



Review Article

Insights into the application of microfluidic platforms in enhanced oil recovery

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ABSTRACT

Enhanced oil recovery (EOR) technologies are used to recover most of the trapped crude oil from our limited reserves. With the escalating energy demand, EOR will achieve substantial economic benefits and greatly help in the exploitation of natural oil reserves. Recent research focused on microfluidic platforms for studying flow behavior during EOR flooding. These platforms are micro-sized, and allow processing and visualization of a minimal amount of fluid, making them an intriguing tool for studying the microscale phenomena in EOR processes. This review presents a comprehensive and concise literature on microfluidic trends and developments in EOR. A particular focus is on the use of these platforms to assess oil recovery via chemical-based flooding methods, to understand the associated emulsification mechanisms, and to mimic subsurface morphology and mineralogy of reservoirs. Furthermore, an outlook on the advancement of microfluidics utilization in EOR applications is discussed, covering development efficient micro-scale separators, 3D printing, and Artificial Intelligence applications. Microfluidic platforms provide valuable insights into EOR processes, and ongoing advancements in microfluidics hold the potential to enhance oil recovery efficiency and optimize EOR techniques.

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1. Introduction

The production of global crude oil from mature fields is declining, while the discovery of new hydrocarbon reserves is insufficient to meet the increasing energy demand. Therefore, new technologies and breakthroughs are needed to ensure an affordable supply of hydrocarbons and minimize the environmental impact of hydrocarbon extraction. Carbonate reservoirs are estimated to contain 40% of global gas and 60% of world oil reserves [1,2]. In the Middle East, reservoirs are dominated by carbonate rocks and contain approximately 70% and 90% of oil and natural gas reserves, respectively [1–3]. Conventional extraction methods can only recover a limited amount of the trapped oil reserves, with more than 70% still remaining buried [2]. However, it is anticipated that the application of EOR technology, as shown in Fig. 1, will alter

the forecast for oil production, both in the Middle East and internationally.

The process of extracting oil from a reservoir takes place in three stages:

- (1) The initial stage, known as primary recovery, is the oil extraction under the influence of the reservoir pressure.
- (2) In the second stage, known as secondary recovery, brackish or seawater is pumped into the well to raise its pressure and force the oil upward. Despite the recovery in both stages, the amount of oil that can be extracted remains relatively limited (20%–30%), while the majority, more than 70%, remains trapped in the well [2].
- (3) The third stage is the enhanced oil recovery (EOR) stage. In this process, various techniques are used to mobilize the oil from the reservoir's porous structure and transport it to the production well. Depending on the EOR technique, oil recovery can reach up to 80% of the oil initially present in the reservoir [2].

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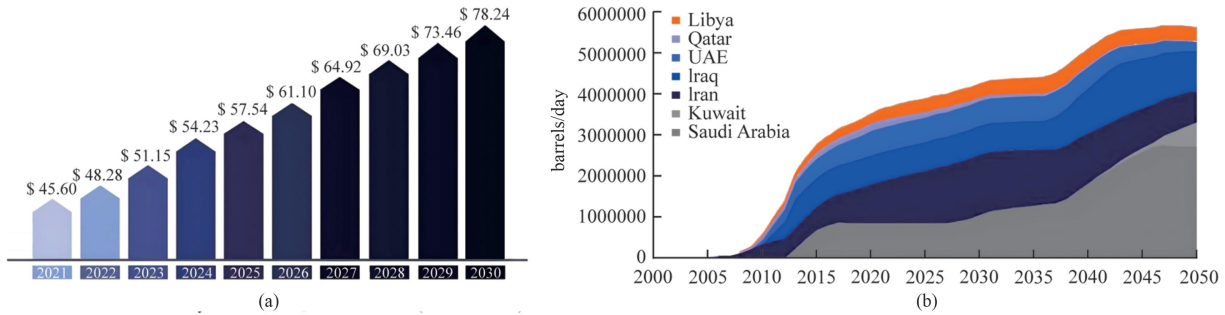


Fig. 1. (a) global enhanced oil recovery market size forecast in USD billion up to the year 2030 by Precedence Research [4], (b) Middle East enhanced oil recovery production forecast in barrel/day up to the year 2050 by Organization of the Petroleum Exporting Countries (OPEC) [5].

There are widely accepted oil recovery techniques that help minimize the loss of crude oil resources and their extraction costs. These techniques, as shown in Fig. 2, are categorized into two categories: thermal and non-thermal techniques, where the former is mainly used in the field [2,6–10]. Thermal techniques include using hot fluids such as hot water flooding or steam injection, electrical heating, or oxygenated gas injection. These methods are costly and environmentally unfriendly because they require external energy and generate combustion gases. On the other hand, non-thermal EOR methods have gained significant attention in recent years due to their potential to improve oil recovery while reducing energy consumption and environmental impact. These methods, categorized as chemical, gaseous, and biological methods, are of great significance and are used worldwide [11].

One of the advantages of non-thermal EOR methods is their ability to target specific reservoir properties and fluid characteristics, such as viscosity, density and interfacial tension [12]. They can also be used in conjunction with conventional EOR methods, such as water or brackish water flooding, to improve their effectiveness [13]. Another advantage is their lower energy requirements compared to thermal EOR methods, which can reduce operating costs and carbon emissions [7]. However, the use of

chemicals, gases and microbes in non-thermal methods can potentially damage the reservoir rock by reducing its permeability [14,15]. Therefore, careful optimization of the injection process and selection of appropriate chemicals, gases, and microorganisms are necessary to achieve optimal results and avoid formation damages. Additionally, some of these methods have long-term environmental impacts, such as groundwater contamination, air pollution, and deterioration of surface waters [16]. This emphasizes the need for careful monitoring and regulation of these methods to ensure their long-term sustainability.

Chemical EOR techniques, including alkaline flooding, surfactant flooding, polymer flooding, alkaline/surfactant/polymer (ASP) flooding, and nanofluid flooding, are the most prominent non-thermal oil recovery techniques. Most chemical EOR methods move the confined oil by reducing the interfacial tension created between the oil and the injected fluid, which results in emulsion formation. A search of database (Scopus) for the keywords “EOR alkali flooding”, “EOR surfactant flooding”, “EOR polymer flooding”, “EOR ASP flooding”, and “EOR nanofluid flooding” indicates that research interest in chemical EOR methods has been increasing since 2005 due to their promising performance for enhanced oil recovery, as shown in Fig. 3.

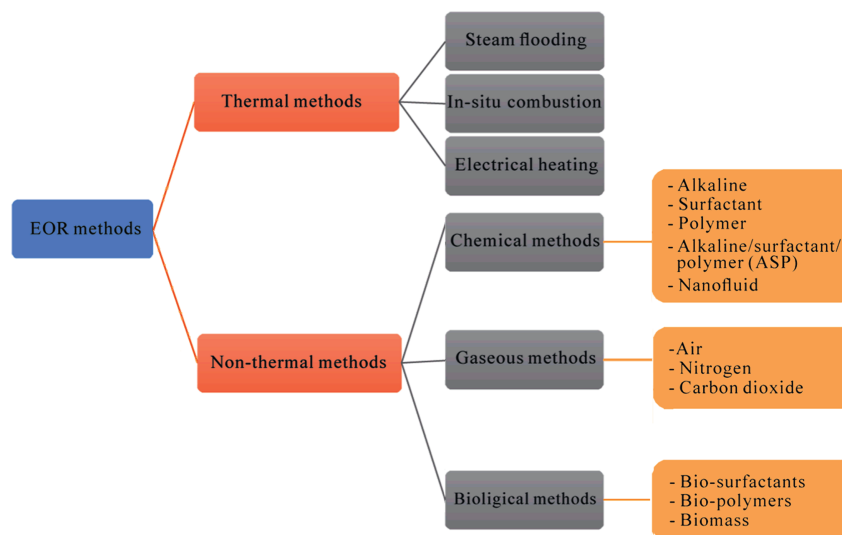


Fig. 2. Schematic of the commonly employed methods of EOR.

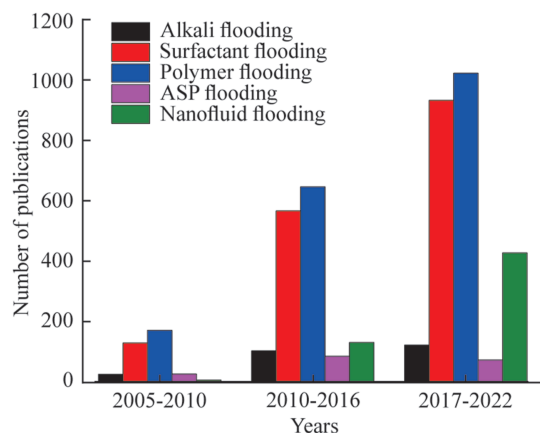


Fig. 3. Number of publications related to chemical flooding methods over the years since 2005.

Chemicals modify the surface energy of porous rocks, lower the interfacial tension (IFT) between the injected water and the oil, or use high viscosity injected fluids to increase the mobility of the oil [11,13,17]. Alkaline flooding, which involves injecting a high pH solution containing sodium hydroxide or sodium carbonate into the reservoir, has been widely used and proven effective for enhanced oil recovery [18,19]. These chemicals react with certain types of crude oil (e.g., acidic crude oil) to produce surfactants or soaps that lower IFT and improve oil recovery efficiency [20,21].

Surfactant flooding is another leading EOR method that is primarily employed in oilfields characterized with low-to-medium crude oil viscosity [22], in which it reduces oil trapping [22] by enhancing oil mobility. Surfactants enhance the oil's mobility by reducing the interfacial energy at the interfaces of water-oil and water-solid, thereby leading to improved recovery of trapped oil. Furthermore, surfactants possess the capability to modify the surface chemistry of porous rock, thereby facilitating enhanced fluid flow and increased displacement of oil. The flooding process involves the use of anionic, cationic, nonionic, and amphoteric surfactants. Among these surfactants, anionic surfactants are widely favored due to their minimal adsorption on sandstone rocks [23], while cationic surfactants are avoided due to their strong adsorption tendency. Nevertheless, cationic surfactants have larger potential to reverse the wettability of carbonate rocks from oil-wet to water-wet compared with anionic surfactants [23]. Nonionic surfactants are neutrally charged and are primarily used as co-surfactants to enhance ionic surfactant compatibility [24]. On the other hand, amphoteric surfactants, possessing both cationic and anionic charged groups, exhibit a broad pH range tolerance, making them effective in both acidic and alkaline environments. Due to the properties imparted from both charged groups, amphoteric surfactants proved to be suitable for both sandstone and carbonate reservoirs [24].

Similar to surfactant flooding, polymer flooding increases the oil's mobility and is preferably employed in oilfields characterized with low-to-medium crude oil viscosity [24]. During flooding, a polymer solution, composed of water-soluble polymers, is introduced into the reservoir in a form of a slug, driven by dilute brine. The water-soluble polymers increase the viscosity of the displacing water, which decreases the water/oil mobility ratio, leading to an increase in oil recovery [25]. Several critical factors to be considered for the selection of the polymers, one of which is polymer architecture, where branched polymers are superior to linear polymers in enhancing the viscosity of the injected solution [24].

Gas injection is another important non-thermal technique for EOR, especially in deep and unconventional reservoirs [2,26,25]. Since the oil price determines the economic viability of the EOR method, gas injection is the best option when oil prices fall [27]. Various gas flooding methods have been used worldwide to improve oil recovery, including air flooding, nitrogen flooding, and carbon dioxide flooding [28]. Gas injection into a reservoir can help maintain pressure and improve oil production. This is achieved by lowering the interfacial tension between oil and water, lowering oil viscosity, and expanding oil volume [25]. However, due to high gas mobility, the recovery factor obtained from gas injection is often lower than expected. A successfully applied method to reduce the mobility of a continuous gas flow and thus increase its volumetric recovery is to foam the gas. Enhanced oil recovery is improved by foaming because the gas viscosity increases significantly, which can stabilize the displacement process, and the interfacial tension is lowered by the presence of surfactants that are added to stabilize the foam, which can reduce capillary forces between oil and water.

For the biological methods, crude oil is extracted using a technique known as microbial enhanced oil recovery (MEOR). MEOR has been tested with various microorganisms that can survive reservoir conditions and exert biological activity [29]. In principle, the MEOR process produces several benefits of EOR through microbial growth and produced metabolites (byproducts), such as the reduction of interfacial tension, formation of stable emulsions, and plugging of high permeability regions [29]. The introduction of these microorganisms, which are responsible for metabolizing certain hydrocarbons, produces various by-products during the process, including alcohols, solvents, acids, gases, bio-surfactants, and biopolymers. These byproducts are biodegradable and of low toxicity, making MEOR an environmentally friendly approach to increasing oil production.

During the oil recovery process, produced oil moves through various channels, including fractures in limestone, pores in the rock, sandstone, and other minerals. These pores and cracks in rocks and minerals are on a micrometer scale where viscous forces, capillary effects, and interfacial tension dominate the effect of gravity. There are two main methods for studying the flow behavior in EOR systems/processes: coreflooding setups and microfluidic platforms. Coreflooding is used in many EOR studies and can provide useful information on the kinetics and amount of oil recovered. The use of coreflooding experiments in the laboratory has great advantages because they use core packs and sand particles that mimic the natural porous reservoir rocks [30]. However, coreflooding can only describe the overall behavior of the system. It is impossible to manipulate the fluids at the pore level and directly observe the underlying mechanisms and behaviors. In addition, the reproducibility of experiments in coreflooding is challenging [31,32]. On the other hand, microfluidic platforms, also called reservoir-on-a-chip, are powerful tools to directly observe the flow behavior and transport phenomena through porous media, where the fluid behavior in a microchannel or a network of microchannels can be mimicked, controlled, studied, and recorded with an optical microscope coupled with a camera [33].

In this paper, the applications of microfluidic platforms in understanding non-thermal EOR processes are reviewed and discussed. We focus on chemical EOR methods and on efforts to visualize and understand the emulsification mechanisms for these methods, as well as on microfluidic surface modifications to mimic the actual reservoir structure. Furthermore, we also reviewed the efforts toward destabilization emulsions in microfluidic platforms to guide future studies on coalescence mechanisms of EOR surfactant-stabilized emulsions that will advance the

understanding of the oil separation process or/and to develop highly efficient separators.

2. Brief overview of microfluidic platforms for EOR

The term “microfluidics” refers to systems in which small volumes of fluids in the range of 10^{-18} to 10^{-9} L are manipulated in small channels with a scale of tens to hundreds of microns [34], known as microchannels. The flow of fluid in these channels is laminar characterized by a low Reynolds number (Re), $Re < 2100$, which is a ratio of inertial forces to viscous forces [35,36]. This makes them useful because the movement of the fluid can be accurately predicted and modeled, offering advantages in terms of fluid control and analysis. In addition, the ability to fabricate transparent platforms allows observing the movement of the fluids, enabling to study phenomena such as mixing, diffusion, and reaction kinetics in real time.

2.1. Microfluidic system setup

A typical microfluidic setup is demonstrated in Fig. 4, consisting of the following essential parts: micromodel chips, a camera and microscope, syringe pumps, pressure sensors, and collecting flasks. The micromodel chips act as the artificial core instead of real rocks.

The camera and microscope will ensure image acquisition and close monitoring of the flow of fluids through a live feed. The syringe pump serves for fluid injection and helps the fluid circulate in the microchip. The sensor controls the pressure in the system, the inlet and outlet are used to supply and discharge the fluid, respectively, and the computer is used to control the flow rates in the syringe pump, receives the pressure data, and analyze the images.

2.2. Measuring key parameters for EOR using microfluidic platforms

Microfluidic platforms are becoming essential in the petroleum industry [37] due to the ability to control fluids in confined spaces within a short period of time, which is not possible using the conventional reservoir scale models that include rock or core samples. Compared to coreflooding setups, microfluidic systems

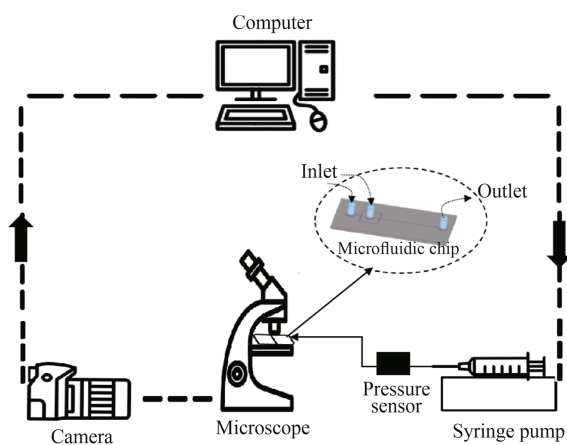


Fig. 4. Schematic of a typical microfluidic system setup composed of: a syringe pump, a pressure sensor, a microfluidic chip with 2 inlets and 1 outlet placed on a microscope equipped with a camera, and a computer. The dashed lines in the scheme shows the digital connections between the different parts of the setup while the continuous ones show the physical connections.

have very small footprints. In addition, the use of chemicals is highly reduced, while energy efficiency is highly improved [38]. In EOR studies, researchers aim to evaluate the effectiveness and mechanisms of different EOR techniques. To achieve this, microfluidic platforms enable the measurement of various key parameters, providing valuable insights into the optimization and understanding of EOR processes. Oil recovery efficiency is a primary parameter of interest in EOR studies, which depends on the volume of the reservoir that has been replaced by the displacing fluid. Microfluidic platforms allow for the measurement of oil recovery efficiency by quantifying the remaining oil saturation after the injection process. This assessment provides a quantitative measure of the effectiveness of different EOR techniques and aids in comparing their performance.

The main forces affecting oil production in EOR at the microscopic scale are viscous and capillary forces [39], which predominate on the scale of microfluidic systems. The capillary number (Ca), which represents the ratio of viscous force to capillary force, is used as a key indicator of the amount of residual oil. This relationship is illustrated in Fig. 5, where it can be seen that the amount of residual oil decreases as the capillary number increases beyond a critical value [40–42]. Prior to this value, the amount of residual oil is high with a constant residual oil saturation.

The capillary number can be mathematically expressed as the ratio of the product of the velocity (v) and dynamic viscosity (μ) of the displacing fluid to the interfacial tension (γ) between oil and the displacing fluid [39], as shown in Eq. (1)

$$Ca = \frac{v\mu}{\gamma} \tag{1}$$

The capillary number is found to increase as the injection velocity is increased, the viscosity of the fluid is increased, or the interfacial tension between the oil and the displacing fluid is decreased through the formation of emulsions.

Surface wettability affects capillary pressure, interfacial tension, and fluid flow behavior, making it a critical parameter to consider in EOR studies [44]. Microfluidic platforms allow for the visualization of fluid-fluid and fluid-solid interactions at the pore scale, enabling direct observation of wetting patterns and the effect of surface wettability on fluid displacement. The characterization of wettability can be performed by studying the contact angle between fluids and solid surfaces in the microfluidic channels [45].

Moreover, chemical and thermal effects play a significant role in EOR techniques. Microfluidic platforms provide a controlled environment to study the impact of different chemicals and thermal conditions on oil displacement. One aspect of chemical effects in EOR studies involves the use of chemical agents, such as surfactants, polymers, and alkalis, to alter the properties of the injected fluids and enhance oil recovery. Additionally, thermal

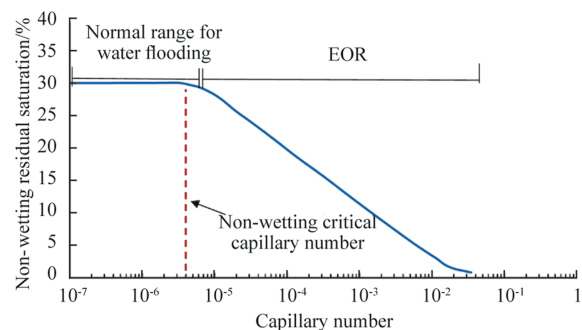


Fig. 5. Effect of capillary number on the amount of trapped oil (%) [43].

effects play a significant role in certain EOR techniques, such as steam flooding and in-situ combustion. Therefore, controlling and manipulating parameters like temperature, pH, salinity, and concentration gradients in microfluidic platforms allows researchers to simulate and study a wide range of chemical and thermal conditions relevant to EOR.

2.3. Limitations of microfluidic platforms for EOR

Despite the advantages discussed, microfluidics has not yet advanced to a stage where it can substantially impact the oil and gas industry due to several limitations. One limitation is the difficulty in scaling up microfluidic experiments to field-scale conditions. Microfluidic devices are typically designed for small-scale experiments, limiting their ability to accurately simulate the complex fluid dynamics and flow patterns that occur in a reservoir [46]. Another limitation is the lack of representation of the reservoir rock properties in microfluidic devices. The properties of the rock surface, such as wettability and roughness, can significantly affect the performance of EOR processes, but they are difficult to replicate in microfluidic devices [47]. To overcome these limitations, several strategies can be considered in the fabrication of microfluidic devices. One approach is to design microfluidic devices with more realistic geometries and dimensions closer to those of actual reservoirs. This can be achieved by using advanced fabrication techniques such as 3D printing or hot embossing, to develop microfluidic devices that replicate the complex geometries of reservoir rocks. Another strategy is to use microfluidic devices that have multiple interconnected channels, allowing for more realistic flow patterns and fluid–fluid interactions. In addition, incorporation of real reservoir fluids, such as crude oil or brine, into microfluidic experiments can provide a more accurate representation of fluid properties and their interactions than would be possible with simplified models.

2.4. Materials and techniques for microfluidic device fabrication

There are several materials used in the fabrication of microfluidic devices, such as silicon, glass, and polymers. The choice of material depends on a number of factors, including the temperature and pressure applied, the chemicals used, and the functionalization and patterning methods followed. Table 1 shows the advantages and disadvantages of these materials. In most EOR studies, glass and polymer materials are used, depending on the experimental conditions and the variables that need to be studied. The wettability of microfluidic channels can significantly affect capillary forces, fingering mechanism, relative permeability, and saturation during EOR flooding experiments. Therefore, modifying the surface wettability of the microfluidic device is a necessity for the complete wetting of the channel walls (water-wet or oil-wet), so that it can be used for precise mimicking of the reservoir's pores. Recently, polymeric materials such as polydimethylsiloxane (PDMS), cyclic olefin copolymer (COC), poly(methyl methacrylate) (PMMA), and Norland optical adhesive (NOA) were used in several studies due to their favorable characteristics, which includes affordability, biological inertness, optical transparency and non-toxicity, making them suitable for use in microfluidic devices [48,49].

Microfluidic devices are typically fabricated using one of several techniques, including soft lithography, hot embossing, injection molding, 3D Printing, and laser ablation. Soft lithography is a popular technique that utilizes a mold made of an SU-8-based negative photoresist to create microchannels and other microstructures on a substrate [47]. The mold is typically created using photolithography and then used to transfer the pattern to the

substrate via replica molding. In the hot embossing method, a polymer material is heated to a temperature above its glass transition temperature and then pressed using a mold. The mold contains microscale patterns that are transferred onto the polymer material. The polymer material is then cooled and solidified, and the mold is removed, leaving behind the desired microfluidic channels and features [49]. Injection molding is a mass-production technique, used to fabricate microfluidic devices, due to its ability to create complex microfluidic devices quickly and efficiently. It involves injecting a molten polymer into a mold containing microscale patterns to create the desired channels and features [49]. 3D printing is a rapidly growing technique for the fabrication of microfluidic devices by using a printer to deposit layers of material and build up the desired structure [50]. It can create complex microfluidic devices with a high degree of precision, but with a resolution typically lower than the resolution of other techniques. Laser ablation is another technique used to fabricate microfluidic devices by using a laser to selectively remove material from a substrate to create microfluidic channels and features [51]. The laser can be used to remove or vaporize material from the substrate, creating precise patterns with high resolution and accuracy. It can be performed on a variety of materials including metals, polymers, ceramics, and glass. The type of laser used depends on the material being removed and the desired characteristics of the microfluidic device. Some common types of lasers used for ablation include excimer lasers, Nd:YAG lasers, and CO₂ lasers [51].

3. Application of microfluidic platforms in EOR

3.1. Microfluidic platforms for oil recovery assessment using non-thermal methods

The concept of low salinity brine flooding as a method for enhanced oil recovery (EOR) was first proposed by Tang and Morrow in 1997 [52]. Since then, this concept has attracted considerable interest, and numerous research papers have demonstrated its effectiveness in improving oil recovery efficiency in sandstone and carbonate reservoirs [53,54]. Saadat et al. [55] developed a reliable and reproducible method to assess the sweeping efficiency of EOR brine flooding in a microfluidic platform. The authors conducted the oil recovery tests using two types of borosilicate glass microfluidic platforms supplied by Micronit Microtechnologies. One type consists of a uniform porous networks, and the other type consists of a rock-like (heterogeneous) porous networks which gives a closer resemblance of the reservoir pore morphology. Various parameters such as oil properties, injection rate, brine concentration, and wettability of the micro-model were studied using this method. The low salinity solutions were found to be effective and had a high oil recovery factor in the water wetted microfluidic device. They also found that the rock-like porous network platform gave lower oil recovery and higher recorded pressures than the uniform porous network, which is anticipated due to the irregular shape of the pores and the presence of dead-end pores in the rock-like platform. They found that the results obtained were reproducible, consistent, and comparable with the previous conventional techniques and literature, confirming the reliability and feasibility of using microfluidic platforms in EOR studies. In another study by Saadat et al. [32], the authors developed a microfluidic approach to study oil displacement by brine flooding at elevated temperatures and pressures. The authors performed the oil recovery tests using a hydrophilic borosilicate glass microfluidic platform, consisting of uniform porous networks. Two types of crude oils with different chemical compositions of resin and asphaltene were used. The chips were

Table 1
Advantages and disadvantages of materials used in fabrication of microfluidic devices.

Materials	Advantages	Disadvantages
Silicon and glass	High resistance in organic solvents Stable electroosmotic mobility Good thermal conductivity Precise fabrication of microchannel	High fabrication cost Low gas permeability Complicated fabrication procedure
PDMS	Low fabrication cost High elasticity Simple and fast bonding	Incompatible with organic solvents Adsorption of biomolecules Hydrophobicity
Polymers (COC and PMMA)	High mechanical strength High optical transparency Inexpensive Low moisture absorption Good chemical resistance Various easy fabrication methods	Complicated strategy for bonding Difficult for surface modification Difficult to assemble under mild conditions Hydrophobicity

supplied by Micronit Microtechnologies and fabricated by isotropic etching. The results indicated that increasing the pressure from 1 to 10 bar had no effect on the displacement pattern and recovery factor, whereas temperature significantly affected oil recovery, where the two crude oil samples exhibited opposite trends. For the crude oil with an API number of 19.2, the recovery factor increased when the temperature increased from 22 to 120 °C, while for the crude oil with an API number of 23, it decreased for the same increase in temperature. This was explained by the effect of oil properties, such as chemical structure and alkali and acid content, on wetting conditions as a function of temperature. In another study by Tahir et al. [56], the potential impact of sulfate-based water flooding was investigated using a microfluidic platform and coreflood experiments. A glass-silicon-glass (GSG) micromodel with oil-wet or mixed/complex wet conditions was used for the flooding experiments. Wettability was modified by utilizing a fluorinated silane to the interior surfaces of the micromodels, with the water contact angle of glass increasing from below 20° to 112° after treatment with the silane. The microfluidic models used in this study had a uniform structure and network with an average porosity and permeability of 27.6% and 13 Darcy, respectively. Table 2 shows the characteristics of the micromodels used in this work. The findings indicate that the recovery factor data from the two methods is comparable, and the two approaches confirm that wettability and interfacial tension are key factors in the mechanism of oil recovery, suggesting that the use of microfluidic models is an excellent way to evaluate EOR processes and assess fluid-fluid interactions.

Dong and co-workers [57] have proposed an alkaline flooding approach using a water-wetted glass micromodel to study the extraction of heavy oil. The glass micromodel consists of two plates, with pores and throats etched into the upper plate. The alkaline solution consists of a mixture of Na₂CO₃ and NaOH. The results show that oil extraction and sweeping performance were improved, and an additional recovery of 20% was obtained when alkaline solutions were used. The sweeping efficiency of alkaline flooding was 90% compared to water flooding, which was 70%. Pei et al. [58] conducted an experimental study on alkaline flooding in

sand packs and etched glass micromodels to study the displacement mechanism and determine the injection parameters' effect on oil sweeping efficiency. They utilized a photochemical technique to etch a two-dimensional network consisting of pores and throats onto glass plates, which were patterned to mimic the actual pore structure that appears in the reservoir. The findings suggest that water-in-oil emulsions are produced when crude oil and an alkaline solution interact, which can improve sweep efficiency by obstructing high-permeability areas and redirecting injected water to oil-trapped zones. The alkaline solution was found to improve oil recovery, achieving an additional recovery of up to 20% of the initial oil in place (IOIP). It was also found that alkaline flooding has an optimal injection rate that can maximize EOR.

Nilsson et al. [59] developed a microfluidic platform to test the effectiveness of different surfactant solutions for EOR, taking into account their rheological characteristics. The microfluidic device was fabricated with PDMS using a simple photolithography technique and consists of random capillaries and pores with an average size of 10–200 μm (Fig. 6). In their work, they used miglyol oil to prevent swelling of the PDMS microfluidic device. The results indicate that, compared to water and the same flow conditions, the surfactant based solutions can increase oil recovery by 15% while reduce IFT by a factor of 10. The results also emphasized that the microfluidic platform is a powerful diagnostic tool for investigating the effects of EOR chemical flooding and enables faster selection of tailored oil recovery fluids.

Saadat et al. [60] also worked on the field of surfactant flooding. In their study, they aimed to evaluate the effects of key factors such as flooding type, concentration and composition of brine, and oil composition on oil recovery efficiency. The experiments were conducted to better understand the relationship between these factors and surface wettability. In their study, they used a microfluidic approach to visually capture their observations of the recovery process. A glass microfluidic device was used to simulate the hydrophilic quartz surface of sandstone rocks with a uniform network of pores and capillaries. The hydrophilic glass device was chemically modified with a hydrophobic coating of octadecyltrichlorosilane (OTS) to alter the wettability towards lipophilic. Their findings indicated that the oil recovery efficiency of brine flooding in the presence of surfactants (sodium dodecylbenzenesulfonate and odium dioctyl sulfosuccinate) is higher than in their absence, indicating that surfactant flooding is more effective than brine alone as an EOR method. The authors concluded that flooding with surfactants has been found to continuously improve oil recovery by increasing the surfactant concentration, while flooding with brine alone achieves a certain recovery value that cannot be improved even by a further increase of brine concentration.

Table 2
Properties of GSG micromodels used by Tahir et al. [56].

Parameter	Glass-silicon-glass (GSG) micromodel homogenous (random circles)
Porosity (%)	27.60
Brine permeability (mD)	13000.00
Min. pore diameter (μm)	8.00
Max. pore diameter (μm)	2610.00
Avg. pore diameter (μm)	178.20

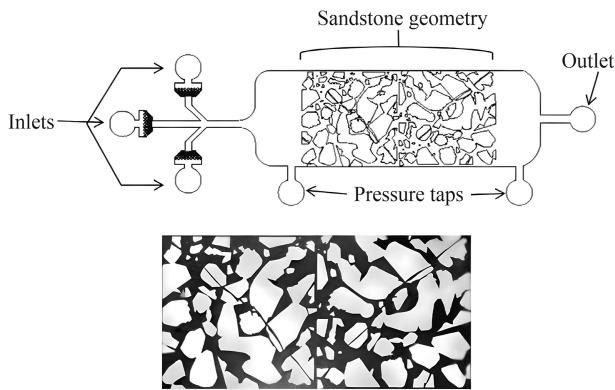


Fig. 6. Schematic of developed microfluidic platforms for studying oil recovery using surfactant flooding. The lower image depicts the sandstone filled with the miglyol oil colored with Sudan blue. Reproduced with permission from Ref. [59]. Copyrights © 2013 Elsevier.

One of the limitations of using coreflooding setup is studying the influence of thief zones on EOR. Thief zones are escape regions for the injected fluid in the reservoir. Their higher permeability compared to the nearby regions, and thus their low flow resistance, allows the injected fluid to flow to them easily. In the core and sandpack experiments, isolating the effect of thief zones on the overall oil recovery performance is quite challenging. To understand the extent to which thief zones affect the flooding performance of polymers, Qi et al. [61] developed a microfluidic platform for evaluating polymer flooding in reservoirs with heterogeneous layers (Fig. 7), including thief zones. The device consists of a random porous network in four different interconnected regions with different properties. The results show that polymer flooding has higher sweep efficiency in all four regions, resulting in significantly higher oil recovery compared to the case of water flooding, as shown in Table 3.

In a work by Rosero et al. [63], to understand the mechanism of polymer flooding during EOR, the authors developed microfluidic platform with different channel porosity and permeability that can simulate real oil reservoirs. The authors fabricated the microfluidic

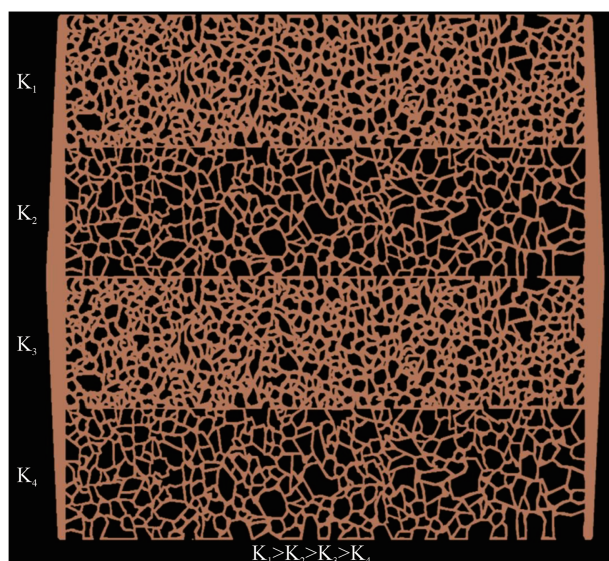


Fig. 7. Representation of different permeability zones used to study oil recovery by polymer flooding. Reproduced with permission from Ref. [61]. Copyrights © 2022 Elsevier.

chip using a standard lithography process and designed the chip's features using layout editor software. A developed microfluidic platform has three different permeability zones (low, medium and high) (Fig. 8). To create the different permeabilities, the authors used the design of three regular octagons of different sizes with repeated distances between them. In their study, they used PDMS material to fabricate the microfluidic devices. The results show that the polymers improve oil recovery by reducing the mobility ratio and redirecting the injected water to regions with low permeability. After flooding with water and flooding with polymers, the residual oil content decreased to 32% and 5.4%, respectively.

Microfluidic devices have proven useful in studying the effects of ASP flooding, which involves injecting alkali, surfactant, and polymer chemicals together for enhanced oil recovery. Alzahid et al. [64] developed a microfluidic approach to evaluate surfactant, alkali/surfactant, and alkali/surfactant/polymer flooding (ASP) using a PDMS micromodel consisting of a sandstone or fracture network. Microfluidic device networks were etched into silicon wafers by deep reactive-ion etching (DRIE) and used to fabricate microfluidic PDMS devices. The chemical flooding oil recovery was evaluated in terms of incremental oil recovery (IOR). The results showed that all the chemical flooding used in this work were efficient for oil recovery. However, ASP flooding showed the best oil recovery compared to other chemical floods, reaching a maximum value of about 31% of recovered oil.

Nanofluids can effectively improve oil recovery by changing the surface chemistry of the rock surface, increasing the viscosity ratio between fluids and changing the characteristics of the oil-water interface. Maghzi et al. [65] studied the effect of dispersed silica nanoparticles (DSNW) on changing the wettability of porous surfaces in EOR. They used a glass micromodel and fabricated the microfluidic chip using a CO₂ laser technique [66] and designed the chip patterns based on a thin section of a sandstone rock oil reservoir. Flooding tests were performed with distilled water and DSNW solutions. The glass surface was initially in an oil-wet condition achieved by saturating the channels with heavy crude oil for 20 days. The researchers found that coating the glass surface with DSNW solutions caused the surface to become superhydrophilic, with a contact angle less than 5°, which led to higher oil recovery compared to flooding with water alone. The optimal nanoparticle concentration was found to be 3 wt%, resulting in an additional 26% oil recovery. The researchers attributed this improvement to the hydrophilic nature of the silica nanoparticles, which transformed the micromodel's wettability from oil-wetted to water-wetted. However, they also observed that as the concentration of nanoparticles increased, the permeability decreased due to their adsorption on the glass surface. Xu et al. [67] conducted a study on enhanced oil recovery (EOR) using silica nanoparticles in a glass T-junction microfluidic chip (Fig. 9). The microfluidic chip was fabricated via a conventional lithography process, where hydrofluoric acid was utilized for the etching process. In their study, they generated monodisperse oil droplets in water while using the aqueous phase with nanoparticles as a displacing fluid. The study showed that the oil droplet size decreased with increasing the concentration of NPs, suggesting that the recovery process is plausible in a large-scale reservoir. While this influence of NPs on the recovery process is not fully deciphered, it is believed to be due to alterations in the rock wettability, modifications in the continuous phase's viscosity, and/or a reduction in the interfacial tension (IFT) between the two phases.

Several authors investigated displacement experiments with foam flooding. The more stable the foam, the greater the flow resistance, resulting in a greater reduction in mobility. Conn et al.

Table 3
Characteristics of all zones and recovery factors achieved after water and polymer flooding [62].

Zone	Channel depth (μm)	Porosity (%)	Permeability (D)	Recovery factor-water (%)	IRF ^a -polymer(%)	Total recovery (%)
k1	25	61	945	46.1	27	73.1
k2	25	39	101	29	41	70
k3	2.8	61	12	21.4	34.5	55.9
k4	2.8	39	1.3	3.6	49.3	52.9

^a Incremental recovery factor-polymer.

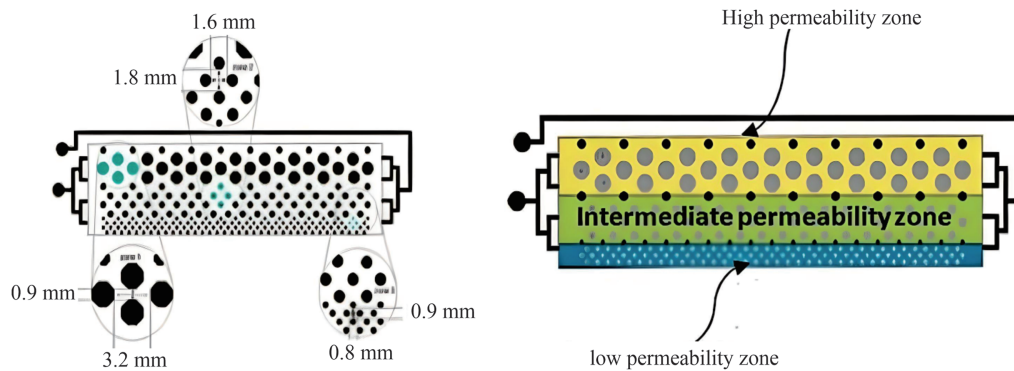


Fig. 8. Schematic of developed microfluidic platforms with different permeability zones for studying oil recovery using polymer flooding [63].

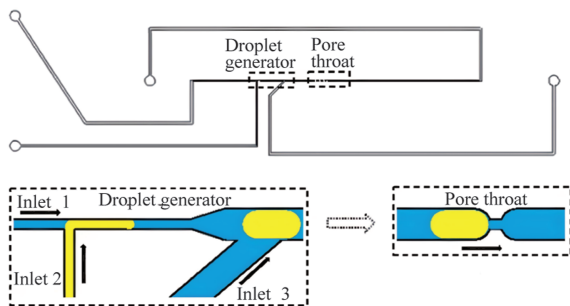


Fig. 9. Schematic of developed microfluidic platforms for studying oil recovery using nanofluid flooding. Reproduced with permission from Ref. [67]. Copyright © 2015 American Chemical Society.

[68] conducted a study to examine how foam flooding affects sweep efficiency. Two separate microfluidic chips made of PDMS were used, one to generate foam using air and the other to perform the flooding experiment (Fig. 10). The microfluidic chips were fabricated using a standard lithography process. The authors found that the foam successfully displaced the oil from the low permeability zones and attributed the successful displacement to the presence of bubbles in the foam, which resulted in a viscosity increase and an enhanced the pressure drop. The authors also concluded that the performance of foam flooding exceeded that of flooding with gas, water, and surfactants under similar conditions.

Jian et al. [69] developed a simple and cost-effective microfluidic method (Fig. 11) to study surfactant-stabilized CO₂ foams using microfluidic platforms. This method was used to study various factors such as surfactant concentration, foam quality, and oil content and their effects on foam behavior and stability. The authors used commercial glass microfluidic models, consisting of either a rock-like network to mimic the pore geometries of rocks or a homogeneous network with a uniform rectangular grain shape. They found that the results obtained with this method provided a good understanding of the foam-fluid transport phenomenon and gather useful information that can be used to improve CO₂

mobility performance. They also found that this microfluidic setup can reduce time and cost by at least 90% compared to conventional coreflooding methods.

Microfluidic devices have been also employed as screening tools for the MEOR process. Armstrong et al. [70] conducted a study using a micromodel to assess the effectiveness of MEOR by analyzing the wettability and capillary number of microchannels. The authors used etched silicon micromodels for their studies. A photochemical method using a glass bead pack was used to etch microchannels onto silicon substrates. They found that using biomass and biosurfactants to perform tertiary oil displacement on the micromodel system can optimize oil recovery by decreasing surface tension and bioclogging of pore spaces. They also found that MEOR gave the best results in microchannels that exhibited high water-wettability. Gaol et al. [71] also conducted microbial flooding experiments to study MEOR mechanisms such as bioclogging and changes in fluid mobility and their effects on oil recovery. The authors used artificial (homogeneous) and real structure (heterogeneous) glass-silicon-glass (GSG) micromodels for their studies. The flooding experiments were carried out at a temperature of 37 °C and a pressure of up to 6 bar. The results indicated bacterial growth during MEOR flooding, leading to bioclogging and a reduction in permeability factors in artificial and real structural micromodels, and subsequently improving oil sweeping efficiency. For a real structural micromodel, an additional 4.2% oil recovery was observed after MEOR flooding.

3.2. Microfluidic platforms as visualization tools for the mechanism of emulsion formation in reservoirs

Emulsion formation is a complex mechanism and is influenced by many factors, such as crude oil properties, flooding chemicals, rock wettability, pore throat structure, and residual oil type and quantity [72]. The formation process becomes more complicated due to the reservoir porosity. Visualization devices such as the microscope [73,74], the Hele-Shaw cell [75], the pressure/volume/temperature cell(PVT) [76], and microfluidic platforms [77] have been used in a limited number of studies to investigate emulsion

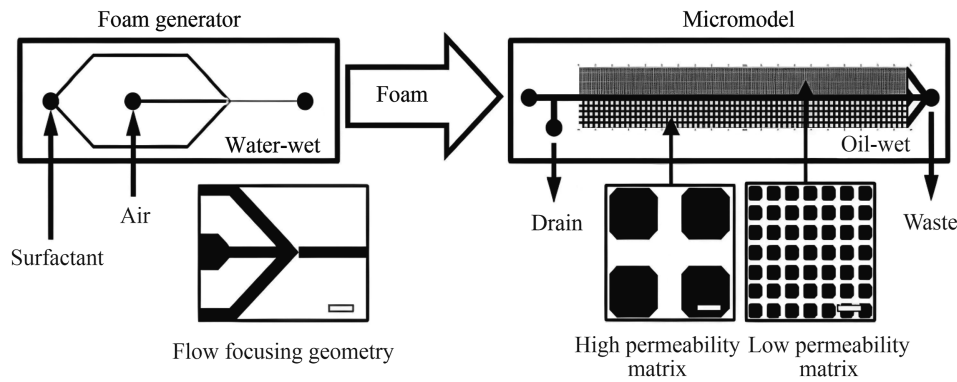


Fig. 10. Schematic of developed microfluidic platforms for studying oil recovery using foam flooding. The oil and foam were injected from opposite ends of the micromodel and allowed to drain until a stable foam formed in the transfer tubes. Reproduced with permission from Ref. [68]. Copyright© 2014 Royal Society of Chemistry.

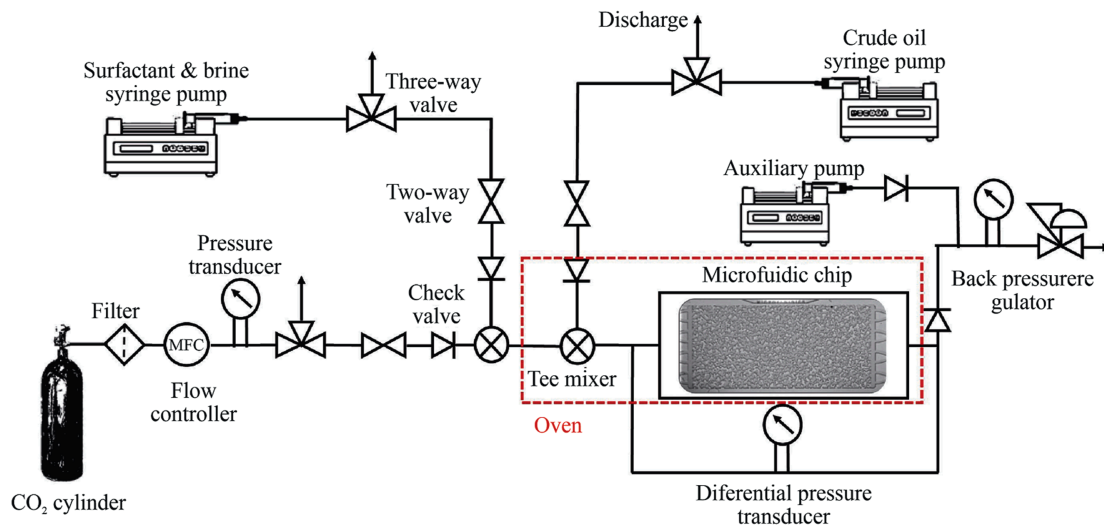


Fig. 11. Schematic of developed microfluidic setup for studying oil recovery using foam flooding. Reproduced with permission from Ref. [69]. Copyrights © 2021 Elsevier.

formation in porous media. Zhou et al. [74] utilized a digital biological microscope to visualize the emulsion formation mechanism during a coreflooding experiment. They identified two primary mechanisms, namely the shear action of an emulsifier solution and the snap action of the residual oil, which contribute to the formation of emulsions or droplets. The study also demonstrated that displacement distance/core length, emulsifier concentration, and injection rate significantly impact the particle size and stability of the formed emulsions. They observed that smaller displacement distances, such as a 6 cm core length, resulted in smaller particle sizes and lower emulsion stability due to the limited amount of residual oil in the well-bore region. When the displacement distance is increased to more than 10 cm core length, an emulsion with quite high stability is formed with the scale of the pore throat (5–15 μm). They also found that increasing the emulsifier concentration led to larger particle sizes and greater emulsion stability. At an emulsifier concentration of 0.4% or 0.5%, the researchers noted that a viscoelastic emulsion with desirable properties could be formed within the pore throat scale. In addition, they found that emulsions with a small particle size formed at both low and high injection rates.

The snap-off process, which is responsible for the entrapment and disconnecting of the non-wetting phase (hydrocarbons) through the pores of the reservoir [78], occurs when the oil interfacial tension is greater than the shear forces resulting in an oil droplet break off and entrapment of that droplet. The process is affected by various factors, such as viscosity ratio, pore-throat, and

capillary number. Fig. 12 illustrates the mechanisms of emulsion formation by snap-off and shearing actions [22].

Kokal et al. [76] reported a technique to examine emulsion properties and features that mimic the extreme environmental conditions of a reservoir. In their experiment, a visual pressure/volume/temperature (PVT) cell was utilized, which included windows that enabled visualization of the fluids inside the cell (PVT cell setup representation, Fig. 13). The findings indicated that emulsions could be generated at high pressure and temperature. The authors also found that the content of asphaltene in crude oil played a significant role in emulsion formation.

Among all the visualization devices, microfluidics has great potential to study the mechanism and behavior of emulsion formation during EOR flooding. Pena et al. [80] conducted a study on the behavior of oil droplets using tapered glass capillary tubes with a capillary diameter of 200 μm and a necking diameter of 50 μm . The authors proposed that the formation of emulsions in porous media can be explained by the snap-off process. According to their findings, the snap-off process depends mainly on the capillary and viscous forces acting on the saturated oil. Emulsions were observed throughout the capillary number range (7×10^{-5} – 7×10^{-4}) when the viscosity ratio was low (oil/water), while snap-off was suppressed, and no emulsions were formed when the viscosity ratio was higher. The authors also noted that snap-off occurred only in a low capillary number range at moderate viscosity ratios.

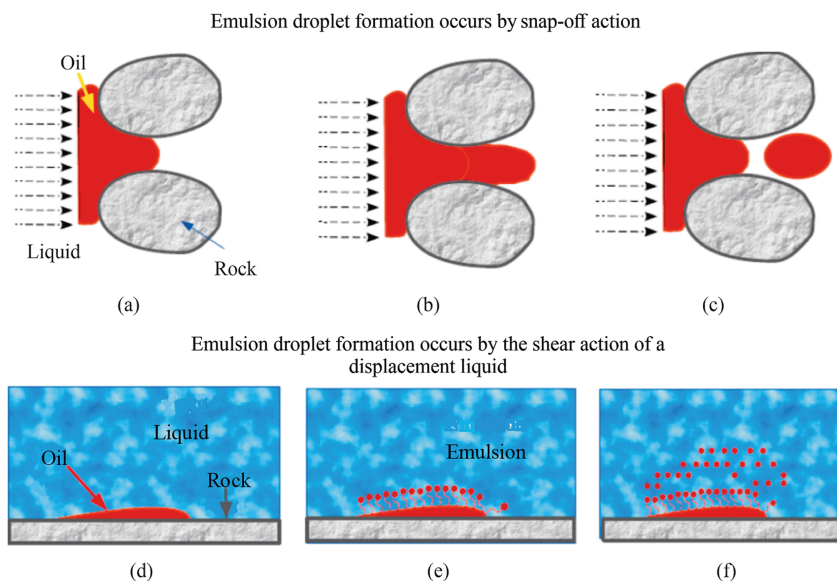


Fig. 12. Snap off-action: (a) oil residual is trapped in the rock grains. (b) the trapped oil interacts with surfactants in the displacement fluid and expands. (c) the oil breaks off and forms an emulsion. Shear action: (d) the oil film is trapped as a residual. (e) emulsion formation by the shear action of a displacement liquid that has surfactants. (f) more oil-water emulsions are formed and dispersed in the liquid phase by a shear mechanism, resulting in a reduction of the oil film. Reproduced with permission from Ref. [22]. Copyright ©2022 American Chemical Society.

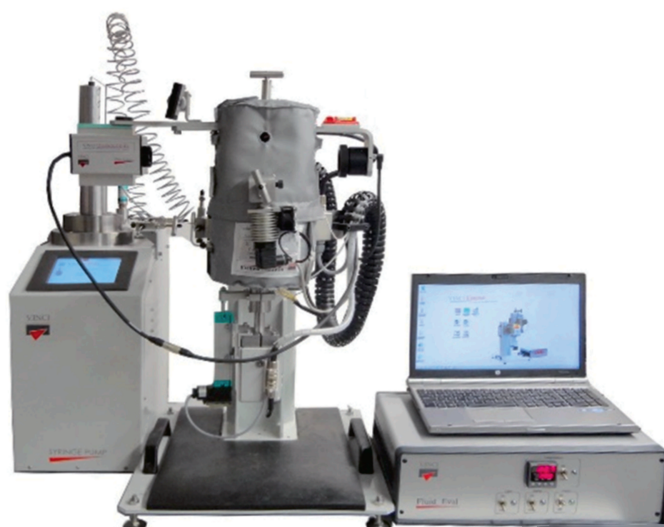


Fig. 13. PVT cell setup by VINCI TECHNOLOGIES [79].

In a study to evaluate the potential of nanofluid flooding on EOR sweep efficiency, Li et al. [81] conducted a study to investigate the impact of hydrophilic silica nanoparticle-based nanofluids on the EOR mechanism. To achieve this, they utilized a hydrophilic etched glass micromodel and a coreflooding setup. The micromodel consisted of a two-dimensional pore structure etched on a flat glass plate, which was then covered by a second glass plate to form a closed pore space. During the flooding experiments, the authors noticed the formation of emulsions, where nanoparticles assisted in stabilizing and releasing oil droplets by lowering the interfacial tension between oil and water. Furthermore, they observed that at higher concentrations of nanofluids (0.1 wt%) large oil droplets disintegrated/broke off into smaller ones, which was attributed to the nanoparticles' ability to stabilize oil-water emulsions and

enhance oil recovery. Lele et al. [82] presented a study on the formation of emulsions during steam injection using a glass microfluidic platforms. The chips were fabricated by the wet etching method. The formation of emulsions was investigated in geometries that mimic pores with a size of approximately 100 μm , both with and without the presence of alkaline additives. The results indicated that the addition of alkaline additives to the steam led to the formation of finer emulsions. In addition, the authors suggest that the constructed microfluidic platform can be used to study emulsions formed during transport through valves, pumps, and pipelines. In a work by Howe et al. [83], they conducted a study to examine the impact of anionic surfactants on EOR sweeping efficiency. They used a microfluidic platform provided by Epigem Ltd. Consisting of a uniform SU8 pore network with a total volume of 17 μL embedded in PMMA to illustrate their observations. The results indicated that the primary EOR mechanism involved the generation of microemulsions caused by the shear effect of the surfactant solution. It was also observed that the affinity of surfactants for oil and water affected the formation of oil-in-water, water-in-oil, and bicontinuous emulsions. Bicontinuous and water-in-oil emulsions had the highest sweep efficiency, whereas oil-in-water emulsions left large amounts of residual oil resulting in only moderate recovery. Al Zahid et al. [78] developed a geomaterial based microfluidic device (functionalized with real rock surface) to investigate the behavior of multiphase flows, including corner flows and snap-off mechanisms occurring in rock reservoirs. They observed a snap-off event after injecting fluids into the chip, and found that the snap-off process is influenced by the pore-solid interface wettability and geometry. The results also suggest that there is a pressure difference between the neck region and the two pore bodies that leads to the snap-off process. Wang et al. [84] used a microfluidic platform (Fig. 14), made of PMMA, to investigate the emulsification mechanism of heavy oil during flooding with water and surfactants. They observed that the emulsification process occurred in three main stages: the first stage was the creation of the head and neck of the oil droplet, the second stage was the development of oil emulsion droplets due to

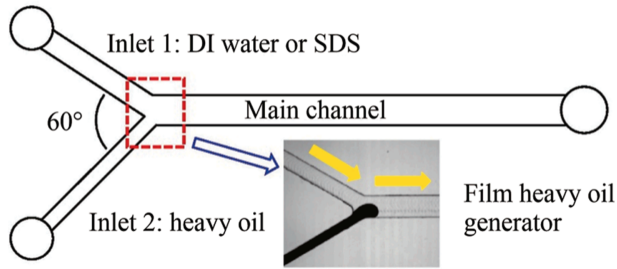


Fig. 14. Layout of a microfluidic device for studying the emulsification mechanism of heavy oil. Reproduced with permission from Ref. [84]. Copyrights © 2021 Elsevier.

the shear action of the surfactant solution, and in the third stage, the remaining heavy oil droplet was subsequently broken by the influence of the flowing surfactant solution.

3.3. Microfluidic platforms with mimicking subsurface morphology and mineralogy of reservoirs

The interaction between the porous surface of a reservoir and the two-phase fluid is a crucial phenomenon in enhanced oil recovery. Oil production efficiency depends on several factors, with the most important factor is the wettability of the surface [72]. Surface wettability is a direct measure of surface energy that can be quantified by measuring the contact angle of a liquid on a smooth solid surface. Although calcite is the main component of carbonate reservoirs and is naturally water-wet, the surface wettability of carbonate reservoir rocks is usually oil-wet due to the aging effect of trapped oil. This changes the surface wettability of the rock, making it hydrophobic [1,85,86]. According to Treiber et al. [87], an analysis of fifty-five samples collected from carbonate reservoirs revealed that 84% of them are oil-wet, 8% are water-wet, and 8% are medium-wet. The heterogeneous surface wettability, as a result of ageing carbonate reservoirs, will influence the dynamics and stability of emulsions formed during the displacement process [88].

Several geomaterial chip fabrication methods were proposed in the literature to produce microfluidic devices that mimic real reservoirs. To study the fluid-solid interactions, Song et al. [89] introduced a method to functionalize the pore surface in a 2D silicon micromodel with kaolinite clay to impart the properties of sandstone reservoirs. The microfluidic device was fabricated by etching the silicon wafer with a sandstone pore structure using a simple photolithography technique. To coat the microdevice with kaolinite, a well-dispersed kaolinite suspension of 1 wt% was injected into the micromodel under sonication after completely saturating the micromodel with DI water. After the micromodel was coated with kaolinite, air was applied to the system to eliminate any clogged particles at the pore openings. The authors were able to visualize brine-flooding experiments to understand the important mechanisms governing the detachment and release of clay particles from the pore surface and their impact on hydrocarbon recovery efficiency. The findings indicate that the clay particles can be mobilized in brines having salinities between 4000 and 6000 ppm, which is consistent with coreflooding experiments performed on Berea sandstones. Moreover, the clay particles significantly alter the wettability of the pore-space, changing it from a highly water-wetted surface to a mixed-wetted surface, which results in the formation of emulsions and in the enhancement of oil recovered from flooding with low salinity water. The same authors in another study [90] used the

same functionalized microfluidic device to investigate the direct effects of low-salt brine injection on clay. They conducted brine flooding experiments with and without oil, and observed various critical mechanisms that lead to an increase in oil recovery during low-salt brine flooding. These include the interaction between brine and clay, the change in wettability caused by the mobilized clay, and the clogging of the pores due to detached clay particles. They found that clogging of the pores by the detached clay particles during brine flooding is the most important mechanism, where the particles block preferential flow paths and redirect injected fluids to non-flowing areas, thereby enhancing oil recovery. Grami et al. [91] developed a microfluidic chip made of coal material by utilizing three-dimensional laser micromachining to etch fracture patterns into the geometrical surface of the coal. The patterns had a size ranging from 14 to 80 μm . After creating the fracture patterns over the coal sample, they bonded the etched coal substrate to a slide of COC and punched the inlet and outlet holes. The fabrication process is shown in Fig. 15. Another conventional microchip was fabricated with the same fracture patterns on PDMS-based material using a simple lithographic fabrication method. The wettability and surface roughness of the conventional and developed microfluidic models were analysed and compared to the actual coal cleats. The authors used the static and dynamic contact angle characterization techniques to quantify the wetting behavior of the developed microstructures, and the developed microchip was used to perform water/gas displacement experiments. The results show that all the properties of the developed microfluidic device, including wettability and surface roughness, are comparable to real coal. The conventional microchip, on the other hand, exhibits incomparable properties.

Similarly, Porter et al. [92] presented a fabrication method using a custom-built femtosecond laser direct-write (LDW) system to create fractures in thin sections of various rock types such as sandstone, siltstone, and shale. In addition, the authors have developed a microfluidic system to study displacement flooding in a reservoir-like environment under high temperature and pressure conditions. To fabricate the microfluidic device, a large rock core was cut into thin slices measuring 46 mm \times 26 mm \times 3 mm (length, width, and thickness). The cut slices were then attached to

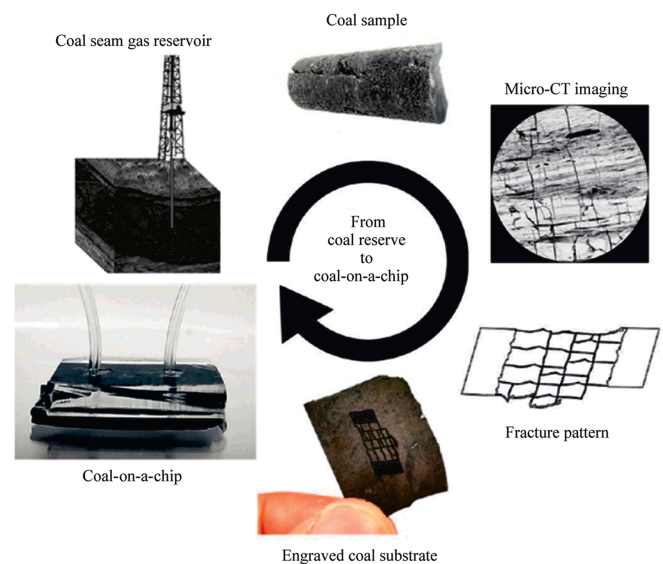


Fig. 15. Illustration of the fabrication process of coal geomaterial microfluidic device. Reproduced with permission from Ref. [91]. Copyright©2017 American Chemical Society.

a glass substrate. Then the pores and fractures were etched using the LDW system, and finally the top of the patterned micromodels was sealed with a glass slide. Although the microfluidic devices were successfully fabricated from geomaterials, the authors were unable to reconcile the wettability of the developed micromodels with the glass material used to seal the top of the micromodel, which affected the observations of the flow and transport processes they tested. The microfluidic device can be further modified to represent real rocks, including tuning the wettability of the porous network surface. Lee et al. [93] successfully fabricated glass microfluidic devices with a network representing geological porous media with controlled wetting conditions by photolithography and UV polymerization. The authors used hydrophilic and oleophilic crosslinking agents with different wetting ratios together with additives to modify and control the degree of wettability. They measured the wetting behavior of the copolymerized microstructures using the contact angle characterization technique, and conducted immiscible oil/water displacement experiments using the modified microchip. The results show that different ratios of hydrophilic and oleophilic cross linkers in the precursor solution lead to a change in the wettability state, and that the use of additives (2-hydroxyethyl acrylate and lauryl acrylate) in the precursor solution further improves the wettability state over a wider range due to the copolymerization effect (e.g., water contact angle in the decane range from 60° to 144°). They also found that wettability has a significant impact on improving the displacement process. A larger volume of the displaced phase is formed when the displacing fluid wets the device wall.

Wang et al. [94] presented a method for coating microchannels of a microfluidic glass chip with a desired thickness of a nanocrystalline calcite (CaCO_3) layer. Chemical surface modifications with sodium hydroxide and silane coupling agent were performed to functionalize the glass surface and enable the growth of CaCO_3 nanocrystals on the inner surface. The characterization results from contact angle measurements, optical microscopy, SEM, Raman spectroscopy validated the successful growth of a nanocrystalline calcite layer in the developed micromodels.

Al Zahid et al. [78] developed a fabrication process to attach rock minerals with connected pathways of corners and crevices onto a PDMS micromodel to mimic multi-phase flow in rocks. The fabrication process involves coating the PDMS surface with a sandstone or carbonate dispersion after oxygen plasma treatment (Fig. 16). The authors employed different techniques, including SEM, EDX, surface profilometer, and contact angle measurement, to evaluate and compare the microfluidic device made of geomaterial with actual sandstone and carbonate rocks. Their findings demonstrated that all properties of the microfluidic device, including mineral composition, wettability, and roughness, are comparable to real rock.

Li et al. [95] developed a nanofabrication method to create a uniform layer of calcite (CaCO_3) on the surface of a 3D micromodel made of hexanediol diacrylate polymer (HDDA), mimicking the natural mineralogy of carbonate reservoirs. The fabrication process involves printing the porous microdevice with a monomer ink of HDDA, introducing calcite nanoparticles into the inner surface of the microdevice, and growing calcite crystals inside the microdevice. After successfully coating the inner surface with calcite, they used the contact angle characterization to test the surface wettability of the modified surface. The results showed a significant change in surface wettability of the calcite coated surface. The surface becomes super hydrophilic, and compared with the nearly hydrophobic surface of pure HDDA with a contact angle of $87 \pm 3^\circ$, water droplet spreads immediately on the surface.

4. Coalescence of emulsions by droplet-based microfluidic platforms for EOR emulsion destabilization

Recently, many researchers focused on the use of microfluidics for controlling droplets' behavior in microchannels. Coalescence of droplets is influenced by multiple factors, such as fluid properties, flow type, and the existence of surfactants. In oilfield emulsions, the presence of surfactants is crucial for stable emulsions during surfactant flooding, as they reduce interfacial tension at the oil-water interface and can form particle films that hinder the destabilization process and complicate the subsequent process of oil-water separation. To separate these emulsions, various destabilization methods are used in industry and investigated in laboratories, including chemical, biological, and mechanical demulsification. However, these methods are limited to describing the system's overall performance and do not provide details on the mechanisms or the behavior of the emulsions during coalescence. Droplet-based microfluidic platforms, on the other hand, can realize the behavior of two-phase flow and control the kinetics of droplet transportation, formation, fusion, and splitting [96]. Therefore, they can serve as a tool to visualize and understand the coalescence mechanisms of EOR effluent emulsions during destabilization, and can provide theoretical guidance for further development of highly efficient micro-scale separators whose throughput can be intensified by the numbering up concept [97–99].

There are two main methods to achieve droplet coalescence in microfluidic platforms, namely: passive and active methods [96]. Active methods use external forces such as magnetic fields, electric fields, temperature fields, and ultrasound waves to induce instability and coalescence of droplets. These methods are more costly and complicated than passive methods because they require external forces and electrode fabrication [96]. On the other hand, passive methods are designed to slow down the front droplet velocity or capture it at a specific location temporarily by adding special microstructures, changing the microchannel structure, adjusting the rate of droplet generation, or changing the wettability of the channel surface [96]. This makes it possible for the rear droplets to reach and merge with the front droplet at a designated point. During this process, the continuous fluid phase between two droplets will gradually drain out as they move closer to each other. Once the droplets come in contact, their interfaces destabilize due to shear forces, causing the droplets to rapidly coalesce (Fig. 17). In comparison to active methods, passive methods are simpler and do not require external forces. The reduced possibility of droplet contamination is a significant benefit of passive methods compared to active methods, which may be contaminated by electrodes.

Several studies have been conducted to induce coalescence of emulsions stabilized by surface-active compounds (surfactants), for enhanced oil recovery applications [101–103]. Therefore, in this section, we demonstrate several passive methods that can be applied to microfluidic platforms to achieve high separation efficiency.

The study of droplet coalescence by changing the geometry of the microchannels has attracted many researchers because the design can be easily modified to improve the separation efficiency. Tan et al. [104] developed three channel geometries to slow down the flow of front droplets (Fig. 18). Two of these geometries depend on a geometrical expansion, where the channel dimensions increase at a specific region to decelerate the droplets. These are the rectangular and tapered expansion designs. The rectangular expansion design allows droplets to enter the channels from opposite directions while facing each other, and merge into an expanded rectangular area, thereby reducing the distance between

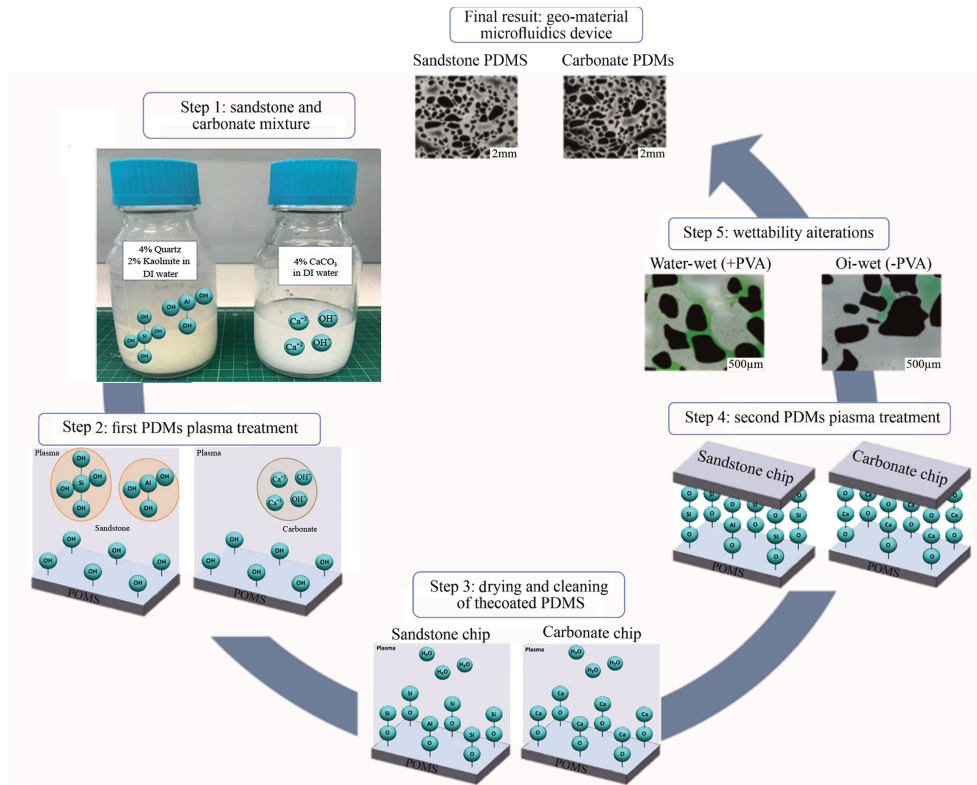


Fig. 16. Schematic of the fabrication process of sandstone and carbonate geomaterial microfluidic device [78].

droplets allowing them to coalesce. It has been found that the expansion area (length and width) and the rate of the two-phase flow are important factors affecting the fusion of droplets. In the tapered expansion design, the droplets enter through different inlets from the same direction and merge into a single channel that is suddenly expanding along its width. Although the tapered expansion worked for a broader range of droplet sizes and flow rates compared to rectangular expansion, it was found that sudden expansion causes a rapid reduction in droplet velocity, allowing undesirable multiple fusions that cannot be controlled. Compared with the previous two designs, the third geometry, called flow rectifying design, provided the most flexibility to control the fusion process of subsequent droplets. Its design consists of a cross flow junction with the side channels having larger dimensions. The flow in the side channels can be manipulated to control the velocity of the droplets. Due to its ability to control the flow rate of the separating fluids at the side channels, it allows a desired droplet fusion rate to occur at the intersection.

Another important passive method for droplet coalescence is by adding special microstructures. Niu et al. [105] designed a droplet merging device with two rows of microcolumns (pillars), that are positioned at a distance smaller than the droplet size to control the spacing between subsequent droplets and facilitate droplet fusion. The use of the pillars induces a mismatch between the surface tension of the dispersed phase and the hydrodynamic resistance of the continuous phase, which leads to droplet merging. Due to the fluid resistance element (pillars), the droplets slow down and wait for subsequent ones to merge with them. Once the droplets are fused, they exit the merging chamber when the continuous phase pressure exceeds the surface tension of the fused droplet. This approach is effective in merging two or more droplets and can be controlled by manipulating the mass flow rate and the ratio of the volume of the droplets to that of the merging chamber. Emulsion separation was applied by Ayoub et al. [106],

where a visual milli/microfluidic device was developed to separate emulsions from EOR coreflood effluents to quantify surfactants. The device includes a millifluidic platform for transferring surfactants in the aqueous phase and a microfluidic separator for separating oil from the aqueous phase. The microfluidic separator consists of two glass based microfluidic chips with a hydrophilic membrane sandwiched between them (Fig. 19). The glass chip contains a serpentine channel with a length, width, and height of 21.2 cm × 900 μm × 150 μm, respectively. The authors evaluated the performance of the separator at different flow rates (1–10 mL/h) and salinities (0–15 g/L NaCl). The study showed that 90% of the fluid collected downstream of the microfluidic separator is water, confirming the effectiveness of the device over a wide range of operating conditions.

Another effective passive technique for lowering the water content of oilfield emulsions is droplet coalescence induced by surface modification. By altering the surface characteristics of the microfluidic channel, attractive forces between the droplets and the surface are induced, thereby disrupting the stability of the

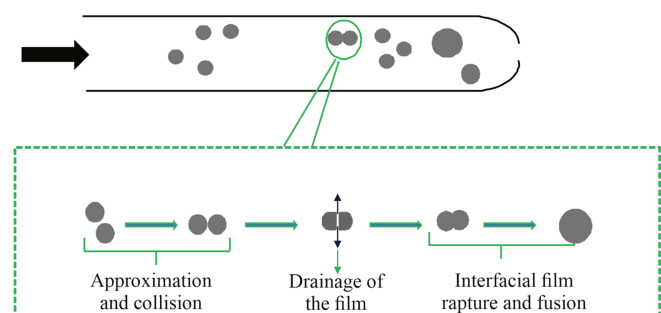


Fig. 17. Schematic of the coalescence mechanism (adapted from Ref. [100]).

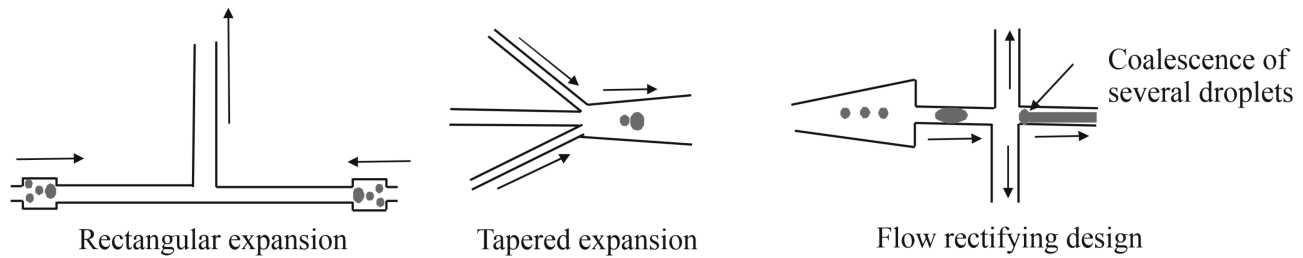


Fig. 18. Different geometries of droplet fusion microchannels (adapted from Ref. [104]).

emulsion. This instability can be exploited to develop a new microfluidic technological approach that helps to induce coalescence of EOR emulsions.

The transport of droplets can be substantially affected by a wall with heterogeneous wetting conditions. Few studies involve the use of microfluidic platforms to modify microcapillaries with desired heterogeneous wettability [88,107], i.e., alternating hydrophobic and hydrophilic regions, to control and manipulate emulsion stability without applying an external force (electrical or acoustic). Fidalgo et al. [108] designed a droplet merging device with a patterned hydrophilic segment of polyacrylic acid (PAA). In this study, they used a photografting method in which the PAA was grafted onto planar benzophenone-containing PDMS substrates by UV photopolymerization to capture the aqueous droplets. They found that droplet fusion is achieved by two sequential steps: droplet trapping and droplet detachment. This process depends on two competing forces: the surface energy and the viscous drag force. In a typical case, the droplet enters the fusion zone with the modified surface, gradually slows down, and adsorbs on the modified surface. It is trapped there and increases in size as it fuses with the following droplet. As the size of the droplet increases, the overall attraction forces between the droplet and the surface decreases, causing the droplet to detach once the viscous drag force of the continuous phase dominates the surface attraction force. Chen et al. [109] reported the coalescence of emulsion droplets caused by their adhesion to the patterned surface of a microfluidic channel. In their study, oil-in-water emulsions were generated within a glass capillary device with a hydrophobic patterned surface of octadecyltrichlorosilane (OTS). The results indicated that the adhesion of oil droplets occurs in the patterned hydrophobic regions, leading to droplet coalescence. Meng et al. [88] successfully fabricated a glass microchip with heterogeneous surface wettability to study the impact of surface wettability and flow

rates on oil/water emulsion dynamics, morphology, and stability. The hydrophobic regions of octyltriethoxysilane (OTES) were patterned on a glass microcapillary using photolithography. The results show that when the oil/water droplets are at a high speed, i.e., high drag force, the emulsion stability is high, while the emulsion dynamics remain the same as the emulsion travels across the hydrophilic and hydrophobic segments. On the contrary, during the slow movement of the oil droplets, the patterned surface energy becomes higher than the viscous drag force, and as a result, the oil droplets adhere to the hydrophobic wall resulting in the conversion, adhesion, or breakup of the oil/water emulsions.

More recently, Alamoodi and Alazzam [110] proposed a new approach to fabricating droplet coalescence devices with patterned hydrophilic segments of graphene oxide (GO). They used a plasma-enhanced liftoff method to generate the surface energy pattern. In this method, photolithography is used to pattern a photoresist layer deposited on a COC substrate, and GO is deposited on the COC substrate after exposing the pattern to oxygen/Ar plasma. The COC patterned substrate was then bonded to microchannels patterned on PDMS. They identified a three-step process for droplet coalescence that involves trapping, fusion, and detachment of the merged droplets. Their findings revealed that the fusion mechanism depends on the development of a thin water film on the surface of the GO-modified section of the channel, which is due to the hydrogen bonding between the oxygen-containing functional groups in the GO and water molecules. This film caused the trapping process to begin as a droplet passes through a pattern of GO. Furthermore, simultaneous fusion and transport of droplets was achieved by manipulating the relationship between viscous drag force and patterned surface energy.

In summary, the coalescence kinetics and mechanisms of EOR coreflow emulsions require further investigation. The droplet-based microfluidic platform holds a crucial role in visualizing and understanding the coalescence behavior of emulsions to develop highly efficient separators.

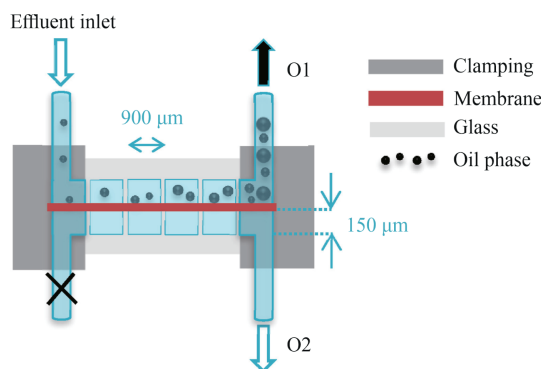


Fig. 19. Schematic of a microfluidic separator consisting of two microfluidic glass chips with a hydrophilic membrane in between for separating oil droplets from the aqueous phase. Reproduced with permission from Ref. [106]. Copyrights © 2022 Elsevier.

5. Outlook

While microfluidic platforms offer potential advantages for studying processes and mechanisms at the rock pore level, micromodels are considered two-dimensional porous media, making precise mimicking of the actual reservoir conditions a major challenge. Developments and improvements in microfluidic technology to address EOR challenges are continuously increasing, especially when it comes to mimicking reservoir temperature and pressure, wettability, fluid-rock interaction, and pore clogging.

Microfluidics can still offer more to EOR processes than understanding fundamental phenomena. Chemical flooding results in the formation of stable emulsions, due to the presence of surfactants, which will continue to be a problem in downstream processing. To avoid economic losses and operational problems, these emulsions must be destabilized before the crude oil is

transported or refined. Current demulsification methods for EOR emulsions mainly include chemical, physical, and biological methods. However, the kinetics, mechanisms and the factors affecting the demulsification process are not yet fully known. A promising application for the use of microfluidic platforms is to study the coalescence behavior and kinetics of surfactant-stabilized EOR emulsions to facilitate the separation process. Then, with the knowledge gained from these studies highly efficient micro-scale separators can be developed. There is a rich literature on controlling coalescence of emulsions in microfluidic platforms as discussed in section 4, which can be the basis for a new application of using passive methods in microfluidics to facilitate the coalescence of EOR effluent emulsions.

In addition, the integration of 3D printing technology with microfluidics has opened up new possibilities in the fabrication of complex microscale structures. By utilizing 3D printing technology, researchers can design and print intricate microfluidic devices with precise control over their geometry, channel dimensions, and surface properties. This customization allows for the creation of microfluidic devices that closely mimic the mineralogy and porous structure of oil reservoirs, enabling more accurate simulations and testing of EOR methods. For example, researchers have used 3D printing to fabricate microfluidic models that replicate the intricate pore networks and mineralogy found in reservoir rocks [111–113]. These models can be used to study fluid flow, displacement mechanisms, and the interaction between injected fluids and reservoir fluids to gain valuable insights into the behavior of different EOR techniques in order to optimize EOR strategies and improve oil recovery efficiency. Moreover, 3D printing enables the integration of multiple functionalities within a single microfluidic device. For instance, researchers have developed 3D-printed microfluidic devices that incorporate sensors for real-time monitoring of fluid properties, such as pH, temperature, and pressure [46]. These sensors provide valuable data for process optimization and control during EOR operations. While 3D printing has been successful in creating microfluidic devices with the desired pore structure, they often involve complex and time-consuming processes. As a result, there is a need for new, simpler techniques for fabricating 3D pore structure in microfluidics for EOR applications. Recently, we developed a new photolithography technique for fabricating microstructures in microfluidics using hydrocarbon swelling in cyclic olefin copolymer (COC) [114,115]. This technique involves using lithography to pattern the desired microstructure on a photoresist-coated substrate, followed by immersing the substrate in dodecane to create the desired structure in the COC. The hydrocarbon swelling technique in COC can be utilized to create a desired pore structure in the reservoir. This technique is simple, fast, and requires minimal equipment and can be performed in a laboratory setting. Additionally, it allows for the creation of a wide range of pore sizes and shapes, enabling the fabrication of microfluidic devices with a more realistic pore network to better mimic natural reservoirs.

Moreover, a research direction that is gaining momentum in microfluidics is the integration of artificial intelligence and microfluidic devices. This holds strong potential for optimizing EOR operations and increasing oil production rates. Using machine learning algorithms, researchers can analyze vast amounts of data generated by microfluidic experiments to optimize fluid flow in porous rock media. The automatic identification, categorization, and monitoring of specific fluids within microfluidic systems can be achieved using AI-based image analysis methods [116]. This provides valuable insights into the behavior of such fluids and facilitates the prediction of their performance. Another aspect is

the artificial intelligence-powered microfluidics which can be used to facilitate the optimization of injection strategies, optimization of chemical concentrations and combination, and fine-tuning of operating parameters, which can be utilized to improve the efficiency of oil displacement in reservoirs and potentially reducing costs and environmental impact. Finally, combining artificial intelligence with computational fluid dynamics techniques enables the development of predictive models that simulate fluid behavior in complex reservoirs to evaluate and optimize different enhanced oil recovery methods.

6. Conclusions

This review provided an overview of the current applications of microfluidics in the EOR process. We presented insights and premises for using micromodels to study various dynamics and mechanisms of fluid-fluid and fluid-solid interactions during the oil displacement process, and demonstrated the reliability and feasibility of implementing micromodels for EOR studies. The promising performance of these microfluidic platforms results from its ability to resemble the pore scale, the surface structure and properties of actual reservoirs, and the small space required to conduct the experiments. The convenience that the experiments can be repeated several times without damaging the microfluidic platform is also a major advantage. We also presented future research direction for the use of microfluidic systems for EOR applications in three domains, namely in designing passive micro-scale separators for destabilization of EOR emulsions, the use of 3D printing to mimic complex microscale structures of reservoir rocks, and the use of AI-microfluidic based systems for an optimized oil recovery.

Nomenclature

ASP	Alkaline/surfactant/polymer
COC	Cyclic olefin copolymer
Ca	Capillary number
DRIE	Deep reactive-ion etching
DSNW	Dispersed silica nanoparticles in water
EOR	Enhanced oil recovery
GSG	Glass-silicon-glass
GO	Graphene oxide
HDDA	Hexanediol diacrylate polymer
IOIP	Initial oil in place
IOR	Incremental oil recovery
IFT	Interfacial tension
LDW	Laser direct-write
MEOR	Microbial enhanced oil recovery
NOA	Norland optical adhesive
OPEC	Organization of the Petroleum Exporting Countries
OTS	Octadecyltrichlorosilane
OTES	Octyltriethoxysilane
PDMS	Polydimethylsiloxane
PMMA	Poly(methyl methacrylate)
PVT	Pressure/volume/temperature cell
PAA	Polyacrylic acid
Re	Reynolds number
SDS	Sodium dodecyl sulfate

CRedit authorship contribution statement

Fadi Dawaymeh: Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Elie Ayoub:** Formal

analysis, Writing – review & editing. **Maryam Khaleel:** Supervision, Writing – review & editing. **Nahla Alamoody:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

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

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