the separation of precious metals from spent catalysts [49].

Currently, a wide range of organic and inorganic compounds are used as SCF, such as a nitric oxide (N_2O), ammonia (NH_3), fluoromethane (CH_3F), difluoromethane (CH_2F_2), trifluoromethane (CHF_3), benzene (C_6H_6), and sulfur hexafluoride (SF_6). Table 1 outlines compounds widely used for research and the practical application of SCF. In terms of energy input and economic feasibility, carbon dioxide is the most attractive substance; it is non-toxic and non-combustible. For these reasons, more than 80% of all research in the field of supercritical fluid technologies and processes is based on the use of carbon dioxide [8].

**Table 1.** Critical state parameters of various substances.

Solvent	Critical Parameters		
	Temperature, °C	Pressure, MPa	Density, kg/m³
Carbon dioxide	31.3	7.29	468
Ammonia	123.3	11.13	235
Water	374.4	22.65	322
Methanol	240.5	7.89	278
Ethanol	243.4	6.3	276
Isopropanol	235.2	4.7	274
Ethan	32.4	4.83	203
Propane	96.8	4.2	217
n-Butane	152	3.75	225
n-Pentane	196.6	3.33	232
n-Hexane	234.2	2.96	234
Benzene	288.9	4.83	302
Chlorotrifluoromethane	28.8	3.9	579
Nitric oxide	36.5	7.14	450

To date, there are two process diagrams for the extraction of carbon dioxide: using high-pressure pumps, and employing compressors. The generalized method of supercritical extraction using carbon dioxide includes condensation, extraction, and separation processes (Figure 4).
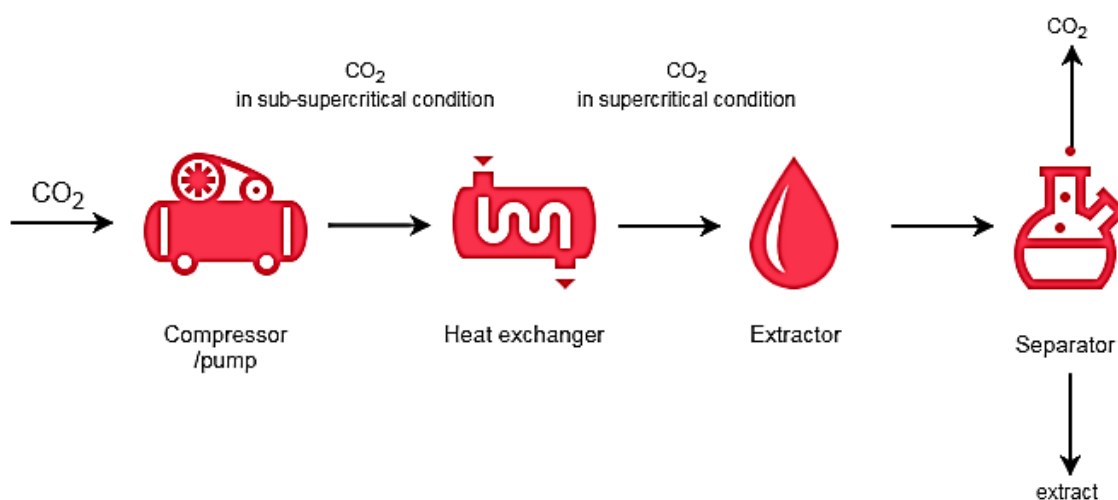
Figure 4. Generalized block diagram of a process plant for carbon dioxide extraction.

First, the liquid carbon dioxide CO_2 is cooled down to zero temperatures and fed to a pump or compressor. By strongly compressing above 31 MPa, the CO_2 is simultaneously heated and converted into a supercritical state. Due to its high fluidity, supercritical CO_2 penetrates the smallest pores of the products and dissolves the desired substances, extracting them from the raw materials. Then, by depressurizing and heating, the supercritical CO_2 is converted back to a gaseous state and completely evaporates, leaving only the pure extract. Due to its inherent non-reactivity, CO_2 does not react with the extract and does not change its properties. It should be noted that special plunger pumps have been developed for CO_2 extraction to a supercritical state [50].

In works [51,52], it is noted that, in terms of the energy input, using a compressor is more expensive than using a pump. In the case of the pump, condensation has a greater impact, while in the case of the compressor, the electricity required to operate the compressor is more expensive (Figure 5). The pump will be cheaper than the compressor in terms of power consumption. At the same time, compressor systems do not require a low-temperature cooling medium (refrigeration unit), include less equipment, are less complex and easy to use, and also take up less space than pumping systems [53]. Notably, energy costs for compressor and pumping systems are almost the same at low pressures. Electricity costs for the compressor system will only increase with increasing pressure.
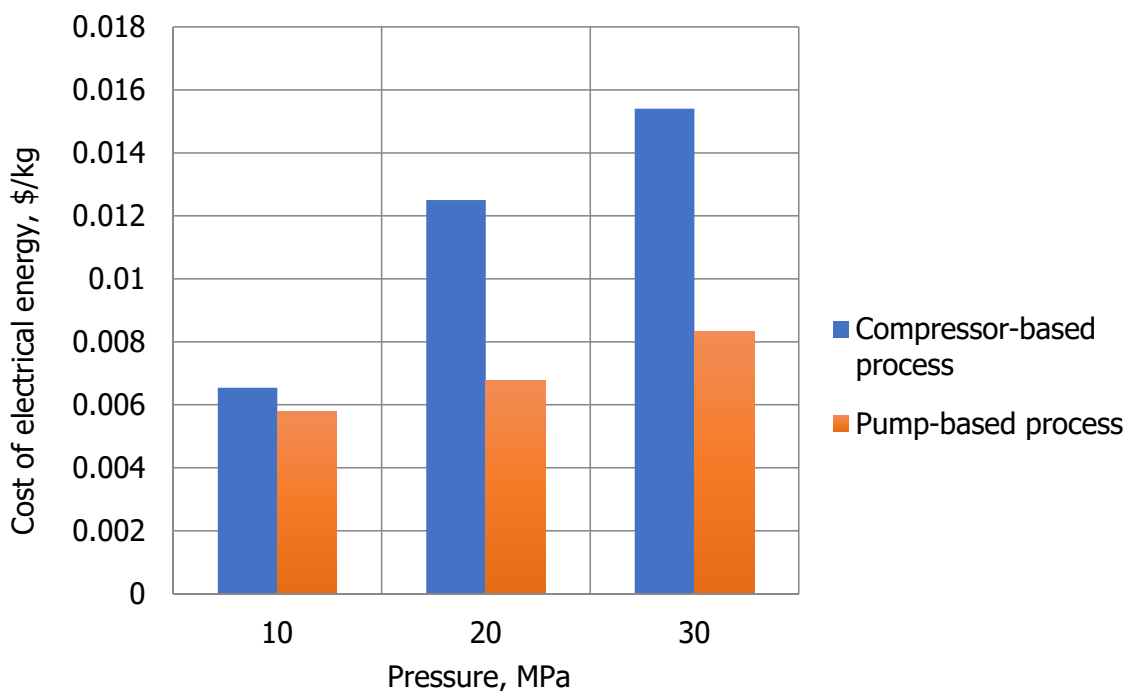
Figure 5. The cost of electrical energy input for the circulation of 1 kg of CO_2, depending on the pressure.

The most important factor when using supercritical fluids is predicting the solubility of substances depending on temperature, pressure, and density. To date, the solubility of a certain substance in a supercritical fluid is calculated using theoretical and empirical formulas, presented in the Appendix A (Table A1) [54–60].

It should be noted that the theoretical and experimental formulas describe the supercritical extraction processes with reliable accuracy. The supercritical extraction method can be used to obtain base oils, fuels, and other products [61].

The most important condition for supercritical extraction is the choice of solvent. The density of gases decreases as the temperature increases at constant pressure, due to which the solubility of gases decreases. The concentration of the dissolved substances in a dense gas increases as a result of the interaction of the dissolved substances and an increase in the vapor pressure of the dissolved substances, with an increase in temperature and pressure. Therefore, the effect of temperature on the solubility of a substance in a supercritical fluid changes with pressure. As a rule, substances with high critical temperatures have better solubility, for example, water, than gases with low critical temperatures [61].

The authors of [62] investigated the solubility of first-pressed coconut oil in SC-CO_2 at temperatures and pressures ranging from 39.85 °C to 79.85 °C and from 20.7 MPa to 34.5 MPa, respectively. The highest solubility (0.0408 g/g) was obtained at 79.85 °C and 34.5 MPa. In the study [63], the highest solubility of paprika extract in SC-CO_2 was achieved at a temperature of 60 °C and a pressure of 50 MPa.

3. Increasing Oil Recovery by Carbon Dioxide Pumped into the Reservoir

In the oil and gas industry, carbon dioxide is widely used to increase oil recovery of the reservoir. There are different approaches for the application of carbon dioxide, namely, injection into a reservoir in the form of carbonated water (water saturated with carbon dioxide), continuous injection of CO_2, cyclic injection of carbon dioxide into the injection wells, injection of a CO_2 rim followed by injection of water; oil displacement by alternating CO_2 and water injection; oil displacement by injection of combined chemicals and CO_2 rims; and alternating injection of carbon dioxide and oil production from the same wellbore (Huff-n-Puff process) [64].

When injecting carbon dioxide into the reservoir, different displacement modes can be implemented, depending on the thermobaric conditions and the oil composition; these involve fully miscible, partially miscible, and immiscible oil displacement. For reservoir conditions of high-viscosity oil deposits, as a rule, immiscible displacement is implemented.

One of the main parameters when using gas methods of EOR, which affect their efficiency, is the Minimum Miscibility Pressure (MMP) of the oil and gas injected into the reservoir. This is the pressure at which the complete miscibility of oil and gas (or the pressure at which the mechanism of mixing displacement begins to be realized). There are experimental methods [65–67] and correlation formulas [68,69], and scientific work is underway to develop a calculation algorithm, through the use of artificial intelligence [70], to calculate the MMP. The use of artificial intelligence to calculate the MMP has reduced the average absolute error of calculations to 6.6%, whereas when calculating with correlation formulas, calculation errors can be 15–20% [70].

The MMP for carbon dioxide pure with reservoir oil varies in the range from 15 to 25 MPa, depending on the temperature. Impurities present in carbon dioxide increase the MDS to 30–40 MPa or more; for example, injection together with water and/or associated gas. The authors of the work [71] found that for oil-CO_2 MMP is equal to 11.9 MPa and all other gases higher than 30 MPa. There may also be a lower MMP value, depending on the type of oil; for example, 8.3 MPa, as in the article [72].

In general, immiscible displacement is realized when the pressure in the reservoir is lower than the MMP, for reservoir conditions of high-viscosity or heavy crude oil deposits.

Moreover, the main mechanisms for increasing oil recovery include decreasing viscosity during the dissolution of carbon dioxide in reservoir oil, increasing oil volume (swelling), implementing the dissolved gas regime, extracting light and medium oil components and their transition to the light (carbon dioxide) phase, as well as decreasing surface tension at the in-place oil-CO_2 interface.

The solubility is one of the important parameters that occur between gas and oil when injecting immiscible gas in the oil reservoir. The solubility parameter demonstrates the ability of a substance to form homogeneous systems with other substances, as in the processes of oil extraction.

According to [11], as of 2014, 136 projects for carbon dioxide injection were implemented in the world, which were carried out by 30 operating companies. Of these, 88 were considered successful and 18 were considered advanced projects, while the remaining 20 were started recently. Ten projects failed to be implemented effectively. Most of them, namely, 128 out of 136, were implemented in the USA. The Weyburn-Midale CO_2 Monitoring Project is the world's first and largest initiative to measure, monitor, and verify CO_2 injection and was conducted alongside EOR operations between 2000 and 2011 [73]. The recent (youngest) carbon dioxide injection projects are those started in 2017 at the Petra Nova, which is located in Texas, USA, the first and only U.S. fossil-fueled power plant generating electricity and capturing CO_2 in large quantities [74]. The plant began capturing approximately 5000 tons of CO_2 per day from its 240-megawatt-equivalent slipstream using post combustion capture technology. The captured CO_2 is transported via an 82-mile pipeline to the West Ranch oil field, where it is injected for EOR. Core Energy's CO_2 injection projects at the Charlton 19 and Chester 16 fields in Michigan, USA, were launched in 2014. According to estimates [75], projects on immiscible oil displacement by

carbon dioxide can increase the oil recovery factor to 9.14%, with an increasing withdrawal rate of high-viscosity oil, to an average of 3.7 m^3/day per well.

The injection of supercritical carbon dioxide into the reservoir is the most promising technology studied in the laboratory. Experimental and theoretical studies into the use of SCF are currently being conducted for hydraulic fracturing and oil displacement from the reservoir. The ability of supercritical fluids to penetrate porous media makes them attractive for extracting hard-to-recover crude hydrocarbons from the subsurface. According to [12,76], wells with a pressure of more than 20 MPa (a depth of about 5000 feet (1524 m)) can be suitable for injecting supercritical CO_2. Wells with such parameters are unsuitable for steam injection because the thermal parameters in the well are above the critical point for water, and heat losses make steam injection disadvantageous. The researchers also note that at pressures below 20 MPa, the effect of temperature when producing SCF will only increase.

The authors of laboratory studies [64,77,78] note the effectiveness of applying supercritical fluid technology, using supercritical carbon dioxide as a displacing agent to extract residual hydrocarbon reserves from various solid porous media.

In the article [18], experimental studies were conducted to compare the displacement of heavy oil by supercritical water, steam, and hot water. The dimensionless time was estimated as the ratio of the total volume of injected water to the pore volume of the active area. The results of the laboratory experiment have demonstrated that reservoir flooding with supercritical water has improved oil recovery by 17%, and reduced heat inputs by 34% compared to classical steam flooding (Figure 6).
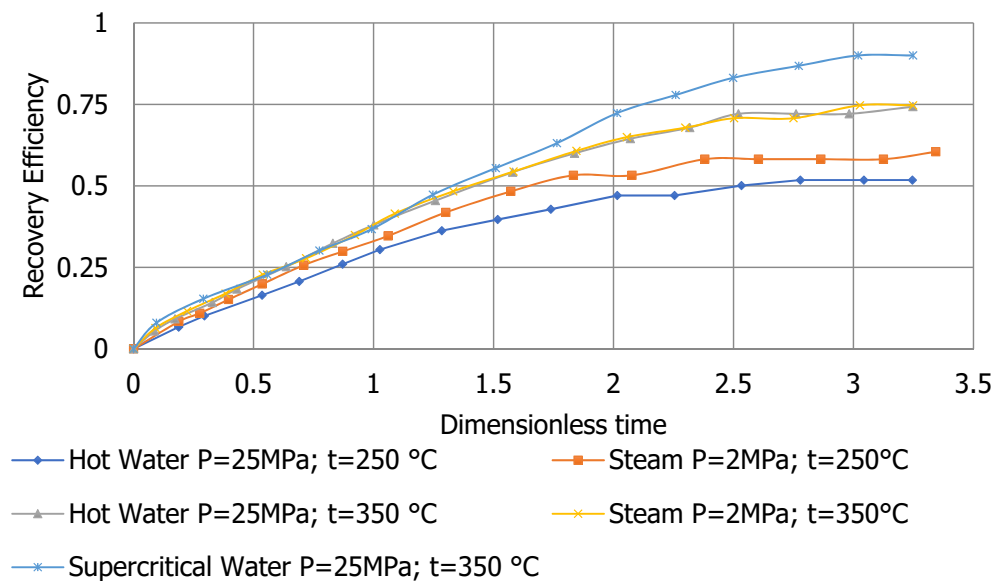
Figure 6. The results obtained in a laboratory experimental study [18].

Using a microfluidic experiment, the authors of [64] compared the efficiency of water, nitrogen, and supercritical carbon dioxide for oil displacement, simulating the Huff-n-Puff process. Injection of supercritical CO_2 has allowed recovery of 90% of oil from the network of connected fractures, and 60% of oil for the closed fractures network. Nitrogen has demonstrated a lower oil recovery rate of 40% from the connected fractures network, and 25% in the closed fractures network. Water injection had no effect on oil recovery from the simulated fractures.

The results of the experimental study [13] have demonstrated that supercritical CO_2 has a higher diffusion coefficient and interfacial mass transfer coefficient compared to those of gaseous carbon dioxide. For example, it took two hours for the oil to swell by 30% when in contact with supercritical CO_2, compared to ten hours when in contact with CO_2 in a

gaseous state. Exposure to supercritical CO_2 for nine hours resulted in a 58% reduction in oil viscosity, while the impact of gaseous CO_2 resulted in a 25% reduction.

The authors of [79] also note that at high pressure and temperature, the observed diffusion process is faster and more intense. The combined effects of reduced pressure, reduced heavy components contained in the oil, reduced viscosity, and high solubility of supercritical CO_2 cause the diffusion coefficients to increase over time and then reach a plateau. When decreasing the pressure from 18.2 to 12.11 MPa, the CO_2 diffusion coefficient increased from 4.38×10^{-9} to 6.21×10^{-9} for the gas phase, and from 6.16×10^{-10} to 9.21×10^{-10} m^2/s—for the liquid phase.

The authors of the work [78] conducted an experimental study of the displacement of oil by supercritical carbon dioxide from sandstone core formations with a Minimum Miscibility Pressure of 12.4 MPa. Carbon dioxide was injected at pressures of 17.2 MPa (miscible displacement) and 9.6 MPa (immiscible displacement) at a temperature of 69.85 °C K. It was determined that up to 93.5% of oil was recovered from a homogeneous sand core by supercritical carbon dioxide in a miscible displacement, and for an immiscible one, oil recovery was 76%. This result was explained by the fact that gravitational-viscous forces prevail in mixing conditions, while the balance between capillary and gravitational forces prevails in the immiscible displacement of CO_2.

There is movement of CO_2 in oil for immiscible displacement by gaseous CO_2 on the difference in their viscosity and density, and a piston displacement with a uniform displacement front is observed for supercritical CO_2, due to which the oil recovery coefficient increases [80].

In this [78] study, a series of experiments were conducted on the injection of supercritical CO_2 at various pressures (17.23, 19.31, 20.68, and 24.13 MPa) in order to extract oil from a core sample from the Bakken formation. Experimental studies demonstrate that when the injection pressure of supercritical CO_2 increases the oil recovery coefficient from the core increases from 8.8% to 33%. In addition, it was proven that the system of macropores and natural cracks makes a greater contribution to oil recovery. Mesopores and micropores are included in the process of supercritical displacement. The oil located in mesopores and micropores after reaching the miscible phase between CO_2 begin to contribute to the recovery potential.

In ref. [81] laboratory tests of immiscible displacement for supercritical carbon dioxide were carried out. Experimental results have shown that immiscible scCO$_2$ is able to mobilize oil in an environment with very low permeability (0.16 mD). However, at the same time, asphaltene deposition was observed, and the injection of scCO$_2$ into limestone cores led to calcite deposition. The authors note that in order to more effectively displace scCO$_2$, it is necessary to start the injection process earlier (i.e., at a higher oil saturation).

In the scientific article [82], the effect of cracks for mixing and immiscible displacement by scCO$_2$ is considered. The presence of cracks increases oil extraction recovery (ER) when injecting scCO$_2$, but it is established that a larger number of cracks do not necessarily lead to an increase in ER. Moreover, a higher injection pressure leads to a higher ER under immiscible conditions, but the increase in oil ER tends to decrease. After reaching the MMP a further increase in the injection pressure does not have a strong effect on the final result. In this experimental study, mesopores make the main contribution to the specific surface area (62.3~75.5%) in the core sample.

Table 2 summarizes the results of experimental studies on the injection of CO_2, N_2, and H_2O for EOR. A comparison of experimental data demonstrates that supercritical CO_2 has the best indicators of increasing oil recovery at optimal pressure and temperature parameters (for example, compared to supercritical water).

Table 2. Summary on the experimental study of injection CO_2, N_2, and H_2O for EOR.

Ref.	Type of Fluid	Condition of Fluid	Pressure, MPa	Temperature, °C	Type of Displacement	Type of Core	Results
Qiuyang Zhao et al., 2020 [18]	H_2O	SCF	25	400	Miscible	Sand	Improved oil recovery by 17% compared to steam
Phong Nguyen et al., 2018 [64]	CO_2	SCF	about 5 to 8	50	Miscible	Microfluidic chips, the connected fracture network	Oil recovery 90%
	CO_2	SCF	about 5 to 8	50	Miscible	Microfluidic chips, the dead-end fracture network	Oil recovery 60%
	N_2	Gas	about 5 to 8	50	Miscible	Microfluidic chips, the connected fracture network	Oil recovery 40%
	N_2	Gas	about 5 to 8	50	Miscible	Microfluidic chips, the dead-end fracture network	Oil recovery 25%
	H_2O	Liquid	about 5 to 8	50	Immiscible	Microfluidic chips, the connected fracture network	Not effective
	H_2O	Liquid	about 5 to 8	50	Immiscible	Microfluidic chips, the dead-end fracture network	Not effective
Duraid Al-Bayati et al., 2017 [77]	CO_2	SCF	17.2	69.85	Miscible	Sand	Oil recovery 93.5%
	CO_2	SCF	9.6	69.85	Immiscible		Oil recovery 76%
Sai Wang et al., 2019 [78]	CO_2	SCF	17.23	40	Immiscible	Core from the Bakken formation	Oil recovery ~ 8.8%
	CO_2	SCF	19.3	40	Miscible		Oil recovery ~12%
	CO_2	SCF	20.68	40	Miscible		Oil recovery ~12.3%
	CO_2	SCF	22.06	40	Miscible		Oil recovery ~33%
Abdulrazag Yusef Zekri; Reyadh A. Almehaideb; Shedid A. Shedid 2006 [80]	CO_2	SCF	11.03	52.78	Immiscible	0.16 mD permeability, carbonate rocks	Oil recovery ~45%
	CO_2	SCF	11.03	52.78	Immiscible	11.99 mD permeability, carbonate rocks	Oil recovery ~95%

Table 2. *Cont.*

Ref.	Type of Fluid	Condition of Fluid	Pressure, MPa	Temperature, °C	Type of Displacement	Type of Core	Results
F. Irawan, S. Irawan & M. Awang 2012 [82]	CO_2	Liquid	10.34	20	No information	Berea sandstone	Oil recovery 67.7%
	CO_2	Liquid	10.34	11.67			Oil recovery 69.1%
	CO_2	Liquid	10.34	5			Oil recovery 72.6%
Manoj Kumar Valluri et al., 2020 [83]	CO_2	Gas	<9.14	32.78	Immiscible	12.56 mD permeability, Copper Ridge Dolomite	Average oil recovery 16%
	CO_2	SCF	>9.14	32.78	Miscible	12.56 mD permeability, Copper Ridge Dolomite	Average oil recovery 26%
	H_2O	Liquid	9.14	32.78	-	12.56 mD permeability, Copper Ridge Dolomite	Average oil recovery 30%
	CO_2	SCF	<9.14	32.78	Immiscible	2,74 mD permeability, Clinton Sandstone	Average oil recovery 29%
	CO_2	SCF	>9.14	32.78	Miscibility	2.74 mD permeability, Clinton Sandstone	Average oil recovery 26%
	H_2O	Liquid	9.14	32.78	-	2.74 mD permeability, Clinton Sandstone	Average oil recovery 20%
Mehdi Fahandezhsaadi et al., 2019 [84]	N_2	Gas	6.89	70	Immiscible	Carbonate rocks	Oil recovery ~40%

The outcome is that when using supercritical carbon dioxide to increase EOR, the solubility and MMP are important parameters. The size of pores and cracks will also affect the result of oil extraction from the reservoir. Of course, the miscible displacement with supercritical carbon dioxide demonstrates the highest oil recovery coefficient (up to 95%). However, immiscible displacement with supercritical carbon dioxide can be effective for extracting high-viscosity or heavy crude oil due to its ability to dissolve substances, as well as for extracting oil from dense formations. Other reasons for studying immiscible displacement are a lower injection pressure compared to miscible displacement, which reduces the amount of substance used and the energy for its injection into the formation. These advantages are economically attractive compared to miscible displacement.

4. Using SCF for Processing and Disposal of Oil Sludge

The oil industry operation is associated with the formation of oil sludge, which is one of the toxic and environmentally hazardous wastes. Oil sludge is formed in the course of drilling wells, oil production, and refining. Solid wastes from the oil and gas industry include bottom sediments from tanks, drilling sludge, drilling mud, oil sludge from spills, oil sludge generated during oil refining, and oil sludge from pipelines.

Oil sludge mainly consists of water, oil, and solid particles. It may also contain toxic substances in the form of cycloalkanes, benzene series, polycyclic aromatic hydrocarbons, etc. [21]. However, for oil-containing sludge, the valuable component is oil, which can be used as secondary raw material.

For oil sludge treatment and disposal, a variety of methods are developed, such as burning, gravitational sedimentation, separation in the centrifugal field, oxidation and biodegradation, solvent extraction, mixing with additives and adsorbents to produce marketable products, biological decomposition by microorganisms, etc. [21,21]. Using SCF-based technologies is another important and promising area of recycling and sludge disposal.

Oil sludge treatment can be carried out by supercritical oxidation and supercritical extraction. Supercritical oxidation is usually performed using supercritical water when the pressure and temperature parameters are above its critical point (Tc = 374 °C, Pc = 22.1)

Supercritical Water Oxidation (SCWO), which was first proposed by Modell at the Massachusetts Institute of Technology in the mid-1980s, is an efficient and advanced oxidation technology for the destruction of organic substances by utilizing the unique properties of supercritical water under typical operating conditions of 450–600 °C, 24–28 MPa [85]. Supercritical water has physical properties that differ from those of liquid water, including high diffusion capacity and low viscosity, density, and dielectric permittivity [86].

In the article [87], supercritical oxidation of water (SCWO) for oil sludge processing was comprehensively investigated in a batch reactor under conditions of various oxygen coefficients (OC, 1.5–3.5), temperatures (T, 400–500 °C), and reaction time (t, 0.5–10 min). The removal efficiency of total organic carbon can reach 89.2% within 10 min at a temperature of 500 °C. Analysis of the reaction pathways suggests that both homogeneous and heterogeneous reactions take place in the reactor. The homogeneous reaction is a typical SCWO reaction that is controlled by a free radical mechanism, and the heterogeneous reaction is dominated by mass transfer.

The authors of [88] conducted laboratory experiments to study the effect of supercritical oxidation on oil sludge treatment. It was found that, using supercritical oxidation, it is possible to neutralize 92% of oil sludge in 10 min.

The authors of the work [89] proposed continuous oxidation of drilling mud with supercritical water, demonstrating that, due to the improvement of the supercritical oxidation technology, the efficiency of organic carbon removal can reach 98.44%.

Another research is mainly conducted to study the use of carbon dioxide for supercritical extraction of oil sludge. The article provides a description [90] of a method for extracting oil from oil sludge by supercritical CO_2 extraction. At an operating temperature

of 35 °C, the pressure is 20 MPa, and the mass ratio of the liquid to the oil-based drilling mud is 3; the extraction rate of crude oil after 60 min of extraction reached 98.6%.

The authors of the work [91] found that the extraction pressure, extraction temperature, and separation temperature affect the coefficient of oil recovery from oil sludge using supercritical carbon dioxide extraction. The authors of the study found that for their oil sludge sample, the optimal values are extraction pressure 21 MPa, extraction temperature 55 °C, and separation temperature 64 °C. The coefficient of oil recovery from oil sludge was 99.65%.

Concerning the supercritical extraction of oil sludge, studies are mainly carried out using carbon dioxide. However, as the authors of [92] note, the propane-butane mixture also has a high solvent capacity for petroleum products. As an extractant, the authors used a propane-butane mixture containing 75 wt.% of propane and 25 wt.% of butane. The composition of the used propane-butane mixture had the following critical parameters: T_c = 112.85 °C, P_c = 4.31 MPa. Depending on the pressure and temperature, the yield of petroleum products varied from 40 to 70 wt.%. It is noted that, within the pressure range of 6.5–12 MPa, the yield of oil products was decreasing with increasing temperature, but at p > 12.5 MPa and the increase in temperature, the yield of oil products, on the contrary, increased. Thus, the application of supercritical technologies for oil sludge processing is extremely promising.

In ref. [93], the extis currently underway. Thue by propane-butane mixture was studied. The original oil sludge contained 30 wt.% water, 5.9 wt.% of mechanical impurities, and 5.7 wt.% of asphaltenes. Extraction with a propane-butane mixture in a ratio of 3:1 (wt.%) at a temperature of 85–120 °C and a pressure of 10 and 15 MPa allowed to for obtainment of petroleum products with significantly low viscosity and low sulfur and water content. The results indicate that the mass content of sulfur after supercritical extraction decreased by half, the content of asphaltenes decreased by five times, and the kinematic viscosity decreases by 10 times, compared to the original oil sludge.

As a result, we can say that the effective destruction of oil during supercritical oxidation and supercritical extraction depends on the physical properties of the oil sludge, extraction time, pressure, and temperature. We believe that effective mathematical models are required for future research to predict the process of oil sludge extraction. Scientific work in this direction is underway. For example, the authors of [94,95] suggest using a relaxation calculation method to simulate the periodic extraction process. This method is based on equations that are written for non-stationary conditions. It should be noted that supercritical oxidation requires less oil sludge extraction time but requires more pressure and temperature compared to supercritical carbon dioxide, which will affect the cost of equipment.

5. Using SCF for Hydraulic Fracturing

To date, hydraulic fracturing using water-based gels is the most common method. However, one of the promising areas is considered to be fracturing using supercritical carbon dioxide (abbreviated as SC-CO_2). An important advantage of SC-CO_2, compared to traditional methods, is reducing environmental pollution by reducing CO_2 emissions, as well as reducing or excluding water during hydraulic fracturing, reducing chemical additives, and eliminating the problem of clay swelling.

The composition of the fracturing fluid at SC-CO_2 includes pure carbon dioxide or a binary liquid consisting of a mixture of liquid CO_2 and N_2 to reduce costs.

In recent years, experimental studies have been conducted to investigate hydraulic fracturing using liquids, such as viscous oil, water, CO_2, N_2, and supercritical CO_2 for granitic, sand, and shale rocks [96,97]. Experimental installations for SC-CO_2 are well described in the review [98].

In experimental works [99,100], the authors have demonstrated that hydraulic fracturing using supercritical CO_2 can create three-dimensional sinuous fractures with a large number of secondary branches. A model of thermal effects during hydraulic fracturing

using supercritical carbon dioxide was developed in [14]. Simulations demonstrate that, in terms of thermal stress, shale is a better rock for hydraulic fracturing with supercritical CO_2 than sandstone. The authors revealed a linear relationship between the hydraulic fracturing pressure and the initial temperature of supercritical CO_2. The hydraulic fracturing pressure increases significantly with an increase in the temperature of supercritical CO_2. Therefore, CO_2 with high initial pressure and a low initial temperature has the greatest margin for increasing the hydraulic fracturing pressure.

To study the fracturing characteristics, experimental work [15] was carried out on the sandstone formation fracturing using water, N_2, liquid CO_2, and supercritical CO_2. Cracks were analyzed using computer tomography, which allowed quantifying the micromorphology of fractures, including the structure of the fracture network, fractal size, aperture, area ratio, fracture volume, etc.

Experimental studies have found that water and N_2 could only form a simple fracture pattern, while supercritical CO_2 formed complex and sinuous fractures. According to the developed methodology, the authors concluded that supercritical CO_2 had up to 4.4 times greater fracture capacity, and could create fractures up to 2.6 times more complex and 23.4% more tortuous than water-based hydraulic fracturing (Figure 7).
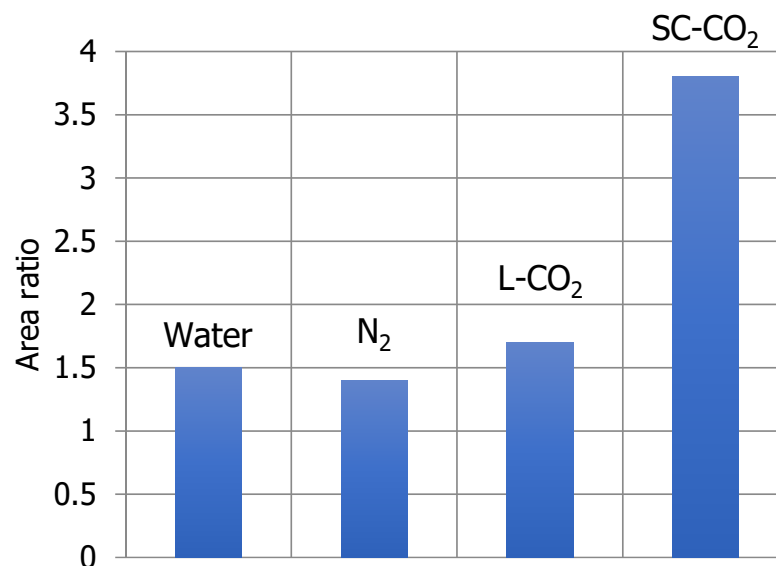
Figure 7. The area ratio of fractures formed by different liquids [17].

Experimental studies on the effect of the viscosity of supercritical CO_2 on the formation of fractures in granitic rocks were conducted in [17]. The research results demonstrated that CO_2 easily migrated and increased the occurrence of fractures in existing channels.

The authors of the article [99] conducted experimental studies of hydraulic fracturing of a shale formation with supercritical carbon dioxide, depending on the drilling depth of a well. In addition, the morphology of cracks was analyzed using computed tomography. As a result, it was found that the rupture pressure decreases with the depth of drilling. A comparison of the crack morphology before and after the fracturing experiments demonstrated that supercritical CO_2 can lead to the appearance of a "winged" crack. The complex crack may form when the drilling depth increases.

It is believed that the low viscosity of liquid CO_2 [100,101] is the main problem when transporting and pumping the propping agent used in hydraulic fracturing. However, that work to eliminate this drawback of SC-CO_2 is currently underway. Thus, ref. [16] reports on the creation of a novel multi-surface fluid system, namely, the solid-free viscoelastic surfactant (VES), designed specifically for transporting a propping agent with supercritical CO_2. The results of experimental tests demonstrate that the new system is compatible

with CO_2 and has all the characteristics of VES systems. The preserved conductivity of the propping agent package was more than 95%.

In ref. [102], due to an independently developed physical modeling system consisting of acoustic emission (AE) and computed tomography (CT), the pressure of the onset of fracture and the mechanism of crack propagation in shale during hydraulic fracturing of SC-CO_2 were measured. The results demonstrated that for shale without pre-existing cracks, it is possible to theoretically calculate the pressure of the beginning of fracture of cracks. Deviations between experimental and theoretical values were in the range of 11%.

The authors of [103] have found that SC-CO_2 has a higher ability to erode rocks and requires a much lower threshold pressure than hydraulic fracturing. The pressure of the beginning of the SC-CO_2 rupture was about 50% lower than during hydraulic fracturing, and the volume of rock destroyed by SC-CO_2 is several times larger.

It is noted in [104], hydraulic fracturing of SC-CO_2 is more labor-intensive, taking about 20 times longer than hydraulic fracturing using water, due to the fact that the injection rate of SC-CO_2 pressure increases gradually as a result of CO_2 compressibility.

As a result, we can say that SC-CO_2 for fracturing has demonstrated great potential for increasing the production of unconventional reservoirs, such as shale gas, dense gas, and coalbed methane. SC-CO_2 fracturing can create very complex networks of fractures with a lower fracture pressure than water, which is economically advantageous to a certain extent.

6. Using SCF for Cleaning Heavy Oil Deposits

The formation of heavy oil deposits (HOD) in oil production is a serious problem, since it reduces the system performance and the efficiency of the oil equipment. Mechanical, thermal, physical, and chemical methods have been developed to remove and combat HOD. However, at the same time, HOD in its composition has many valuable components that can be used after processing as additives to fuel oil in the construction industry, in the preparation of lubricating compositions [101].

The HOD is a mixture of asphaltenes, resins, and paraffins. The asphalt-resin substances (ARS) that are part of the HOD composition are heterocyclic compounds of a complex hybrid structure, which include nitrogen, sulfur, oxygen, and metals (Fe, Mg, V, Ni, Ca, Ti, Mo, Cu, Cr, etc.) [105–107].

The supercritical extraction process is considered to be a promising technology for oil deasphaltizing. Experimental studies on the extraction of asphaltene using carbon dioxide as a solvent were conducted in [108]. The authors have demonstrated that 12% of asphaltenes were extracted with supercritical carbon dioxide, and the resulting extract contained alkanes, and aromatic and polar compounds. The temperature variations within the range of 40 to 50 °C did not significantly affect the extraction efficiency, while the pressure change from 13 to 30 MPa and the use of co-solvents (toluene and dichloromethane) allowed for extraction of heavier n-alkanes and aromatic compounds, as well as more branched and cyclic alkanes.

The authors of [109] conducted a study of the deposition of heavy fractions and the separation of asphaltenes from an oil sample using SC-CO_2. The experiments were carried out at a temperature of 50 to 140 °C and a pressure of 10 to 30 MPa. An increase in temperature at a pressure above 20 MPa, as well as the addition of small amounts of toluene to the initial oil sample, provided greater selectivity of separation, and a greater concentration of asphaltenes in the precipitated fractions and drier solids.

In an experimental study [110], the composition of waxy crude oil after SC-CO_2 treatment was studied, and changes in rheological properties such as pour point, viscosity, yield strength, and wax deposition characteristics caused by changes in composition, were analyzed. The results demonstrated an increase in the content of heavy components, such as asphaltenes, resins, and hydrocarbons with a high carbon number, as a result of the extraction of light components by supercritical carbon dioxide. This led to an increase in the pour point, as well as an increase in apparent viscosity and yield strength. The stability of the emulsion of crude oil treated with SC-CO_2 also increased, and the effectiveness of

its demulsification after dosing with the same demulsifier decreased. According to the authors of the work, all these changes may adversely affect the safe transportation of the extracted liquid in oil fields where SC-CO$_2$ is injected.

The authors of [111] studied the dissolution of asphaltenes in supercritical water. As a result, it was found that petroleum asphaltenes under the impact of supercritical water were easily subjected to hydrothermal destruction with the formation of liquid (up to 30%), gaseous (up to 4.3%), and solid products (up to 64.9%).

In the experiment [112], it was demonstrated that the inclusion of hematite nanoparticles with supercritical water and formic acid demonstrates a higher degree of formation of the light fraction of the product and low coke formation in heavy oil, which indicates the dissolution of asphaltenes.

Understanding the flow behavior and mixing of heavy oil in supercritical water is necessary to increase the efficiency of this process. Thus, the authors of [113] conducted an experiment to visualize the behavior of heavy oil in supercritical water using neutron radiography. Heavy oil and supercritical water were supplied by counterflow in a 1/2-inch diameter tubular reactor filled with 3 mm diameter Al$_2$O$_3$ particles; pressure and temperature were set at 25 MPa and 400 °C. The authors found that the behavior of heavy oil in supercritical water depended on the flow rate of oil and water. This study demonstrates that neutron radiography is an acceptable method for imaging and investigating the behavior of heavy oil in supercritical water.

The article [114] presents the results of processing heavy crude oil in the presence of activated carbon and supercritical aqueous liquid. Experimental studies have demonstrated that, as a result, it is possible to significantly reduce the content of sulfurous and resinous-asphaltene substances and increase the number of light fuel fractions. The paper reveals the distinctive features of changes in the composition and properties of liquid products of the conversion of crude oil into hydrothermal fluid at 420 °C, as well as in the presence of activated carbon at a process temperature of 375 °C. It is established that light fractions are formed in transformed heavy crude oil in hydrothermal fluid in the presence of activated carbon, due to the destruction of resins and asphaltene components.

The authors of [115] investigated the structural and group characteristics of resins and asphaltenes isolated from high-sulfur natural asphaltite and liquid products of its transformation in a stream of supercritical water at 400 °C and 30 MPa, with and without zinc or aluminum admixture. It was found that, as a result of SCW treatment, the molecular weight of resins and asphaltenes is reduced by two to five times compared to the components of the initial asphaltite. The authors attribute this decrease primarily to a decrease in the number of naphthenic and aromatic rings, accompanied by a sharp increase in the proportion of the latter. In the presence of metals, the differences between the components of the initial asphaltite were more pronounced.

In the survey paper [116], it is reported about the formation of HOD in oil reservoirs, which leads to a decrease in the permeability and oil recovery of the rock. However, this mechanism of HOD formation in oil reservoirs is studied insufficiently. The authors of the work believe that the reaction between the reservoir oil, salt solutions, and the formation rock during the injection of carbon dioxide can lead to the dissolution of the rocks (i.e., an increase in the permeability and porosity of the formation), but, at the same time, to the precipitation of asphaltenes, which lead to the opposite effect. In this regard, the authors conducted an experimental study on the effect of supercritical carbon dioxide on carbonate cores saturated with oil and salt solutions. The results of the work have demonstrated that the amount of damage to the core depends on the rock structure, salt solution, and core permeability, while the damage is caused by the interaction of CO$_2$ with the rock. Accordingly, it is recommended to conduct individual studies on the impact of supercritical carbon dioxide injection for each oil field.

To study the asphaltene formation mechanism, the authors of [117] performed molecular-dynamic simulations of the reservoir oil-supercritical carbon dioxide system to explain the mechanism of asphaltene formation in the rock. Molecular dynamics simulations

have found that supercritical carbon dioxide dissolves resinous, aromatic, and saturated substances, but leads to the formation of asphaltene nanoaggregates. In the beginning, the asphaltenes are separated from each other due to the extraction impact of supercritical CO_2. Then, the asphaltenes bind to each other to form nanoaggregates that can persist in supercritical CO_2. In this regard, the authors of the work recommend adding inhibiting agents at the first stage of aggregation when pumping supercritical carbon dioxide into the formation.

In conclusion, we can say that the injection of supercritical carbon dioxide into the oil reservoir can lead to the formation and precipitation of asphaltenants as a result of the volatilization of lighter fractions. However, at the same time, asphaltenes are not waste products of the oil industry. Due to the use of supercritical water extraction, valuable components of asphaltenes can be extracted.

7. The Effect of SCF on the Equipment Corrosion

To apply SCF technology in the oil and gas industry, it is necessary to consider the issue of its corrosion impact on the equipment.

The authors of [118] considered the problem of corrosion monitoring caused by carbon dioxide in the oil and gas industry, since the supercritical state of CO_2 is widely found in the processes of oil transportation, injection, and production.

Carbon dioxide can be transported in various aggregate states, but during pumping through the pipeline, a single-phase flow is preferred for safety reasons. The supercritical phase or the gas phase is usually chosen because less energy is required to pump carbon dioxide over long distances. As a rule, CO_2 delivery pressure through the pipeline varies within the range from 5 to 20 MPa. Besides using corrosion-resistant materials and corrosion inhibitors, the authors suggest limiting the water concentration, reducing the flow velocity, and shortening the contact time of CO_2 with transport and injection systems, which can mitigate the corrosion of carbon steels. For an oil-producing system, it is recommended to increase the water entrainment velocity and flow turbulence, and mitigate the corrosion environment to increase the enhancement of the water entrainment and flow turbulence, and mitigate the corrosion environment, if carbon dioxide is injected with alternating water.

Pure and dry supercritical CO_2 does not cause corrosion [119]. However, studies [118,120–123] demonstrate that supercritical carbon dioxide saturated with water corrodes carbon steels. It is noted in [124] that the maximum corrosion point is observed at a point just below the critical point. The authors of [125] also observed significant corrosion in the subcritical region of CO_2. Practically, this means that parts and pipelines that are used for preheating or cooling will be more intensively confirmed by corrosion. Obtaining relatively pure carbon dioxide is an expensive technology, especially when it comes to receiving it from flue gases [126]. From this perspective, carbon dioxide in addition to H_2O during transportation and injection may include various impurities, such as SO_x, NO_x, HCl, CO, O_2, Ar, H_2, H_2S, CH_4, and N_2.

It is reported [127] that SO_2, H_2O, and O_2 can form sulfurous and sulfuric acid (H_2SO_3 and H_2SO_4). Experimental studies have found that $FeSO_3$ and/or $FeSO_4$, which are present on steel surfaces when exposed to a dense phase of CO_2 at low water content (less than 500 ppmv), are corroded at a rate of 0.005–0.02 mm/y at 100–344 ppmv SO_2. The corrosion rate increased to 0.017 mm/y when NO_2 was added to the system.

Experimental studies in [119] indicate that the impurities H_2O, O_2, and NO are the most influential on the corrosion of carbon steel in the CO_2 stream. The authors recommend reducing the water concentration in carbon dioxide below 600 ppmv.

In ref. [128], alloys of ferritic-martensitic steel (Gr. 91), austenitic stainless steel (316L), Ni-Fe-based superalloy (HR 120), and Ni-based superalloy (IN625) were studied. The results for the samples demonstrated a parabolic increase in mass over time when exposed to air and CO_2, and supercritical CO_2 was more aggressive. In austenitic alloys exposed to supercritical CO_2, recrystallized zones formed under the oxide.

The authors of [129] studied the corrosion properties of T91 and 316 alloys under SC-CO$_2$ conditions at temperatures of 500 °C, and 600 °C, and a pressure of 20 MPa. T91 corrosion products mainly consisted of external columnar Fe3O4 and internal Fe-Cr spinel, which had a porous structure and had no protective effect. Thin and dense Cr$_2$O$_3$ was formed on the surface of 316 after corrosion at a temperature of 500 °C, while a large number of iron oxide nodules formed on the surface of the chromium-rich scale at 600 °C.

In an experimental study [130], CrMoV steel was exposed to carbon dioxide at temperatures of 500, 550, and 600 °C for 120 h and pressures of 0.1 and 10 MPa. No significant change in the carbon deposition content at 0.1 MPa by carbon dioxide was observed, in contrast to the high carbon content at 550 °C and 10 MPa for supercritical carbon dioxide. The authors believe that the reason for this difference is the formation of internal M$_3$C carbides rich in iron and the oversaturation of steel grains with dissolved carbon at 550 °C, which is not observed at temperatures of 500 and 600 °C.

The corrosion rate can be affected by temperature and pressure. The authors of a number of articles note that the corrosion rate of carbon steel will grow in the CO$_2$ stream with an increase in temperature and pressure [131–133]. It was demonstrated in [119] that in CO$_2$-saturated NaCl solutions, the corrosion rate of carbon steel increases with increasing temperature at the initial stage. However, the corrosion rate tends to decrease over time at a higher temperature (i.e., 60 and 80 °C). This is due to the formation of protective corrosion flakes of FeCO$_3$. Further, with an increase in temperature (more than 60 °C), FeCO$_3$ becomes the dominant corrosion product, with the possible presence of Fe$_2$CO$_3$OH.

The authors of [134] analyzed the internal corrosion of pipelines under the influence of supercritical CO$_2$. They note that it is necessary to pay attention to the point corrosion of metal and stress corrosion in supercritical environments. It is also noted that, until now, the mechanism of formation of FeCO$_3$ by supercritical CO$_2$ has not been fully studied, and further research is required to use its protective properties.

The formation of pitting corrosion of the pipeline by supercritical carbon dioxide with impurities of SO$_2$, NO$_2$, and O$_2$ was considered in [135]. The results demonstrated that, in a water-saturated supercritical environment of carbon dioxide with impurities of SO$_2$, NO$_2$, and O$_2$, the average maximum depth of ulcers stabilized after three days. The influence of the flow on the propagation of pits was insignificant, which indicates a weak influence of the flow on the formation of pitting corrosion.

As a result of the studies, summary recommendations on the maximum concentrations of impurities for the transportation and injection of CO$_2$ have been developed [120–123] (Table 3).

It should be noted that to date there are no comprehensive studies of the effect of these concentrations on the MMP of carbon dioxide and oil. We consider that generalized experimental studies, according to Table 4, would contribute to the creation of a standard for the transportation and injection of carbon dioxide in order to EOR.

The authors of [118,120] summarized the results of practical experience on the injection of carbon dioxide and provided recommendations for mitigating the corrosion of equipment (Table 4). Pump and compressor pipes that are exposed to carbon dioxide saturated with water must be made of 316 SS stainless steel and covered with plastic, or have epoxy liners made of fiberglass or plastic [76,123,136,137]. Direct experience has demonstrated that if corrosion mitigation measures are followed, carbon steel can be safely and effectively applied to casing and production tubing. According to the authors' estimates, the average life of wells operating with carbon dioxide injection will be 20–25 years or more, which is comparable to other oil and gas wells.

Table 3. Recommendations on the maximum concentrations of impurities for the transportation and injection of CO_2.

Component	Concentration	Limitation
H_2O	500 ppm	Technical: below solubility limit of H_2O in CO_2, no significant cross effect of H_2O and H_2S, cross effect of H_2O and CH_4 is significant but within limit for water solubility
H_2S	200 ppm	Health and Safety consideration
CO	200 ppm	Health and Safety consideration
O_2	Aquifer < 4 vol%. EOR 100–1000 ppm	Technical: range for EOR, because of lack of practical experiments on the effects of O_2 underground
CH_4	Aquifer < 4 vol%. EOR <2 vol%	Health and Safety consideration
N_2	<4 vol% (all noncondensable gases)	As proposed in ENCAP project
Ar	<4 vol% (all noncondensable gases)	As proposed in ENCAP project
H_2	<4 vol% (all noncondensable gases)	Further reduction of H_2 is recommended because of its energy content
SO_x	100 ppm	Health and Safety consideration
NO_x	100 ppm	Health and Safety consideration
CO_2	>95.5%	Balance with other compounds in CO_2

Table 4. Recommended materials of equipment, constructions for transportation, and injection of CO_2 [120].

Equipment, Constructions	Materials
Measuring sections of the pipeline	316 SS, fiberglass
Christmas tree (Trim)	316 SS, nickel, monel-metal
Valve packing and seals	Teflon, nylon
Wellhead (Trim)	316 SS, nickel, monel-metal
Tubing Hanger	316 SS, Incoloy
Tubing String	Glass Reinforced Epoxy (GRE), Internal Plastic Coating (IPC), Corrosion-Resistant Alloy (CRA)
Tubing Joint Seals	Seal ring (GRE), Coated threads and collars (IPC)
ON/OFF Tool, Profile Nipple	Nickel plated wetted parts, 316 SS
Packers	Internally coated hardened rubber of 80–90 durometer strength (Buna–N), Nickel plated wetted parts
Cements and cement additives	API cements and/or acid resistant specialty cements and additives

As a result, we can say that in order to reduce the corrosion of equipment during transportation and injection of supercritical carbon dioxide, it is necessary to understand the physical operating conditions and the chemical environment (including the composition of the initial flow) to which the materials of the transported and downhole equipment will be subjected. The most suitable equipment material should be selected from the operating conditions. This means that different materials must be used in various sections (sections and zones) depending on the conditions (temperature and pressure) and the composition of the injected medium. It is necessary to conduct additional studies on the timpurity concentration effects of reducing equipment corrosion in the carbon dioxide injection projects for EOR.

8. Conclusions

The conducted systematic review and analysis of research in the field of application of supercritical technologies for the oil and gas industry has found that supercritical carbon dioxide should be considered the most promising agent in this area, due to its low critical parameters and low cost.

Laboratory and theoretical studies have demonstrated very high efficiency of using supercritical CO_2 to increase oil recovery and hydraulic fracturing, processing, and disposal of oil sludge, as well as dissolution of heavy oil deposits. Moreover, the injection of CO_2 into the reservoir has recently acquired a very important environmental significance associated with carbon dioxide capturing and storing problems.

Therefore, based on the conducted review, one can conclude that using supercritical CO_2 in the oil and gas industry looks very promising. This is evidenced by a large number of publications on this topic carried out in the recent decade.

However, it should be noted that the vast majority of studies in this area were carried out in laboratory conditions or were based on a theoretical background. There is still very little practical experience in using this technology in the real oil fields. This suggests that the considered technology is still under development, and additional research is needed to adapt it to real conditions and already existing oil and gas technologies. In particular, the impact of supercritical fluids on the durability of pipes, pumping equipment, shut-off valves, and other oil and gas equipment is very important. The unique advantages of supercritical fluids suggest that these problems will soon be resolved, and this technology will be widely implemented in the oil and gas industry.

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Appendix A

Table A1. Basic theoretical and empirical formulas to calculate solubility in SCF.

No	Author of the Methodology	Calculation Formula
1	Poynting equation [54]	$\ln \frac{P'_v}{P_v} = \frac{\mu V_L}{RT}(P-1)$ where P_v is the saturation pressure, Pa; P'_v is the saturation pressure of the externally compressed condensed medium, Pa; V_L is the specific volume of the condensed medium, m^3/kg; μ is the molar volume of the condensed medium, m^3/mol; R is the gas constant, J/(kg·K); T is the absolute temperature, K; P is the external pressure, Pa.
2	Bilalov-Gumerov equation [51,54]	$\ln \left(\frac{y \Delta \mu}{y_{\Delta s} \Delta \mu_{\Delta s}} \frac{\rho_r}{T_r} \right) = \varphi_i \left(\frac{H_1 - H_2}{R} \right)^i$ where y is the solubility of the studied substance in the fluid, g/L; $\Delta \mu$ is the chemical potential of supercritical fluid at process temperatures, J/mol; ρ_r is supercritical fluid density, kg/m^3; T_r is supercritical temperature, K; φ is volume fraction of solvent, %; H_1, H_2 are molar entropies, J/(mol·K); $y_{\Delta s} \Delta \mu_{\Delta s}$ is the scale flow of the dissolved component through the unit thickness of the fluid layer when the entropy changes at the interface $S_1 - S_2$; R is the universal gas constant, J/(kg·K); i is the association number.
3	Chrastil equation [55]	$S = \rho^k \exp\left(\frac{a}{T} + b\right)$ where S is the solubility of the solute in dense gas, expressed in g/L; ρ is the density of the solvent, m3/kg; k is the association number; T is the temperature, K; α is the reaction heat; b is the ratio between the molecular masses of the solute and the solvent $a = \frac{\Delta H}{R}$ $b = \ln(M_A + kM_B) + q - k \ln M_B$ where ΔH is the total reaction heat, J/mol; R is the gas constant, J/(kg·K); M_A and M_B are the molecular weights of the solute and of the gas, correspondingly, u; q is a constant.
4	Del Valle-Aguilera equation [56]	$S = \rho^k \exp\left(\frac{a}{T} + b + \frac{c}{T^2}\right)$ where c is an empirical modification introduced by Del Valle-Aguilera to account for the evaporation heat of the solute.

Table A1. *Cont.*

No	Author of the Methodology	Calculation Formula
5	Adachi-Lu equation [57]	$S = \rho^{k+e\rho+d\rho^2} \exp\left(\frac{a}{T} + b\right)$ where k, a, b, c, and d are coefficients adjusted by fitting to experimental data.
6	A modified model of the mass action law for the correlation of solubility of solid and liquid substances in SCF [58]	$S = \rho_{SCF}{}^k m^\gamma \exp\left(\frac{a}{T} + b\right)$ ρ_{SCF} is the density of pure *SCF*, kg/m³; k is the snumber of *SCF* associations; m is the concentration of co-solvent (mole fraction) in a binary mixture consisting of *SCF* and co-solvent; γ is the number of associations for co-solvent.
7	Solubility equation of solid active ingredients in sc-CO$_2$ with and without co-solvents [59]	The new q-Chrastil's equation uses the definition of the q-exponential function expressed as follows [60]: $\exp_q x = [1 + (1-q)x]^{1/1-q}, if[1 + (1-q)x] > 0$ $or \exp_q x = 0, if[1 + (1-q)x] \le 0$ Applying the *q*-exponential function, it is possible to express *q*-Chrastil's equation as $S = \rho_{SCF}{}^k m^\gamma \exp_q\left(\frac{A_q}{T}\right)$ where ρ_{SCF} is the density of pure *SCF*, kg/m³; k is the number of *SCF* associations; m is the concentration of co-solvent (mole fraction) in a binary mixture consisting of *SCF* and co-solvent; γ is the number of associations for co-solvent; the parameter is related to the solvation energy.

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