

A Review on Use of Emulsified Acids for Matrix Acidizing in Carbonate Reservoirs

Muhammad Mohsin Yousufi,* Mysara Eissa Mohyaldinn Elhaj, and Iskandar Bin Dzulkarnain

Cite This: *ACS Omega* 2024, 9, 11027–11049

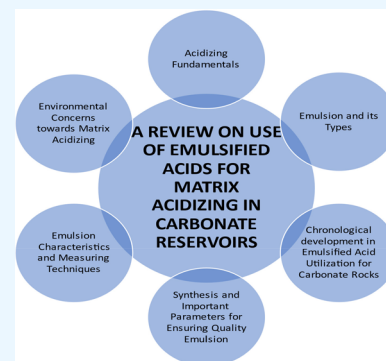
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Almost 60% of oil and 40% of gas reserves worldwide are contained in carbonate reservoirs where acidizing stimulation is more challenging compared to sandstone reservoirs. Utilization of emulsified acids in matrix acidizing operations has been the most effective technique for more than half a century. This is due to the colloidal system's ability to generate deep, narrow conduits toward production zones under controlled retarded reactivity with the rock surface, along with the excellent sweep efficiency and corrosion inhibition of the well equipment. This Review attempts to review the various kinds of emulsified acids that are used for matrix acidizing of carbonate formations. The Review is trying to trace the innovations that have, gradually, been applied for enhancing the performance of emulsified acids for a variety of conditions, their limitations, and the developmental solutions such hybrid emulsifiers and pickering emulsions. In addition, the Review also discusses the parameters, characteristics, and measuring techniques required for the successful synthesis of a stable and quality emulsion while considering the environmental concerns raised toward the application of an emulsified acid system. From the reviewed publications, it can be summarized that macroemulsions are best suited for matrix acidizing applications over microemulsions due to low emulsifier concentrations and high acid volume retention; similarly, water in oil emulsions provide better retardation in a comparison to oil in water emulsions. The small droplet size of the emulsion yields high viscosity and stability. The compositional balance between each component present in the acidizing system is a crucial factor for optimum performance. Moreover, for future practice, much focus is required to design emulsified acids as ecofriendly systems that can leave the least amount of toxicity during and after implementation.



1. INTRODUCTION

Almost 60% of the oil and 40% of the gas worldwide reside in carbonate reservoirs.¹ As the number of reserves is high in carbonate formations, so are the challenges in producing them. It is highly important to fully understand the reaction mechanism that takes place between the acid and the rock's surface to achieve a successfully controlled matrix acidizing operation.²

The process of acidizing is one of the oldest techniques used for well stimulation, dating back to 1895 when Frasch and Van Dyke observed a 300–400% increase in hydrocarbon recovery in a limestone reservoir via successful injection of HCl.^{3–6} The success of this operation, along with a few others, opened the doorway for matrix acidizing applications to be adapted by various companies.^{7–9}

This Review is intended to identify the key challenges involved in matrix acidizing of carbonate rocks. It is an effort to provide a roadmap for addressing the key parameters involved in the synthesis of emulsified acid. Furthermore, it highlights the functional properties involved in the development of a desired quality emulsion, their evaluation methods, and techniques. Finally, we discuss the environmental concerns involving emulsified acids and future recommendations for better utilization of acid emulsification.

2. ACIDIZING FUNDAMENTALS

Matrix acidizing can improve or restore permeability of the region near the wellbore without fracturing the formation. Matrix acidizing is most useful where shale break and natural flow boundaries need to be maintained to minimize gas and water production to yield a high percentage of oil production without an increase in gas or water production. The increase in permeability will reduce the pressure drop associated with injection or production of fluid by enlargement of the pore throat or removal of formation damage.

The production increase caused by acidizing depends on the reservoir pressure and whether the formation near the wellbore is damaged. In an undamaged formation, the permeability increase from acidizing will be insignificant; however, in the case of a damaged formation (naturally or artificially induced), permeability can be increased tremendously up to 10–100×

Received: September 17, 2023

Revised: January 30, 2024

Accepted: February 2, 2024

Published: March 1, 2024



upon damage removal. In exceptional circumstances, matrix acidizing treatments can give significant stimulation in undamaged zones. This can occur in naturally fractured formations where acid can travel along existing fractures.

In a producing well, a zone of damaged permeability near the wellbore chokes the converging radial flow and decreases production drastically. The goal of matrix acidizing is to achieve radial acid penetration into the formation by enlarging pore spaces or dissolving damaging particles from near wellbore zones.

Matrix acidizing for clastic and nonclastic rocks is different due to the difference in lithology, as acid has a different propensity for the two types. For sandstone, the purpose is to eliminate and minimize formation damage, while for carbonates it to bypass the formation damage via inducing wormholes (flow channels).¹⁰

The reaction between carbonate and acid is mass-transfer-limited, meaning that the acid consumption rate at the rock–acid interface is faster than the mass transfer. In sandstone it is reaction-rate-limited, as the mass transfer at rock–acid interface is faster than the reaction rate of the acid.⁵ This is because acid reacts more quickly with carbonates than sandstones, since carbonates have a fast dissolution rate and provide more mass for dissolution. In sandstone, only interstitial material is dissolved, while constituents such as quartz and feldspar have a very slow reaction with the acid. From here onward the focus will be more on carbonated rocks as per the scope of this Review.

Carbonate rocks have different dissolution rates from one another, which are dependent on lithology and temperature. Limestone is mass-transfer-limited at temperatures greater than 32 °F, while dolomite is mass-transfer-limited at temperatures exceeding 302 °F.^{11,12} In addition, dolomites are less ductile and have a slower reaction rate than limestone and often have multiple permeable zones. Matrix acidizing is not suitable for reservoirs with a porosity greater than 35% or for brittle formations such as chalk-based formations. Moreover, it is important to identify what type of rock is to be stimulated and the amount of heterogeneity in it, which allows for proper chemical selection and optimization during the design stage. Some carbonates rocks are pure, while others contain siliceous materials. The components may be precipitated chert, siliceous fossils, clastic grains of quartz, or shaly material. As the concentration of siliceous material increases, the rock is then classed as either sandy, cherty, or shaly limestone. Similarly, in the case of two carbonate rocks, limestone and dolomitic rocks, that might be interbedded, the calcium content of limestone may have been partially replaced by magnesium; thus, the rock would be classified as magnesian or dolomitic limestone.

A conventional form of matrix acidizing treatment uses 15–200 gallons of acid per foot. The acid is injected at pressures below the formation parting pressure. HCl is generally used in strengths from 5 to 15 wt % to remove carbonate and iron scales and as preconditioner for a mud acid (a combination of HCl and HF)-based treatment to treat clay damage and to remove drilling mud. A 15 wt % concentration of mud acid is utilized that contains hydrofluoric acid in concentrations of 1.5–3 wt %, while the rest is hydrochloric acid (12–13.5 wt %).

2.1. Acid Selection Factors. There are three interrelated chemical factors for the selection of an appropriate acid for a particular treatment,¹³ as presented in Figure 1.

2.1.1. Stoichiometry. Stoichiometry is the ratio between the reactants and reaction products of an acid reaction with reservoir materials. A parameter that helps in stoichiometry is the

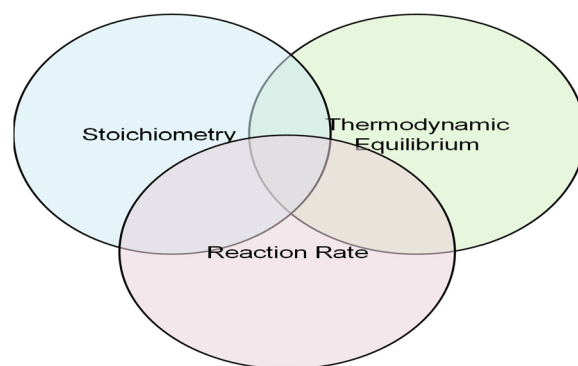


Figure 1. Interrelated chemical factors affecting the selection of an acid for a treatment.

dissolving power of the acid, as it reflects the capacity of an acid to dissolve a particular material. It depends on factors like the acid's concentration and strength and the nature of the material being dissolved. A higher dissolving power implies the acid can dissolve more material per unit volume.

2.1.2. Thermodynamic Equilibrium. Thermodynamic equilibrium is a state in a chemical reaction when the forward and reverse reactions occur at equal rates, resulting in no net change in the concentrations of reactants and products; this can limit the extent of the reaction and prevent complete utilization of the reactants. Thermodynamic equilibrium can be reached in many acid reactions before the acid is fully reacted, particularly in the case of organic acids reaction with limestone and dolomite formations. Equilibrium consideration controls the precipitation of reactant products that may negate treatment benefits in either carbonate or sandstone formations.

2.1.3. Reaction Rate. The reaction rate of an acid with a formation fixes the amount of time required for an acid to react. The time the acid takes along the reservoir geometry within which the reaction occurs allows for the estimation of the acid penetration distance.

1.2. Type of Acids Utilized in Matrix Acidizing. The acid used during any acidizing operation depends on various factors, such as temperature, stability, lithology, dissolving power, reaction rate, and the products formed using that acid. Acids are used either individually or as mixtures while keeping the conditions under consideration. In general, the acids used for any stimulation process belong to one of two types, namely, mineral and organic acids. Hydrochloric acid (HCl) and hydrofluoric acid (HF) are examples of mineral acids extensively used in industry. Organic acids that are prominently used are formic acid and acetic acid. In addition, industrially designed acids such chloroacetic acid and sulfamic acid have also been employed.¹³

Acidizing of carbonate rocks such as limestone (CaCO_3) and dolomite $\text{CaMg}(\text{CO}_3)_2$ is conducted utilizing hydrochloric acid. Hydrofluoric acid is not used on carbonate formations because it reacts in an unfavorable manner that creates insoluble calcium fluoride.

For sandstone formations, a mixture of hydrochloric acid and hydrofluoric acid, commonly known as mud acid, is used. Hydrofluoric acid can dissolve quartz and clay but is used in small amounts in the range of 1.5–3%. Hydrochloric acid, being nonreactive with sand or clay, is used for dissolving the calcite content present in sandstone and for maintaining a low pH level in the reservoir to prevent precipitates from forming due to hydrofluoric acid reacting with the formation.

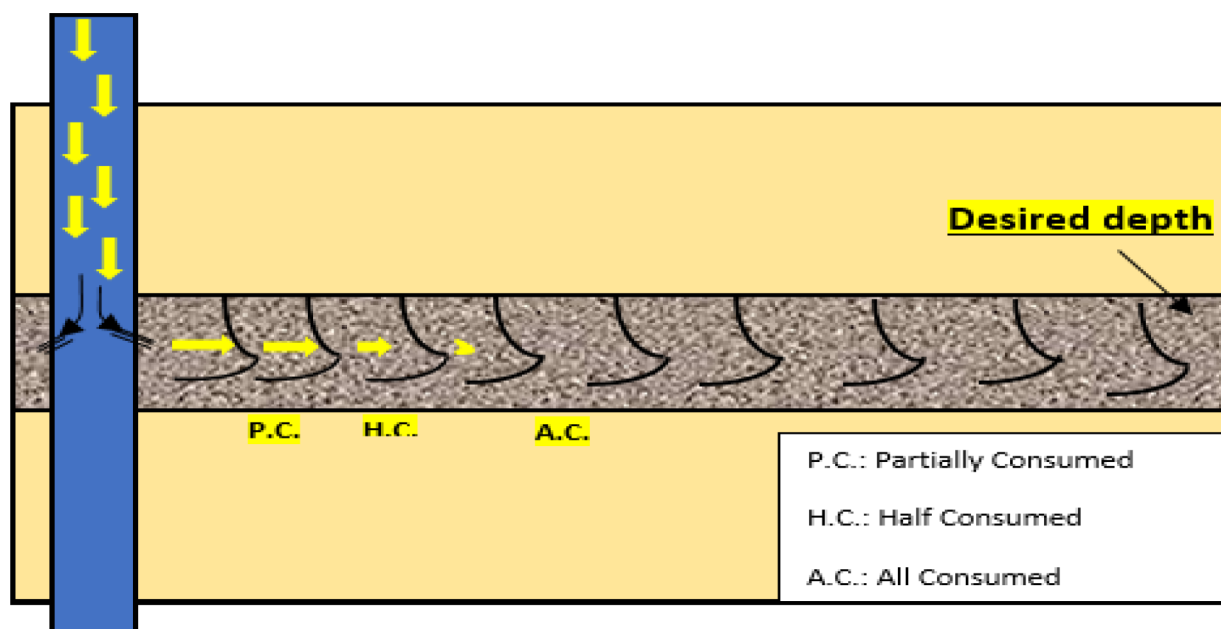


Figure 2. Conventional acid without a retarder performing matrix acidizing.

Formic and acetic acids are stable at high temperatures. Therefore, they are used in such conditions where the reactivity of hydrochloric acid increases and it cannot penetrate up to the targeted zone to create the flow conduit. Organic acids, however, have a major disadvantage of reaching equilibrium before being fully utilized. Moreover, acetic acid and formic acid have weaker dissolving power when compared to hydrochloric acid and are also expensive; hence, they are used in small quantities.

Industrially based acids are valued for their portability on account of preventing the excess use of transportation and pumping; however, they are costly and consequently are rarely used.¹⁴

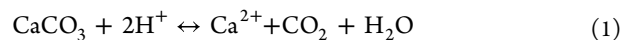
2.3. Matrix Acidizing Operation Stages. A typical matrix acidizing process is accomplished in five steps, namely, (i) wellbore cleanout, (ii) preflush, (iii) main acid treatment diversion, (iv) overflush, and (v) displacement.¹⁵

For a carbonate reservoir, wellbore cleanout is conducted to remove the precipitations like scale and rust and to dissolve wellbore deposits. Various sorts of additives such as mutual solvents, surfactants, and corrosion inhibitors are injected for this purpose. This is followed by a preflush, which is done to create an environment suitable for the main acid stimulation to be carried out satisfactorily. To do so, the preflush fluid creates a barrier between the formation fluid and the main acid fluid so that no emulsion or sludge is formed. After the preflush, the main acid treatment is introduced to create permeability in the reservoir as required. Since carbonates are highly heterogeneous and acid tends to move toward the highly permeable zones, diversion is required in some cases during the stimulation process so that the acid can be placed in low-permeation zones as well. After the main acidizing treatment, overflush is performed to remove residue of the stimulation reaction that may create hindrance. Finally, displacement takes place to ensure that the overflush fluid has reached the reservoir layers and that the flowback of the fluid is taking place efficiently.

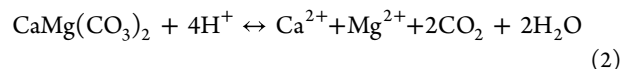
During stimulation, the acid–rock interaction takes place in three stages, as follows: (1) transfer of hydrogen ions (H^+) from the fluid to the rock surface where it spreads, (2) reaction of hydrogen ions (H^+) with calcite or dolomite, (3) generation of

products from the reaction, such as calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}), which travel from the rock surface to the fluids. The reaction with calcite and dolomite can be described by the following chemical reactions:¹⁶

For limestone:



For dolomite:



The slowest step in the reaction controls the reaction rate; this is where temperature is an important parameter to consider. At low temperatures, the reaction of the hydrogen ions (H^+) with the rock becomes slower than the other two steps involving transfer of reactants and products to and from the surface, while at high temperatures the diffusion rate of hydrogen ions (H^+) is responsible for the overall reaction rate, as the reactivity of the acid increases with the increase in temperature.¹⁷

2.4. Technical Concerns Involved in Matrix Acidizing.

In general, there are three major problems involved when conducting a matrix acidizing operation. The first problem is the highly reactive contact of the acid with the rock's surface. The second problem is fluid leakage during the flow because acid goes into natural fractures and thief zones, and the third problem is the formation of precipitates due to acidizing.

With regards to the first problem, reservoir rocks have a high reaction rate at high temperatures. As a result, a limited number of wormholes are generated. The acid gets consumed quickly during the initial stages of transportation from surface to the rock, and the wormholes cannot further form or reach the required depth because of the fast pace of the dissolution that occurs right on the rock's face.¹⁸

With regards to the second problem, fluid leakages are created due to the presence of natural or artificially induced high-permeation zones. These pathways cause acid loss in the initial

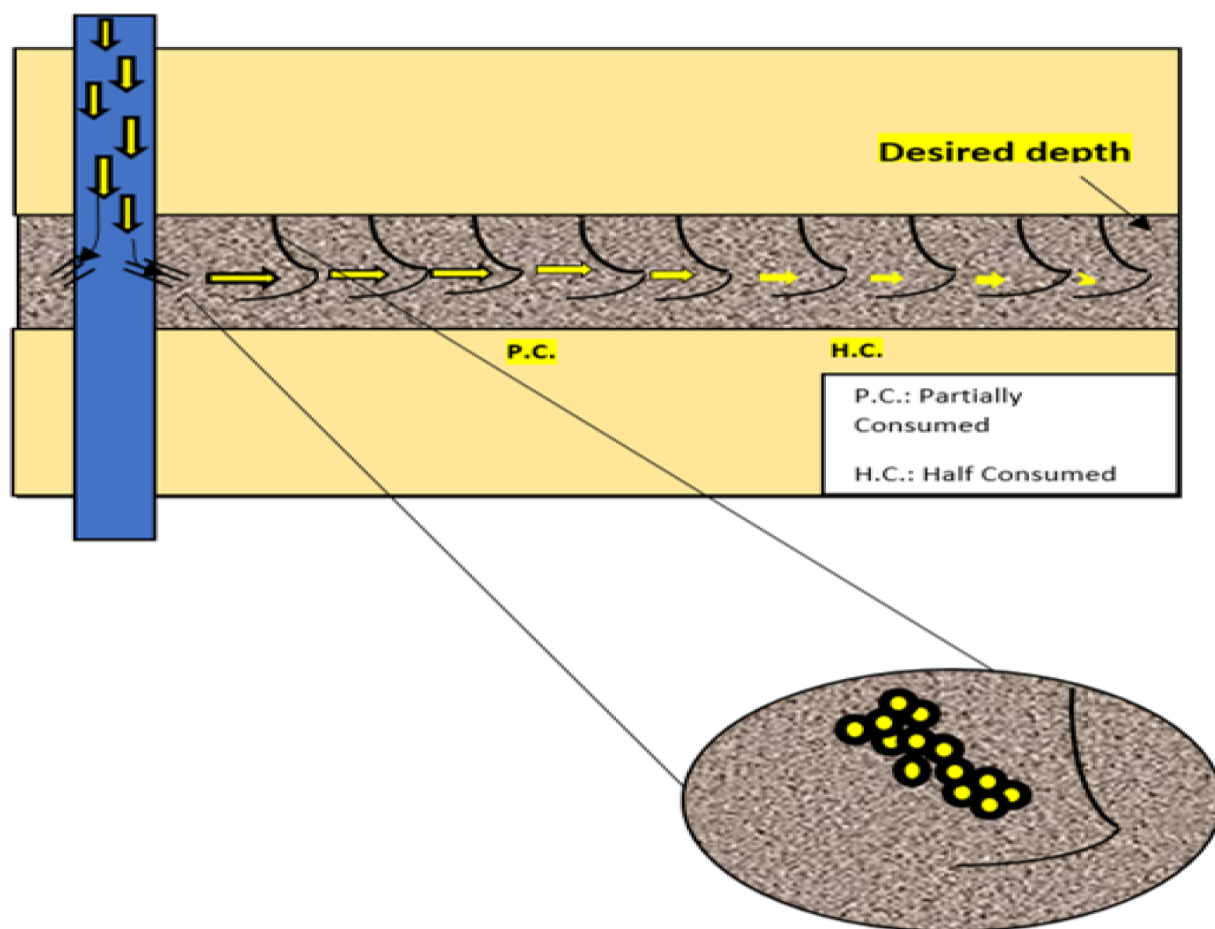


Figure 3. Retarded acid performing matrix acidizing.

stages of the stimulation process, which leads to the generation of low number of wormholes, and in some cases the desired depth is not reached. This is because acid's tendency to move toward high-permeation zones, due to which low-permeation zones are not supplied, and diversion methods are implemented. Mechanical diversion methods such as ball sealers and packers are expensive. Therefore, the use of chemical diverting agents is encouraged.¹⁹

In comparison to sandstone, the effect of precipitation is low in carbonates; still, the existence of precipitates is present, especially in the case of undamaged formations. During matrix acidizing, iron precipitates, asphaltenes, and various other sorts of deposits due to the reaction produce hindrance. This reduces the preexisting permeability of the formation rather than increasing it. That is why for undamaged wells acid fracturing is preferred rather than matrix acidizing. However, if fracturing is a major concern toward well stability, then matrix acidizing is adapted. Additives are used to prevent the formation of precipitates, such as surfactants, mutual solvents, scale and corrosion inhibitors.²⁰

To solve these issues, the acidizing fluid must have a linear and smooth flow and be viscous enough to act as a diverting agent for preventing fluid leakage. It must have a retardation effect to reduce the rate of reaction and must be able to prevent precipitates from forming.

2.5. Retarding Fluids. To minimize dissolution reaction between the acid and the rock surface, acid retardation is required. Figure 2 depicts the acidizing process in the absence of a retarding agent, which results in full consumption of the acid

before it reaches the targeted depth. Figure 3 describes the acidizing process in the presence of a retarding fluid, which helps allow the fluid to reach the targeted depth.

Different types of retarding fluids have been used throughout the years. The general types that are frequently used are as follows:

- (i) Gelled acids: These are used to slow down the rate of reaction between the acid and the formation via high fluid viscosity. Gelled acids are not able to work in high temperature conditions due to the deterioration of polymers used with the acid at temperatures above 130 °F.²¹ Due to their specific high viscosity, these fluids have high injection pressure requirements.
- (ii) Chemically retarded acids: These are made by adding oil-wetting surfactants to the acid in order to create a film that can separate the acid contact with the formation. A lot of oil is injected to maintain the barrier, thus making the material costly. At high temperatures the barrier starts to fade, so it is not adequate for usage under high temperature conditions.
- (iii) Chelating agent-based stimulants: These can reduce the iron precipitation rate, along with giving a retarding effect in stimulation of calcite. However, these additives have low dissolving power in comparison to hydrochloric acid and must be pumped in large amounts, which make their use uneconomical.²²
- (iv) Emulsified acids: These are nowadays considered as a major source of successful matrix acidizing operations due

Table 1. Screening of Retarding Acids for Matrix Acidizing

gelled acids	chemically retarded acids	emulsified acids
slow down the rate of reaction between acid and the walls of the formation via high fluid viscosity	surfactants create a film to separate the acid contact	give high viscosity, prevention against fluid losses, and retardation courtesy of emulsification of oil and water
due to high injection pressure requirement, gelled acids are seldom used in matrix acidizing	costly due to large volumes of oil usage	kinetically and thermally stable
gels have diffusion rates one magnitude lower than straight acid	at high temperatures the film starts to fade	emulsions have diffusion rates two magnitudes lower than straight acid

to their attractive characteristics. Their high viscosity prevents fluid losses. Emulsions have a retarding effect on the dissolution reaction due to the presence of oil. They also provides corrosion inhibition against the well equipment, which caters to low permeable zones, etc. Therefore, they have been used more frequently.

Table 1 compares different retarding fluids and presents the key features that make emulsified acids fit for matrix acidizing operations.

The following section of this Review provides a brief introduction about emulsions, their types relevant to matrix acidizing, and their application in carbonate formations from the start of its implementation to the recent developments.

3. EMULSION AND ITS TYPES

An emulsion is a mixture of two (or more) immiscible fluids (water/aqueous phase and oil phase) combined by an emulsifier.²³ An emulsion is classified on the basis of (i) droplet size of the dispersed phase, (ii) the dispersion medium, and (iii) the emulsifier used.

3.1. Emulsion Type Based on Droplet Size. In terms of droplet size, emulsions are classified into macro-, micro-, and nanoemulsions. The size range along with a visible difference in the turbidity of the fluid differentiates them from one another.

The emulsions mostly involved in matrix acidizing are either macroemulsions (1.5–100 μm droplet size), which have a milky white color, or microemulsions (3–50 nm droplet size), which have a transparent or translucent shade.²⁴ However, in some studies a fluid is considered to be a microemulsion if it has a droplet size less than 1 μm .²⁵ Coarse emulsions have until now been considered more cost efficient in matrix acidizing operations due to having low amount of surfactants and the ability to hold large volume of acid in contrast to microemulsions, which require large volume of surfactants for stability. Hence, very few publications^{26–28} created microemulsions, whereas research studies^{18,29–52} created coarse emulsions, as illustrated in Figure 4.

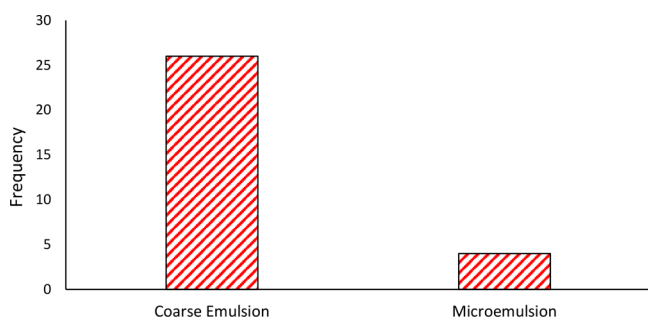


Figure 4. Graphical representation depicting the more favorable emulsion type as per size for matrix acidizing with respect to the literature review.

3.2. Emulsion Type on the Basis of the Dispersion Medium. On the basis of the dispersion medium, an emulsion can either be water in oil (W/O) or oil in water (O/W), depending on which fluid is the external phase and which is the internal phase. Water in oil emulsions provide better retardation due to the low diffusivity created by the oil phase around acid droplets, which allows for minimum acid volume contact with the rock-tubular surface. Thus, most research^{18,26,29–37,39,40,42–51,53} has adapted W/O emulsions due to their desirable retardation effect and corrosion inhibition in comparison to O/W emulsions,^{27,28} as depicted in Figure 5.

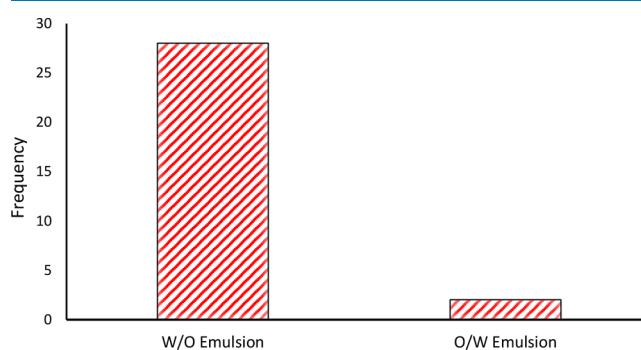
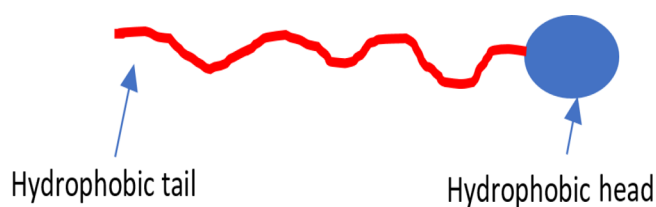


Figure 5. Bar chart representing the most suited emulsion based on phase behavior for matrix acidizing as per the literature review based on field application.

3.3. Emulsion Type on the Basis of the Emulsifier. An emulsifier is an integral component of the emulsion system; it combines the immiscible phases by lowering down the interfacial tension between them. There are mainly two types of emulsifiers: (a) surfactants and (b) pickering agents.

3.3.1. Surfactant-Based Emulsion. Surfactants are liquid-based molecular surface-active agents and have been the conventional emulsifiers in all fields dealing with emulsion synthesis for quite a while. Surfactants are needed in the synthesis of emulsified acids to reduce the interfacial tension between water and oil to make them miscible. Surfactants have a dipolar nature courtesy of the group of amphiphiles they are made from. Amphiphiles are compounds consisting of a hydrophilic head and a lipophilic tail that are responsible for solubilizing water and oil. (Figure 6). The surfactants mostly used in emulsified acid synthesis for well stimulation are categorized into three types: anionic, cationic, and nonionic.⁵⁴

- (i) Anionic surfactant: These are negatively charged surfactants. Anionic surfactants can be sulfates, sulfonates, phosphates, and phosphonates.
- (ii) Cationic surfactant: These are positively charged surfactants. The cationic surfactants are of two types. The first type consists of primary, secondary, and tertiary amines, which are only soluble in acidic solutions, while the second type consists of quaternary amines, which



Amphiphile

Figure 6. Structure of an amphiphile consisting of a hydrophilic head and an oleophilic tail.

solubilize in a wide range of pH solutions. When ionized, both types form long-chain cations.

- (iii) Nonionic surfactant: These types of surfactants do not possess any charge in their hydrophilic group, which is responsible for defining the charge of a surfactant; rather,

the interaction is governed by hydrogen bonding.⁵⁵ The lipophilic group consists of long carbon chains (C12–C18) derived from natural and petroleum oils or from fats and synthesized hydrocarbons. These are able to keep low interfacial tension between the acid and the oil; moreover, they are nontoxic and are used with other surfactant types strengthen their properties.

Both cationic and anionic surfactants are prone to precipitation caused by multivalent ions such as Ca^{2+} and Mg^{2+} present either in additives or released as reaction products, causing phase separation. Cationic and anionic surfactants are incompatible with one another as they tend to precipitate. These are combined with nonionic surfactants which themselves need small amounts of ionic surfactants to increase their cloud point; in turn, return nonionic surfactants enhance the performance of ionic surfactants, thus creating an emulsion that remains stable over longer periods. Moreover, both ionic surfactants are mostly toxic and do not easily degrade.

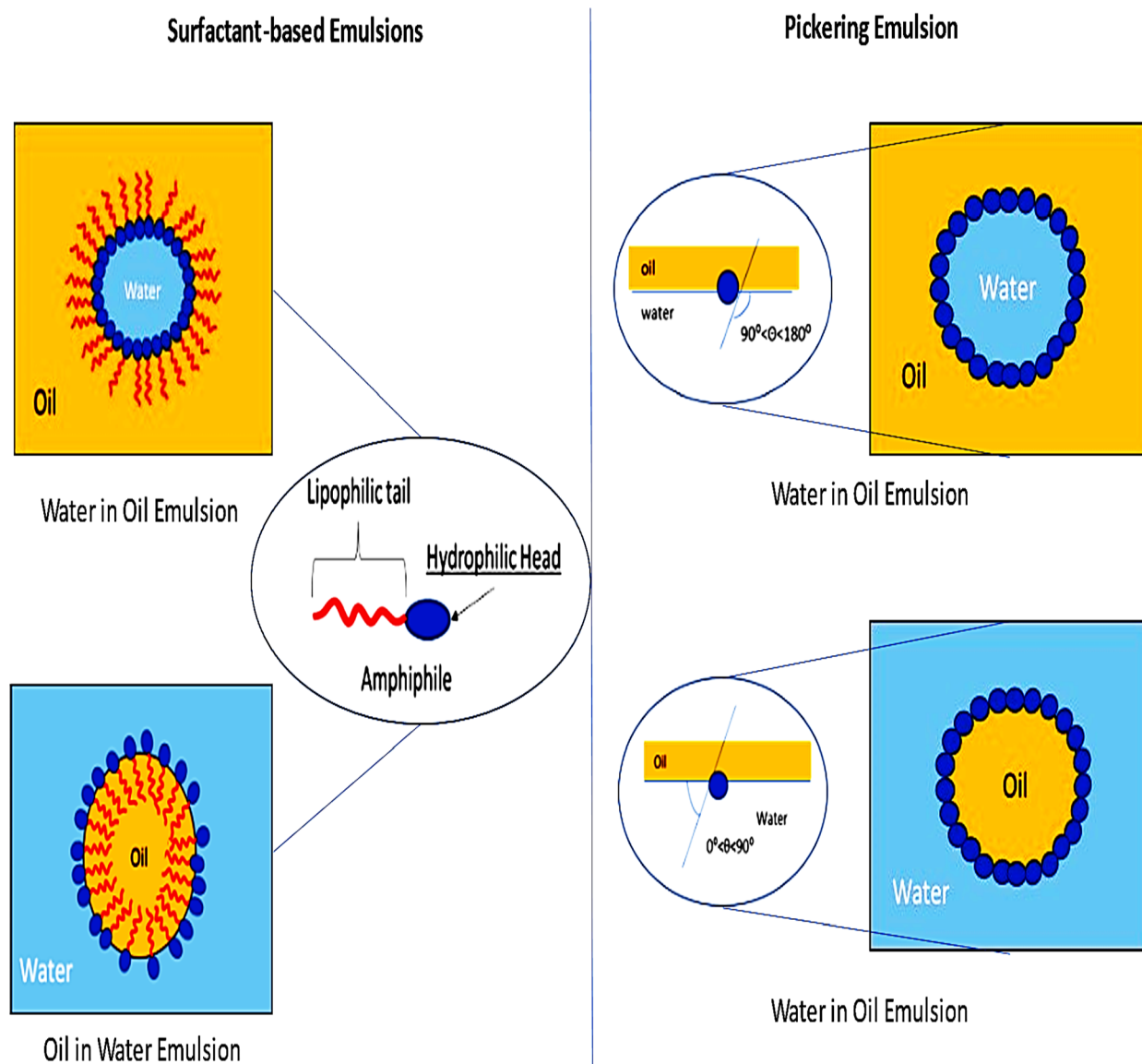


Figure 7. Illustration of the difference between surfactant-based emulsions and pickering emulsions with respect to the difference between the interfacial bonding mechanisms. Surfactants utilize clusters of amphiphiles and their respective HLB value to create a specific type of emulsion, whereas in a pickering emulsion the particle's wettability defines the type of emulsion formed.

Table 2. Chronological Table Highlighting the Progress Made in the Development of Emulsified Acids for Carbonate Rocks

s. no.	authors	emulsion type	composition	type of rock	outcomes
1	Groote, ⁷⁷ 1933	W/O	oil phase: crude oil aqueous phase: 15 wt % HCL emulsifier: asphalt/sulfonic acid	limestone	direct contact between acid and equipment was mitigated while successfully acidizing the formation
2	Davis et al., ⁷⁹ 1965	W/O	oil phase: kerosene aqueous phase: 15 wt % HCl emulsifier	limestone	long permeable conduits were achieved
3	Nierode and Kruk, ⁸⁰ 1973	W/O and O/W	oil phase: kerosene aqueous phase: 28 wt % HCl emulsifier: dodecylbenzenesulfonic acid, proprietary emulsifier		emulsified acids performed better in terms of viscosity, mobility, and retardation
4	Hoefner and Fogler, ⁸⁴ 1987	W/O	oil phase: dodecane aqueous phase: HCl emulsifier surfactant: cetylpyridinium chloride (cationic) cosurfactant: butanol	Damian Chalk	W/O microemulsion created a wormhole in finely grained calcite
5	Guidry et al., ²⁹ 1989	W/N ₂ /O 70:30	oil phase: lease oil aqueous phase: 10 wt % HCL additional internal phase: nitrogen (gaseous) emulsifier: emulsifying agent	limestone	double retardation effect due to nitrogen addition giving penetration depth greater than 20 feet
6	Al-Anazi et al., ⁴⁷ 1998	W/O 70:30	oil phase: diesel oil aqueous phase: 15 wt % HCl emulsifier: cationic surfactant	tight carbonate	permeability increased up to 9× due to smaller droplet size distribution
7	Buijse and Domelen, ⁴⁹ 1998	W/O 50:50, 70:30	oil phase: crude oil aqueous phase: 15 wt % HCl emulsifier	limestone	emulsified acid provided uniform dispersion toward lower permeable zones
8	Navarrete et al., ⁴⁸ 1998	W/O 70:30	oil phase: diesel oil aqueous phase: 15, 20, or 28 wt % HCl emulsifier	dolomite	6.6× more retardation in matrix acidizing and 14–19× more retarding in fracturing than HCl while providing high conductivities at 350 °F
9	Bazin and Abdulahad, ⁵⁰ 1999	W/O 40:60 50:50:00	oil phase: diesel oil (70%) aqueous phase: 7–15 wt % HCl emulsifier: petronate HH (anionic), IPE101 (nonionic)	limestone	increase in oil phase volume, reduction in the acid diffusion rate, and increase in acid concentration gave more penetration and less fluid consumption
10	Nasr-El-Din et al., ⁵¹ 1999	W/O 70:30	cosurfactant: alcohol oil phase: diesel oil aqueous phase: 15 wt % HCl emulsifier: cationic surfactant corrosion inhibitor chelating Agent (EDTA)	dolomite	permeability of the field wells was increased, and corrosion was reduced (iron precipitation) at 55 °C
11	Nasr-El-Din et al., ³⁰ 2001	W/O 70:30	reducing agent (Sodium erythorbate) aqueous phase: 15 wt % HCl emulsifier: cationic surfactant corrosion inhibitor chelating agent (EDTA)	dolomite	eleven vertical wells were fractured successfully, providing a significant increase in gas production

Table 2. continued

s. no.	authors	emulsion type	composition	type of rock	outcomes
12	Kasza et al., 2006 ³¹	W/O 50:50:00	reducing agent (sodium erythorbate) aqueous phase: 15 wt % HCl (70%) emulsifier (2%) corrosion inhibitor (0.2%) oil phase: diesel oil	dolomite	increased productivity index up to two folds while remaining stable at high temperature (248 °F) and pressure conditions
13	Sarma et al., 2007 ³²	W/O 70:30	aqueous phase: 15 wt % HCl emulsifier: surfactant 1 (4.3 HLB), surfactant 2 (15 HLB)	limestone	the synthesized emulsified acid provided effective stimulation having an increased retardation time at 203 °F
14	Nasr-El-Din et al., 2008 ³³	W/O 70:30	oil phase: diesel oil aqueous phase: 28 wt % HCl emulsifier: cationic (tallow amine acetate)	limestone and dolomite with streaks of anhydrite	emulsifier amount was reduced, along with time synthesis on field at 275 °F
15	Zhang, 2008 ²⁷	W/O and O/W 70:30	oil phase: diesel oil aqueous phase: 20 wt % HCl emulsifier: aliphatic ethoxylate alcohol (non-ionic) cetyltrimethylammonium ammonium chloride (cationic) cosurfactant: butanol, <i>n</i> -octanol	limestone	W/O microemulsion proved to be the most thermally stable and corrosion resistant
16	Fatah and Nasr-El-Din, 2010 ³⁵	W/O 70:30	oil phase: xylene aqueous phase: 15 wt % HCl emulsifier: nonionic surfactant corrosion inhibitor	limestone	asphaltenes were removed, and the well was stimulated without operational issues at 160 °F
17	Appicutoli et al., 2010 ³⁶	W/O 70:30	oil phase: xylene oil phase: diesel oil aqueous phase: 15 wt % HCl emulsifier	carbonate rock	the selected emulsion out of various solvent-based emulsified acids reduced acid reactivity and removed asphaltenes at 158 °F
18	Sayed et al., 2012 ³⁹	W/O	oil phase: diesel oil aqueous phase: 15 wt % HCl emulsifier: cationic surfactant with isopropanol and petroleum distillate	limestone with streaks of anhydrite	stimulation of low and high injection rates in varying permeability cores at 220 °F was achieved
19	Zakaria and Nasr-El-Din, 2015 ⁴⁴	W/O 70:30	oil phase: diesel oil (30%) aqueous phase: 15 wt % HCl (70%) emulsifier: partially hydrolyzed polyacrylamide (1.5 vol %)	Indiana limestone	polymer-assisted emulsified acid provided higher stimulation at low injection rates with effective diversion to low permeability zones
20	Sidaoui et al., 2016 ³²	W/O 70:30	oil phase: waste oil (30%) aqueous phase: 15 wt % HCl (70%) emulsifier: cationic emulsifier (1 vol %)		waste oil proved to be more economical and environmentally friendly than diesel oil
21	Tupā et al., 2016 ²⁸	O/W	oil phase: kerosene, xylene (alternatively used) Aqueous phase: 15 wt % HCl emulsifier: ALK90 Nonionic surfactants (ethoxylation grade 9), RNX110 (ethoxylation grade 11) cosurfactant: <i>sec</i> -butanol	limestone (Jandáira Formation)	the selected microemulsion increased the permeability to about 60%
22	Ahmed et al., 2018 ³⁸	W/O	oil phase: waste oil (30%)	Indiana limestone	a lower cost and more stable pickering emulsified acid was able to achieve narrow, branch-free, and deep wormholes comparable in performance to conventional diesel-based emulsion

Table 2. continued

s. no.	authors	emulsion type	composition	type of rock	outcomes
23	Carvalho et al. 2019 ⁸⁶	70:30 W/O, W/O/W, and O/W/O	aqueous phase: 28 wt % HCl (70%) emulsifier: nanoclays oil phase: kerosene and Solbrax Eco 175/235 aqueous phase: HCl emulsifier: ethoxylated nonionic surfactants Ultron L10, L20, L70 and L100 cosurfactant: propanol and butyl glycol		a stable microemulsion was obtained after thorough screening that was able to provide optimum retardation; however, acid volume was generally low
24	Yousufi et al. 2019 ⁸³	W/O 70:30	oil phase: jatropa oil, palm oil and diesel oil aqueous phase: 15 wt % HCl emulsifier: nonionic blend of Span80 and a proprietary linear alcohol-based nonionic surfactant (ethoxylation grade 9)	Indiana limestone	<i>Jatropha curcas</i> oil-based emulsified acid provided suitable performance comparable to the conventional diesel oil-based emulsion while reducing environmental concerns
25	Aly et al. 2023 ⁸⁹	W/O 70:30	oil phase: diesel oil aqueous phase: 15 wt % HCl emulsifier: solid nanoparticle	limestone	the pickering emulsion was evaluated in a large-scale radial testing facility. it provided a remarkably low-pressure differential during moderate and high injection rates with a sudden drop at the point of breakthrough with efficient wormhole generation. at low injection rates, differential pressure decline was slow
26	Mahmoud et al. 2023 ⁹⁰	W/O 70:30	aqueous phase: diesel oil emulsifier: (i) Claytone-SF (strong), (ii) Claytone-EM (medium), and (iii) Lapomite-EP (weak)		out of the three emulsifiers, Claytone-SF proved to be the most stable and shear thinning pickering emulsion up to 120 °C
27	Mohyaldinn et al. ⁹¹	W/O 70:30	oil phase: diesel oil aqueous phase: 15 wt % HCl emulsifier: cetyltrimethylammonium bromide (CTAB)		a shear thinning surfactant-based emulsion was synthesized. however, the emulsion formed failed to maintain long-term stability even at room temperature while utilizing large amount of surfactant concentration

With respect to the hydrophilic–lipophilic strength of the surfactant, a balance value known as the hydrophilic–lipophilic balance (HLB) of that surfactant is obtained, which helps in selecting the right surfactant for the required type of emulsion that needs to be formed. The lower range (4–7) of HLB creates water in oil (W/O) emulsions, whereas a high ranged value (8–18) gives rise to oil in water (O/W) emulsions.^{56–63}

The water in oil (W/O) system has a surfactant with a less hydrophilic nature. Oil gets dissolved as an external phase, and water becomes the internal phase. The water is in the center surrounded by oil bonded together by a low hydrophilic value-based surfactant. In contrast, oil in water (O/W) systems have a surfactant with a highly hydrophilic nature; therefore, water gets dissolved into it as an external phase and oil is in internal phase. In the case of emulsified acids, the aqueous phase is occupied by acid.

3.3.2. Pickering Emulsion. Pickering emulsions utilize fine-sized solid particles to emulsify the two immiscible phases. These particles create a steric barrier by arranging at the oil–water interface, and adherence of particles generates repulsion between the droplets that prevents coalescence.⁶⁴ The interfacial bonding between the particle and the two phases is very strong and thus the energy required for detachment of particles from the interface is very high; thus, the stability is far greater than that provided by surfactant mechanism.⁶⁵ Unlike surfactants, which bond to the immiscible phases via their hydrophilic head and lipophilic tail, in pickering agents the natural wettability (affinity) of the solid particles at the oil–water interface governs the phase placement in an emulsion. The wettability is determined by measuring the contact angle (θ) between the three phases (oil phase, aqueous phase, and solid particle). If $\theta < 90^\circ$, the O/W particle is hydrophilic. If $\theta > 90^\circ$, the W/O particle is lipophilic. If $\theta \sim 90^\circ$, a stable emulsion will be obtained,⁶⁶ as the energy required at 90° to stabilize an emulsion is minimum⁶⁷ and the solid particle is partially wettable by both the surface; therefore, equilibrium bonding is achieved. Particles forming low contact angles have affinity toward the droplets and thus are unable to stop coalescence of the droplets. Particles that are partially hydrophobic ($\theta \sim 90^\circ$) provide better stability, as these particles have affinity for both aqueous and oil phase (i.e., are partially wettable) and act as a barrier between them. This barrier prevents the droplets' coalescence^{68–70} and Ostwald ripening.^{71,72} Figure 7 highlights the difference between surfactant-based and pickering emulsions because of the difference between the wettability mechanisms.

However, individually in different cases individual emulsifiers fail to provide the desired emulsification needed due to concerns such as degradation (especially in the case of surfactants and polymers), shear resistance, and wettability, which arise because of harsh subsurface environmental conditions such as high temperature, pressure salinity, and pH. As a result, the implementation of hybrid emulsifier emulsions that utilize a combination of either surfactants, polymers, or particles achieves a synergistic effect, overcoming the sole drawbacks of emulsifiers while using very minimal concentrations of each.^{55,73–75} For instance, the use of polymers as part of the emulsifiers makes the continuous phase more viscous and generates a structural network to mitigate coalescence.⁷⁶

4. CHRONOLOGICAL DEVELOPMENT IN EMULSIFIED ACID UTILIZATION FOR CARBONATE ROCKS

This section discusses the chronological advancement in emulsified acid systems for matrix acidizing of carbonate formations. The discussion includes attempts made toward developing various forms of emulsified acids, such as macroemulsions and microemulsions, as well as the utilization of different forms of emulsifiers, which can provide better performance under reservoir conditions. Table 2 highlights and summarizes these developments more precisely.

4.1. Macroemulsified Acid. De Groot⁷⁷ (1933) was the first to use emulsified acids, focusing more on preventing corrosive reaction of hydrochloric acid with the subsurface equipment. The use of inhibitors was minimized due to the ability of the emulsion to barricade acid from the well tubing, thus slowing down its reactivity. During the process, the emulsified acid was injected from the surface downward for the purpose of preventing the well tubing from having direct contact with the acid. The constituents of the water in oil emulsion for this stimulation process consisted of 15 wt % hydrochloric acid as the aqueous phase, crude oil as the oil phase, and oil-soluble sulfonic acid or petroleum asphalt as an emulsifier. The water to oil ratio was 1:2.

Harris⁷⁸ (1961) reported the application of acetic acid as an aqueous phase amalgamated with crude oil as the oil phase for well completion and stimulation.

Davis⁷⁹ (1965) used an emulsion to attain maximum penetration depth by reducing fluid loss occurrence and slowing down the reaction of the acid with the formation. A preflush of water carrying fluid loss additives was injected, right after which an emulsified acid solution consisting of (10% by volume) kerosene, 15 wt % hydrochloric acid, and an emulsifier were introduced. The emulsified acid would thicken up meeting the spearheaded water; thus, demulsifiers were mixed in water to maintain the required mobility and viscosity to reduce acid consumption and allow long permeable conduits to be formed.

Nierode⁸⁰ (1973) tested out the effectiveness of water in oil and oil in water emulsions against hydrochloric acid and gelled and chemically retarded acids in terms of fluid loss reduction and reaction retardation. It was observed that emulsified acids had the desired viscosity for preventing fluid losses and exhibited better retardation capabilities compared to other retarding fluids at high temperatures.

It was further observed that water in oil emulsions give better retardation and penetration depth than oil in water emulsions as a result of having oil as an external phase, which provides more hindrance between the acid and the formation. According to this study,⁸⁰ when a 28 wt % concentration of hydrochloric acid is used, a water in oil emulsion has a retarded dissolving power equal to 18 wt % hydrochloric acid, whereas the retarded dissolving power of the oil in water emulsion is half that. Apart from the study of stimulation fluids, closure stress was also highlighted as a force that reduces or shuts down the induced permeable conduits and must be considered during the design of stimulation process. The chemicals used were 28 wt % hydrochloric acid and kerosene as aqueous and oil phases, respectively, in varying ratios to one another for each of the three emulsions: one had acid as an external phase along with a proprietary emulsifier, while the other two possessed oil as an external phase and had dodecylbenzenesulfonic acid or the proprietary emulsifier as the surfactant, respectively.

Guidry²⁹ (1989) came up with a modified version of emulsion acidizing fluid. Referred to as an energized emulsion fluid, it consisted of nitrogen (droplet size of 200 micrometers) along with a dispersed acid (droplet size of 20 micrometer) in a continuous oil phase. This system imposed higher retardation of the acid–rock reactions because of nitrogen's higher energy level of compressibility over acid to contact the formation. As a result, a double retardation effect via an external oil phase and nitrogen allows energized emulsified acid to achieve a penetration depth greater than 20 feet, making it more cost-effective in comparison with regular nonenergized emulsions due to consuming less fluid for an equal etching depth.

Al Anazi⁴⁷ (1998) used a water in diesel oil emulsion for stimulation of a tight carbonate reservoir. The reservoir had not responded to regular hydrochloric acid of 15 wt %. It was observed that the water-in-oil emulsion having a droplet size of 77 μm dominated, created a deeper wormhole rather than shallow etchings such as those generated by regular hydrochloric acid. This resulted in improving the core permeability up to 9 \times in comparison to hydrochloric acid, which only refined it twofold. The corrosion inhibition ability of the emulsion minimized the use of a corrosion inhibitor. A major contribution apart from this application was that the number and size of wormholes were concluded to be a function of the injection rate, which was previously ambiguous. The higher the injection rate affect the size of the wormhole induced, and the number of wormholes generated is also increased.

Another useful coarse emulsion synthesis was presented by Buijse⁴⁹ (1998) for use in carbonate formations at temperatures up to 250 $^{\circ}\text{F}$. The outcome of the process was not only the use of emulsion as a deep penetration medium but also its implementation as a diverter because of the emulsion's high viscosity, which allows it to cater to low-permeability zones. The study compared straight and gelled acids with emulsified acids. Superiority of the emulsion was proved in terms of decreased fluid consumption, a reduced number of post treatment products, and the possibility of pumping at a low injection rate. The retardation in acid reactivity was found to be more effective because diffusion depends on mobility of the dispersed phase droplets in the continuous phase rather than the aspect of molecular diffusion as in other fluids. Biodegradability was proposed to be achieved by substituting conventional oil phase with an environmentally friendly oil.

The study⁴⁹ also gave a comparative analysis between a microemulsion and the synthesized coarse emulsion. Buijse reported that the diffusion retardation and wormholing capability of the two fluids are almost the same. However, he recommended coarse emulsions to be more financially viable due to the microemulsion's limitation of hold a low acid volume (<30%) and its need for a large amount of emulsifier (>20%) compared to coarse emulsion, which is able to hold high quantities of acid (>80%) and requires a lower volume of emulsifying agent (<3%).

Later in the same year, Navarette⁴⁸ (1998) designed an emulsion that was capable of being stable at temperatures up to 350 $^{\circ}\text{F}$. The emulsion formed was a coarse emulsion having a droplet size larger than a microemulsion, with distribution varying between 1 and 77 μm . The proposed system allowed the study of the difference in wormhole generation between straight acid and a retarded emulsion-based acidizing fluid. Similar to ref 47, Navarette also observed the emulsion's low reactivity with the surface of the formation, which allowed for an extended conductive path to be made while reducing the volume of fluid

used at ambient and high temperatures. The diameter made by emulsion was smaller than that made by regular acid, and as evident from Nierode's work⁸⁰ wide wormholes are prone to fast closure under the influence of high closure stresses, rendering the stimulation futile. Narrow wormholes were generated by emulsified acid, which remained open due to decreased face dissolution.

As observed by Buijse,⁴⁹ Navarrete also pointed out that microemulsions, although effective, are uneconomical due to large amount of surfactant used; hence, a coarse emulsion is a better option for field applications.

Another investigation of Buijse⁴⁹ was conducted by Bazin⁴⁶ (1999), who evaluated the effect on wormhole propagation with respect to injection rate by comparing straight and gelled acids with emulsified based acids. It was concluded that an optimum injection rate for wormhole propagation is the least amount of fluid to achieve a breakthrough. This was achieved by emulsified acid that provided a high injection rate over gelled and straight acids. It was also stated that the mere increase in concentration of acid after an observed optimum value did not significantly increase wormhole penetration. However, Bazin contradicted this point in his very next paper the next year,⁵⁰ in which he agreed with increasing acid concentration to achieve a high penetration distance.

As stated above, one year later Bazin⁵⁰ compared emulsions of various compositions to evaluate the effects on stability, viscosity, and propagation. The emulsions were compared with plain acid for their ability to produce long conduits using a minimum volume of fluid, as stated prior by Buijse.⁴⁹ The stability of the emulsion was observed to increase with the increase in oil content; however, after a certain increase in oil concentration, the retardation effect does not increase. Increasing the concentration of acid would increase the propagation, but adding more volume of acid will not increase the breakthrough time of the emulsion. Bazin favored the capability of regular hydrochloric acid to form wider channels rather than the narrow deeper ones as formed by emulsified acid, which provided more open channels. Thus, he neglected the impact of closure stresses, which collapse the wide face conduits made by regular hydrochloric acid.

After having success with emulsified acid in tight carbonates, Nasr-El-Din⁵¹ (2001) used them in disposal wells that suffered from injectivity losses. The study focused on observing the effect of change in surfactant concentration on the stability of the emulsion under reservoir conditions of 131 $^{\circ}\text{F}$. Apart from injection rate,⁴⁷ two new parameters, namely, acid volume and initial core permeability, were discovered to be responsible for affecting the size and number of wormholes induced.

Nasr-El-Din³⁰ discovered a new use of emulsified acids in deep wells consisting of sour gas. Application of both fracture and matrix acidizing was involved in this case scenario. The emulsified acid, in comparison to hydrochloric acid, proved to be capable of forming straight wormholes irrespective of the varying amount of hydrogen sulfide (H_2S) present in the well while providing corrosion resistance and stability at a high temperature of 275 $^{\circ}\text{F}$.

After observing a failed stimulation operation using a solution of hydrochloric acid and acetic acid in a well, which due to the high temperature of 248 $^{\circ}\text{F}$ had a limited reaction rate that was sufficient only for well cleaning, Kasza³¹ (2006) synthesized a water in oil emulsion using the crude oil from the field as an oil phase to reduce the cost and overcome this failure. The emulsion had a 50:50 acid to oil ratio with 0.2% corrosion inhibitor and

2% emulsifier. The emulsified acid remained stable for up to 180 min under high temperature and pressure conditions and increased the oil production on the pilot well up to two times.

Sarma³² (2007), investigated the effect of emulsifier content and temperature on the stability of the emulsion by studying a coarse emulsion of water and oil consisting of 15 wt % hydrochloric acid and diesel oil. It was emphasized that emulsion's stability depends on the quality of the surfactant used. Sarma recommended that a blend of two surfactants, one being highly hydrophilic with a HLB value of 15 and the other being lipophilic with a HLB value of 4.3, can be utilized to obtain an emulsifier of 5.1 HLB value, which provided a stronger bond between the aqueous and oil phases. It was observed that a water in oil emulsion provided better retardation than an oil in water emulsion. A 70:30 ratio of water (acid) and oil was selected because the low amount of oil consumption made it economically viable and also provided better mobility and coverage. At 203 °F, the emulsion with 1.5% surfactant concentration provided 93–95% dissolution of the rock in 25 min, while the emulsified acid having 2% surfactant concentration provided the same percentage of dissolution with a retardation time of 30 min. This signifies that the retardation impact increases with the increase in surfactant concentration.

Nasr-El-Din³³ (2008) designed a highly stable emulsion that utilized a new type of cationic emulsifier consisting of a long carbon chain of C₁₂–C₁₈ which gave a better oil solubility. This provided a smaller droplet size of 35 μm. The emulsifier was made from tallow amine acetate that required merely a quarter of the amount of the previously used cationic emulsifier, which had a smaller carbon chain and a larger droplet size of 69 μm. The highly viscous emulsion remained stable from ambient temperature to 275 °F. The application of this new emulsified acid yield increased the oil production rate up to 34%. Due to high solubility, the synthesis was much easier and less time-consuming. Even though this was meant for fracture acidizing, the development meant taking a step further in the use of emulsion for other well stimulation operations such as in matrix acidizing.

Fatah³⁵ (2010) came up with a multipurpose emulsion consisting of xylene as the oil phase in a water in oil emulsion for removing asphaltene and improving the permeability of the well. Previously, the asphaltenes were removed by the aromatic-based solvent, which was an entire operation itself, after which well stimulation took place. The advantage of xylene as an external phase of the emulsion was that it could remove the asphaltene content, after which the internal phase of acid would dissolve the carbonate. The stability and viscosity of the emulsified acid were checked at ambient temperature as well as at a formation temperature of 160 °F. Although it had lower viscosity and stability than diesel, xylene performed both the services in one job.

Similar to Fatah's work,³⁵ Appiciutoli⁸¹ (2010) synthesized a 70:30 acid to oil ratio emulsion for an environmentally challenging zone, which had a high priority for health and safety measures, especially with the exposure of chemicals to the atmosphere. The emulsion had to not only stimulate at low injection rates but also remove asphaltenes. A number of oil-based solvents, excluding diesel, were tested for the oil phase in comparison with toluene for the solubility of asphaltenes. The main reason for not using diesel as an oil phase was because of its high tendency to react with formation oil, causing it to become unstable and inducing asphaltene. The selected emulsion removed asphaltenes, reduced the reactivity of the acid, and

remained stable in bottomhole conditions of 158 °F as well as at ambient temperature. In addition, the emulsion gave a faster feasible mixing and pumping on field, fulfilled the health and safety requirements, and increased the production rate.

Xiong³⁴ designed an emulsified acid to stimulate formations having a high water content due to water flooding. Formation sections having a high water content mostly have improved permeability because the rock surfaces have a hydrophilic nature. During stimulation, conventional acid-based emulsions are attracted toward the rock surface and do not enter hydrophobic zones containing hydrocarbons. As a result, the permeability of these zones remains the same. The novel water in oil emulsified acid created by Xiong consisted of a combination of hydrochloric acid and fluoroboric acid (HCl and HBF₄) with diesel in a 70:30 water to oil ratio. Fluoroboric acid enhances the retardation reaction with the formation, and products made are capable of stabilizing the clay of the rock's surface rather than causing an abrasive effect. The emulsified acid further emulsifies after encountering water-bearing zones, directing itself toward low-permeation zones automatically. The core flooding tests resulted showed a sufficient increase in the permeability of oil-bearing zones, while a minor increase in permeability was seen in water-bearing regions. Although this stimulation process was for sandstone, the diverting capability of the emulsified acid is worth looking into for future development and implementation in carbonate rocks.

Sayed³⁹ introduced an emulsified acid consisting of a cationic surfactant, isopropanol petroleum distillate (which was only 1.0 vol % in the system), and 15 wt % hydrochloric acid (diluted in deionized water having an 18.2 MΩcm resistivity). The hydrochloric acid was titrated with a 0.1 N sodium hydroxide solution. Special measures were taken to have zero electrical conductivity for the water in oil emulsion. The emulsifier was designed to work at temperatures of up to 220 °F. The proposed system gave an optimum injection rate in the range from 5 to 7 cm³/min, with inducing no face dissolution at low and high injections of up to 10 cm³/min.

Sidaoui⁸² substituted a diesel oil phase with waste oil, as it is less costly and more environmental friendly. The acid in waste oil emulsion consisted of 15 wt % hydrochloric acid, with a cationic emulsifier concentration of 1 vol %. The water to oil ratio was 70:30. The emulsion was tested at various temperatures for droplet size distribution, with a droplet size range of 1.47–3.09 μm dominating, which in comparison to diesel oil was much smaller and thus gave better stability. Apart from waste oil, triglyceride oils were considered as potential replacements for diesel oil in emulsified acids. Jatropha and palm oil-based emulsions were comparatively analyzed against diesel oil-based colloidal acid; the jatropha oil-based system performed comparatively similar to the conventional diesel-based emulsion and upon screening showed a lower toxicity value.⁸³

4.2. Microemulsified Acids. The use of microemulsions specifically in matrix acidizing first started with Hoefner and Fogler,²⁶ who successfully stimulated Danian chalk, which is a naturally grained soft pure calcite and has a low permeability. It was not favorable to perform fracture acidizing on Danian chalk, and it was unresponsive to conventional acidizing by hydrochloric acid. Due to the retardation ability of emulsions, a microemulsified acid was synthesized and tested on the Danian chalk. It was observed that the microemulsion had a diffusion rate magnitude twofold lower than that of regular hydrochloric acid.

Hoefner and Fogler⁸⁴ differentiated between microemulsions and the emulsions of oil and water that were being used before. Since microemulsions have a very small droplet size, they tend to act as one phase when passing through the pores, thus presenting no relative permeability flow. Coarse emulsions, on the other hand, have an average droplet size larger than the pore throat diameter if they flow as a two-phase fluid, thus having a relative permeability effect. Reservoirs consisting of interconnected pore spaces are often require to be connected. This can be done by stimulants having a delayed spending capability of acid to allow live acid placement further from the wellbore to stimulate such zones. As the fluid cannot exist in pores having a smaller size than the fluid droplet size, the microemulsions have an edge over macroemulsions in such cases. The microemulsified acid developed was a water in an oil-based system having a droplet size of 10 nm (micelle state), which yielded an increase in permeability at low flow rates, along with having decreased fluid consumption and giving a greater acidizing depth.

An alcohol in acid microemulsion was developed and patented for well stimulation treatments by Gardener.⁴⁰ It was an innovative method of using a microemulsion consisting of alkyl alcohol as a replacement for crude oil as an oil phase. The patented work was designed to be compatible with various sorts of acids, alkyl alcohols, and emulsifying agents. The compositions were compared with other reference microemulsions and gave similar results.

Zhang,²⁷ following the work of Zhao,⁸⁵ designed a water in oil and oil in water microemulsified acid system, with an acid to oil ratio of 70:30 and a mean droplet size of 10 to 30 nm. The emulsion utilized merely 8% emulsifier concentration in comparison to the emulsifier concentration of 20% used by Zhao.⁸⁵ The emulsifier consisted of a combination of cationic and nonionic surfactants with butanol as a cosurfactant. The use of such a low amount of surfactant was intended to present the microemulsion as an economically feasible solution for well stimulation. The microcolloid showed great retardation ability when tested on calcium carbonate cores and optimum corrosion inhibition when tested with N-80 steel coupons.

Aum²⁸ designed an oil in water microemulsion system for carbonate acidizing by using 15–18.3 wt % hydrochloric acid, with oil phases such as xylene and kerosene and butanol as a cosurfactant. Two systems were tested. The first system (system 1) had a surfactant of ethoxylation grade 9, and the other system (system 2) had a surfactant of ethoxylation grade 11. Xylene was selected out of the two oils for both the systems because it has a longer aqueous phase region due to the increased solubility of the surfactant. The microemulsions were found to perform corrosion inhibition better than regular hydrochloric acid. The droplet size of system 1 (80–133 nm) was smaller in comparison to the droplet size of system 2 (158 to 183 nm), thus giving a more stable emulsion. The dissolution rate of both systems was found to be better than that of conventional 15 wt % hydrochloric acid, which rapidly reacts with calcium carbonate up to 90% within 55 s; in comparison, system 1 reacted up to 95% with the carbonate rock after 1413 s, and system 2 dissolved the same amount in 396 s. The increases in permeability by systems 1 and 2 were 57% and 59%, respectively, without any face dissolution, whereas regular hydrochloric acid increased permeability 120% but caused a major face dissolution. The system of oil in water microemulsion was found not cost-effective due to amount of emulsifier required for synthesis (25–37%).

Similarly, microemulsions were evaluated⁸⁶ using kerosene and Solbrax ECO in combination with nonionic surfactants. A stable emulsion with a fine retardation capability was attained; however, due to the high emulsifier content, the emulsion was able to retain a low acid volume.

4.3. Polymer-Assisted and Pickering Emulsions.

Utilization of nanosized particles (pickering emulsion) for increasing the stability of an emulsion was patented by Huang and his team in 2012⁸⁷ for treating subterranean formations at temperatures of 200 °F. The system consisted of acids (10% or more in concentration), an oil phase, an emulsifier, and acid-insoluble nanoparticles of varying ranges and types (as per the required condition). The nanoparticles could be of montmorillonite- (high purity clay), quartz-, tungsten oxide-, or even carbon-based, such as nanosized graphite, graphene, and carbon nanotubes, and could be used either individually or in an amalgamated form. Due to the small size, these particles would stabilize the emulsion by connecting the different phases with one another more strongly. The most important benefit of this work was the use of any acid or oil for the synthesis, especially mentioning triglyceride-based oils, which promote the use of an environmentally safe fluid for well stimulation.

Emulsified acids, as mentioned previously, are used because of their lower diffusion and retardation rate when compared with gelled acids. Emulsified acids also provide appropriate viscosity for easy flow of the stimulating fluid. However, it is often necessary to inject gel (polymer)-based diverting agents in preflush to achieve better acid placement in highly permeable formations and increase permeability in less permeable zones. For such cases, Zakaria,⁴⁴ created a polymer-assisted emulsified acid. The gelled acid-based emulsion consisted of a gel polymer having a concentration of up to 1.5 vol % in the internal phase along with the 15 wt % acid. Diesel oil was used as the oil phase along with a cationic surfactant. The droplet size of the emulsion became smaller because of the addition of polymer. As a result, the viscosity and stability of the emulsion increased. The diversion of the acid was observed by placing two cores of different permeability in such a manner that the acid could move in either of the cores at a temperature of 230 °F. The polymer-assisted emulsified acid increased the permeability of the low-permeability core much more than that of the high-permeability region. The acid ran only a quarter of the volume of the high-permeability core, whereas in the low-permeability core it moved through the whole length, achieving a breakthrough. Thus, the diversion along with stimulation was effectively achieved by polymer-assisted emulsion.

Following the Sidaoui's work,⁸² Ahmed⁸⁸ utilized waste oil along with nanoclay as stabilizing agent, as done by Huang,⁸⁷ instead of surfactant to further reduce the cost and increase emulsion stability at 190 °C. The emulsion performed well, requiring a lower pore volume of acid to break through and generate a narrow, deep, and branch-free wormhole at high injection rates compared to the diesel oil-based colloidal system at 135 °C. The utilization of nanoclay (organoclay) was further investigated on a large experimental scale⁸⁹ and was later upscaled for openhole wellbore field stimulations. Radial testing on a Saudi limestone outcrop (dimensions of 20 × 16 × 16 in.) was conducted at ambient temperature. Successful wormhole generation was observed while exhibiting an exceptionally low-pressure differential during moderate and high injection rates, with an immediate drop at the breakthrough point and a smooth decline in pressure differential at low injection rates. Further exploration of different clay-based emulsifiers has cemented

their superiority over surfactants, with the results yielding emulsified acid with excellent stability and shear thinning behavior.⁹⁰

5. SYNTHESIS AND IMPORTANT PARAMETERS FOR ENSURING QUALITY EMULSION

The process of emulsification is normally achieved by shear mixing the two immiscible fluids with the aid of an emulsifier. This can be done by using either a magnetic stirrer (for low volume samples) or a mixer/homogenizer (for high volume samples and highly viscous samples); homogenizers are best at breaking down the dispersed phase into a finer size in the continuous phase, providing a more solubilized strong colloid system.⁹²

Emulsion stability is governed/influenced by certain factors during the synthesis process, and these vary with means used for emulsification/mixing. Al Mutairi⁹³ described the challenges faced and the factors affecting the synthesis of an emulsion. The focus was on the effect of droplet size, which affects the surface area, interfacial tension, viscosity, and stability of the emulsion. He recommended that the factors that altered the droplet size were addition rate, speed, emulsifier concentration, and acid volume. It was pointed out that rapid addition of acid to the diesel and emulsifier mixture would produce coarse emulsions having large droplet sizes. Thus, to produce a fine emulsion, acid must be added gradually drop by drop. In this way, droplets can be encapsulated in the continuous phase homogeneously. The emulsifier concentration and acid volume affect the droplet size in opposite ways. Emulsifier concentration technically has a high impact, as an increase in its value increases the dispersion of the discrete phase; however, after a certain increase in emulsifier concentration there is no significant change in droplet size and moreover it limits the percentage for other components, making it a crucial part of the design phase. With increases in the emulsifier concentration, the droplet size decreases, whereas with increases in the acid volume the droplet size increases. Thus, microemulsions cannot acquire high acid volume but coarse emulsions can.

In the case of oils with high viscosity, the emulsifier concentration decreases, as such oils have an ample amount of organic (carboxylic) acids present for emulsification. An ideal emulsion is one that remains stable the longest for the targeted period, has minimum emulsifier content, and contains both the phases (oil and aqueous) in the maximum desired value as per the needed viscosity–mobility ratio. Therefore, it is necessary to select an emulsifier that can provide strong bonding between the two immiscible phases with a minimal amount of it in the emulsion system. Mixing speed and temperature can create an emulsion with good viscoelastic behavior. At ambient conditions, the elastic modulus (G') is not high, meaning shear resistance is not dominant and requires high mixing speeds to generate a thoroughly solubilized stable emulsion, whereas at higher temperatures and slow mixing speeds the emulsion synthesized has good shear resistance and non-Newtonian characteristics, which is because in these conditions droplets further break into smaller sizes.⁶² For heavy oils, the mixing period and speed are higher, as the energy and time for breaking a highly viscous oil are increased.

Emulsifier concentration and mixing speed lose their significance when using homogenizers, as unlike magnetic stirrers a homogenizer is designed for thorough mixing of the phase; these are normally used for large volumes. The factor that is prominent is the droplet injection rate. As mentioned above,

even a small difference can cause behavioral change; therefore, the injection rate should have consistent increment, as the emulsion volume increases when using a buret/pipet.⁴⁵ Therefore, it is better to apply atomic dispersion as mode of injection/addition of the dispersed phase. This is because the droplet size of the dispersed phase should be as small as possible with respect to the application, and introducing the droplets in a mist form enhances the dispersion of the discrete phase.^{93,94} For emulsions with a highly viscous oil, the influence of stirring speed and time must be considered, as these require a homogenizer for mixing just like large-volume emulsions and need sufficient energy and time to synthesize a stable emulsion. Since very minute solid particles are used as pickering agents, it is more feasible to use an ultrasonic bath/mixer/homogenizer to better disperse the pickering agent in the mixture to achieve maximum solubility in the colloid system. The power used to ultrasonicate varies and depends on the nature of particle and its interaction with the fluid.

5.1. Reservoir Heterogeneity. The stability, viscosity, fluidity, and thereby stimulation capability of an emulsified acid depends on the permeability contrast and type of permeable zones, whether fractured or unfractured. The concerns with the fluid injection rate and early consumption near the wellbore as well as sweep efficiency are greatly affected by the reservoir profile. If not considered properly, these can result in near-wellbore cave-in, induction of passages into thief zones yielding fluid loss, failure to penetrate targeted depth, and insufficient zonal coverage.^{49,50}

5.2. Rock Surface Charge. The electrostatic interaction between the stimulant and the rock surface is a major governing parameter toward either a successful stimulation or failure. The reservoir rock and fluid charge are responsible for deciding the type and concentration of different components in the colloidal acidizing agent. Additives such as corrosion inhibitors and emulsifiers can be adsorbed and lost on to the rock surface, resulting in emulsion destabilization, increased chances of formation damage, and unwanted corrosion scale generation.^{37,43}

5.3. Emulsifier Concentration. The concentration of an emulsifier plays a vital role in making an emulsion technically and economically favorable. The droplet size decreases, and its distribution becomes more homogeneous with the increase in emulsifier concentration. This is at the cost of reduction in volume of other phases, for well stimulation acid should be in an adequately large amount, usually occupying 50–70% of the emulsion. The increase in emulsifier concentration, especially if surfactant is used, hugely narrows down the space for acid, which makes the emulsion stable against thermal and mechanical changes but reduces its penetration capability and is economically unfeasible. Beyond critical micelle concentration, droplet size does not decrease; however, in the case of pickering agents, this can lead to increased stability with a relatively lower amount than that used for surfactant. Moreover, macroemulsions are favored for matrix acidizing over microemulsions, which provide sufficient stability with ample acid volume.^{28–51} The use of a pickering emulsion and a hybrid emulsifier (combination pickering particles and surfactants or polymers) greatly minimizes the emulsifier concentration while forming a strong structural network, which provides enhanced stability.^{74,95,96}

5.4. Water- Oil Ratio. For matrix acidizing, the oil phase is merely there to provide retardation and excellent sweep efficiency at low injection rates; therefore, the amount of oil

generally used in emulsified acid ranges from 10% to 50%. The stimulating fluid achieves deep penetration for which more mobility is required; therefore, a 70:30 ratio of water in oil is usually selected. This ratio is favored by many research studies because of lower oil consumption, higher mobility, and moderate acid reaction retardation.

5.5. Oil Viscosity. The viscosity of the oil can potentially increase emulsion stability by reducing droplet mobility to an extent and thereby reducing droplet diffusivity toward the rock surface. However, highly viscous oils tend to drastically slow down movement of aqueous droplets, which can potentially lead to destabilization and cause formation damage.⁹⁷

5.6. Temperature. It is crucial to consider the impact of temperature on the emulsion during the design and deployment phase. Temperature can influence stability, reactivity, and viscosity of an emulsified acid. During synthesis, high temperatures can lead to further breakdown of droplets into smaller sizes, and ionic charges are excited due to the addition of thermal energy, hence increasing colloidal stability. During deployment, however, high-temperature conditions can adversely affect emulsion stability and increase acid reactivity.^{83,94,98}

5.7. Effect of main constituents and additives on Emulsion Performance. Main constituents of an emulsion are mainly comprised of the acidic phase, the oil phase, and the emulsifier. As discussed previously, the type and concentration of these constituents affect each others properties; similarly, additives are used for different purposes, which can often diminish the capability of other additives or constituents, thus hindering overall emulsion performance. For instance, acid type and concentration can reduce the inhibition ability of a corrosion inhibitor; similarly, an increase or decrease in the inhibitor concentration can have an effect on the stability provided by the emulsifier and vice versa.^{37,41,42,99} It is best to keep the additives away from one another by placing them on opposite sides of the oil phase, which reduces their interaction, enhances the life span of the emulsion, and in certain cases increases certain capabilities of the emulsion. For example, Al-Zahrani,⁴³ instead of just focusing on the concentration of inhibitors and emulsifiers, changed the placement of the corrosion inhibitor in the emulsion phases by placing it as an external phase while the acid was encapsulated by oil. This allowed the inhibitor to have direct contact with the well tubing. This innovation provided much better inhibition and stimulation properties than the conventional emulsified acids, which have inhibitors in the internal phase along with the acid. The synthesized emulsion was compared with the emulsified acid having an inhibitor as an internal phase. The regular emulsified acid started to separate after 30 min and was completely separated in 110 min at 248 °F, whereas the synthesized emulsion (having inhibitor as an external phase) worked well for temperatures up to 248 °F. It started separating from the inhibitor after 60 min and was completely separated from it in 140 min. After the inhibitor separation, the emulsified acid at low shear rate functioned as an emulsion having the inhibitor in internal phase, and at a high shear rate the emulsified acid acted as an emulsion without inhibitor. The synthesized emulsion provided a deeper penetration with improved inhibition capability compared to the regular emulsion.

6. EMULSION CHARACTERISTICS AND MEASURING TECHNIQUES

6.1. Stability. Stability is a vital characteristic. If an emulsion is not able to resist the thermal and mechanical changes in its

surroundings during injection, then it will not be able to penetrate the targeted zone. The following parameters ensure a stable emulsified acid formation.

6.1.1. Bottle Test. The bottle test is a testing method based on gravity segregation/separation¹⁰⁰ that is used to determine stability by inspecting the emulsion for separation (creaming or sedimentation) with respect to time at different temperature and salinity conditions.^{83,101} The observed separation layer thickness indicates the volume separation,¹⁰² which is later used to determine the emulsion stability index used for predicting the long-term stability of an emulsion against coalescence or flocculation^{97,103} using the following formula:

$$ESI = \left[1 - \frac{V_o}{V_e} \right] \times 100 \quad (3)$$

where V_o is the volume of oil separated from the emulsion and V_e is the volume of the emulsion

6.1.2. Droplet Size Distribution (DSD). An emulsion is targeted to possess homogeneous distribution of small sized droplets with low variation so that the emulsion acts as a one phase fluid system for a desired time. The heterogeneity in droplet size and level of dispersion indicate to which degree emulsion instability factors such as creaming, flocculation, coalescence, etc. are likely to occur. For this purpose, droplet size and distribution at different regions of the emulsion need to be evaluated. This allows the determination of the instability mechanisms that may be hindering the stability performance of the system. Emulsion stability is susceptible to salinity and temperature; therefore, during the design stage the emulsion needs to be tested for resistance against specific temperature and salinity ranges that would be present in subsurface. The droplet size is governed by the surfactant concentration, pickering particle size, the viscosity and charge of the phases, the mode of dispersion, the mixing speed, and the temperature during synthesis, as well as the reservoir conditions such as salinity, pH, and temperature. Table 3 highlights the droplet size range from a few of the publications. The following techniques can be used to visualize droplet size.

Table 3. Droplet Size of the Emulsified Acids as Per the Literature

authors	year	droplet size	emulsion type
Guidry et al. ²⁹	1989	20 μm HCl, 200 μm N ₂	macroemulsion
Al-Anazi et al. ⁴⁷	1998	77 μm HCl	macroemulsion
Navarrete et al. ⁴⁸	1998	1–77 μm HCl	macroemulsion
Nasr-El-Din et al. ³³	2008	35 μm HCl	macroemulsion
Zakaria and Nasr-El-Din ⁴⁴	2015	1.14–6.34 μm HCl	macroemulsion
Sidaoui et al. ⁸²	2016	1.47–3.09 μm HCl	macroemulsion
Hoefner and Fogler ⁸⁴	1987	10 nm (micelle state)	microemulsion
Zhang et al. ²⁷	2008	54.5 nm	microemulsion
Tupã et al. ²⁸	2016	80–183 nm	microemulsion

6.1.3. Imaging/Microscopy. Instability mechanisms such as coalescence and flocculation can be predicted roughly through the bottle test to an extent. However, instability mechanisms such as these including Ostwald ripening require microscopic imaging techniques for detection, as these involve the evaluation of droplet size distribution and shape.¹⁰² Microscopy helps in observing the dispersed droplets having a size smaller than 100 μm.¹⁰⁴ Imaging techniques such as cross polarized microscopy,

fluorescence microscopy, and cryo-based scanning electron microscopy are some of the techniques that are used to study droplet structure.^{105–107} In terms of precision and detail, electron microscopes such as field emission electron microscopes and transmission electron microscopes are the best choice for this purpose due to their high resolution and ability to capture large surface area images quickly. Given the sample has to be frozen, comparatively the high resolution is most suitable for analyzing individual droplet shape, size, and morphology as well as the distribution of droplets throughout the emulsion and at the interface.^{108,109} Combining microscopic imaging with a more precise droplet size distribution (DSD) technique such as a light scattering-based or acoustic-based technique further strengthens surety regarding the droplet structural features and stability of the emulsion.

6.1.3.1. Light Scattering Method. The light scattering method utilizes a monochromatic beam of near-infrared light that travels through the emulsion sample. It indicates the concentration and size of the droplets via detecting the percentage and angle of backscattered light.¹¹⁰ It is based on Fraunhofer and Mie theory and utilizes the refractive index of the sample to provide the desired results. The samples have to be diluted to avoid multiple scattering effects and provide accurate results.¹⁰² It is important to know that microscopic image analyses give a number-based distribution, whereas particle size analysis techniques provide a volume-based distribution. Although a number-based distribution can be converted to a volume-based distribution, the accuracy the particle size analysis provides is far more acceptable due to being measured directly.¹¹¹ In cases where it is necessary to provide a single-point specification to represent droplet size distribution, then the median value should be presented, as it is the most stable value generated by laser diffraction. The light scattering technique (static/dynamic) can mostly measure sizes in the range of 0.3 nm to 5000 μm .¹¹²

6.1.3.2. Ultrasonic Spectrometry. Ultrasonic spectroscopy is a noninvasive technique that measures attenuation level in the frequency of ultrasonic velocity, through which it calculates particle size distribution and concentration. Unlike the light scattering technique that requires the dilution of the sample, causing a certain amount of compromise in accuracy, the acoustic-based technique allows for high particle concentration measurements due to the measuring mechanism relying on acoustics; it can even measure opaque samples. Generally, ultrasonic spectrometers can measure droplet size ranging from 5 nm to 1000 μm .

6.1.4. Zeta Potential. The zeta potential is related to the attractive and repulsive charge forces experienced by the droplet in the emulsion, which govern the stability of the colloid. The droplets usually repel one another, thus keeping them dispersed throughout the continuous phase, and the emulsion remains stable; slight changes in the polarity of the colloid system can lead to instability, such as an increase in salinity or pH fluctuation. The process is based on the DVLO theory.¹¹³ The zeta potential can be determined by two methods: electrophoretic mobility and electroacoustic spectroscopy. Electrophoretic mobility measures the velocity of the charged particles/droplets by applying an electric field to the dispersion, and the zeta potential is obtained from the velocity measured and the size of the particles. Electroacoustic spectroscopy generates an ultrasonic pulse to the dispersion. This causes droplet movement, thereby inducing an alternating current that is used to calculate zeta potential by considering the current as a

potential between two electrodes.¹⁰² Similar to droplet size analysis, the acoustic technique does not require sample dilution, and concentrated samples can be measured. In contrast, microelectrophoretic techniques often employ the light scattering technique to measure concentration and distribution of the charged droplets in the emulsion and therefore require the dilution of the sample.

6.2. Rheology. Rheology holds great significance in terms of stability and colloidal flow behavior. The viscosity of a fluid defines its degree of mitigation toward instability. The more viscous a fluid is, the lower its tendency to destabilize. This is due to retardation in droplet fluidity, which prevents their intermingling with one another. The flow behavior and ability to resist shear stresses are governed by the mobility/viscosity ratio, which accounts for mixing performance and power required during synthesis and the injection rate during deployment. Rheometers use different plate geometries for determining the rheology of various fluids under different shear stress and temperature conditions.^{102,114} This is to account for slipping behavior and the occurrence of phase evaporation under high thermal conditions in different fluid types. A highly viscous sample can be measured with a parallel plate, but for a low viscous colloid a concentric cylinder is feasible. The wide surface area of the parallel plate generates a high chance for fluid slippage and evaporation in a low viscosity medium; however, this is not of much concern with highly viscous fluids. A concentric cylinder safeguards the fluid within its confines and at a raised level, thereby reducing the induction of such concerns.

6.3. Acid Solubility. Acid solubility is gravimetric test usually performed to evaluate acid reactivity with reservoir rock, which helps assess the effectiveness of an acid in terms of permeability enhancement, formation damage removal, and mineral content (dolomite, limestone, or quartz) in carbonates. This is valuable in determining the sensitivity of the rock toward a certain acid, the reaction rate, the required acid volume for a treatment, and the reaction byproducts.¹¹⁵ The test can be used in the case of emulsified acids as well to evaluate the reaction retardation ability of the emulsion.¹¹⁶ This is conducted by introducing 1 g of rock in powdered form (finer than U.S. sieve 80 mesh) to 150 mL of emulsified acid for 1 h without stirring, as the test is to be conducted in a static state. The solution is then passed through filter paper using a filtration assembly, as the emulsified acid is usually quite viscous. The powder collected on the filter paper is then dried and weighed. The acid solubility percentage is determined using the following equation:

$$\% \text{ Acid Soluble} = \frac{W_1 - W_2}{W_1} \times 100 \quad (4)$$

where W_1 is the initial sample weight and W_2 is the final sample weight

6.4. Electrical Conductivity. To validate that the emulsion formed is water in oil, an electrical conductivity test is performed, which would show near-zero electrical conductivity if oil is the external phase.^{30,44,51,117} If there is slight conductivity, then the emulsion is stirred for an additional 10–20 min maximum to ensure proper homogenization of the phases.^{34,39} This also highlights the resistance to instability by the colloid due to increase in oil percentage and viscosity. As the oil percentage increases, the emulsion viscosity increases, thereby enhancing the severity of emulsification. This is because the droplet fluidity decreases further in the continuous phase, thereby preventing coalescence and flocculation.¹¹⁸

6.5. Corrosion Inhibition. The production facility is prone to corrosion upon interaction with the acidic well stimulation fluid especially at high temperatures downhole. An emulsified acid usually retards reactivity between the acid and the metal tubing assembly.^{119,120} To evaluate its inhibition effectiveness, tests such as weight loss analysis, which is a gravimetric method in which a corrosion coupon is suspended in the emulsified acid for a given period of time and is then cleaned and reweighed, are performed. The weight difference is used to determine and predict corrosion rate and metal loss using the following equation:

$$\text{Metal Loss} = \frac{W \times K}{D \times A} \quad (5)$$

where W is weight loss (g), K is the K-factor, D is the alloy density (g/cm^3), and A is the exposed area (cm^2).

Another more accurate method is the rotating cylinder electrode test, which is basically a dynamic-based test that best emulates field conditions.^{121,122} It consists of a rotating cylinder electrode made up of carbon steel dispersed in a brine solution in a container having a reference and counter electrode, with all electrodes being attached to a potentiostat. Varying concentrations of the test sample are introduced in the solution. The system measures the current and converts it into the corrosion rate.

6.6. Density. Densities of the emulsion and of the immiscible phases must be known. Densities of the aqueous and oleic phase are primarily important for determining the creaming velocity of an emulsion, as shown in the following equation:

$$V_{\text{Stokes}} = (2gr^2(\rho_2 - \rho_1))/(9 \times \eta) \quad (6)$$

where g is acceleration due to gravity, r is radius of the droplet, ρ_1 and ρ_2 are densities of the two immiscible phases, and η is the shear emulsion viscosity. This equation is based on Stoke's law, which mentions how the stability of an emulsion can be measured by observing the creaming velocity of the emulsion droplet either rising or falling (i.e., creaming or sedimentation). The emulsions with high resistance to this phenomenon tend to possess good stability, as this indicates a colloid system having a relatively homogeneous distribution of droplets dispersed evenly. The concentration of the respective phases in the colloid can be changed accordingly to reduce instability occurrence as much as possible.

6.7. pH. The pH during different stages in the design phase (synthesis, core flooding, acid solubility, and corrosion inhibition screening) must be evaluated, as it is responsible for the rate of acid reactivity with the metallic completion assembly and rock surface as well as acid's capacity to hold minerals after reaction. The acidizing medium should hold enough strength to stimulate deep narrow passages while keeping pH-sensitive minerals and ions (irons, calcium, and silicates) intact within itself during flowback to prevent formation damage (precipitation and scale generation), as high pH can lead to instability of the calcium content remaining in the acid. However, it should not be so strong as to create corrosion concerns in the tubular assembly.¹²³ The pH value at the point of injection varies with each formation type from 0.01 to 3. The allowable pH for initially returning acid is between 0.2 and 5, and 50–60% of the fluid returns back while the rest remains inside, which can cause unwanted reduction in production profile by reacting with reservoir rock and fluids. Moreover, there are chances of

contamination of nearby aquifers by migration of displaced acid into such zones.^{124,125}

6.8. Flow through Porous Medium/Core Flooding.

Core flooding is performed to assess fluid propagation through porous regions, acidizing performance, and changes in permeability before and after the stimulation process. This test allows the optimization of treatment design with respect to reservoir conditions by testing out varying emulsion compositions at different injection rates. Although the entire procedure is time-consuming and expensive, it is by far the most accurate means of performance evaluation before field deployment. For matrix acidizing, the stimulant is required to create deep, narrow, and interconnecting wormholes to improve the ease of formation fluid production. Therefore, it is preferred to use rock cores of 6–12" length to observe fluid propagation.^{88,126}

This is usually in combination with techniques such as X-ray computed tomography (CT) or nuclear magnetic resonance (NMR) to gain more insight regarding the flow pattern generated, changes in porosity, permeability, and total fluid content remaining inside the core after flooding.

7. ENVIRONMENTAL CONCERNS TOWARD MATRIX ACIDIZING

Almost 98% of exploration and production waste comes from produced water during the production operations.¹²⁷ The toxicity level is higher in matrix acidizing compared to other stimulation operations. The emulsified acids used for matrix acidizing consist of hydrochloric acid and petroleum-based oils in major quantities, which have been proposed to be accountable for increasing environmental concerns.

The Energy Policy Act of 2005 (Safe Drinking Water Act, Section 322)¹²⁸ has recommended proscribing diesel fuels from usage due to their high carcinogenic content causing an elevation in lung cancer rates, skin damage, vision impairment, clotting deficiency, and many other health-related risk factors and environmental concerns. Diesel-based products include xylene, benzene, toluene, etc.; thus, all are prohibited from usage. In February 2014, the US Environmental Protection Agency (EPA) published the Underground Injection Control program to provide regulators with guidelines when giving permits to operators in order to prevent diesel fuel usage to ensure environmental security in exploration and production operations.¹²⁹

Abdullah¹²⁵ presented a report of the past three years that focused on well stimulation operations other than hydraulic fracturing. The report pointed out that the amount of hazardous chemicals being used in acid fracturing and matrix acidizing are more toxic in nature, being labeled as high concern by the EPA. This is because the chemicals used for acidizing operations have heavier chemical concentrations in the range of 6–18%, whereas hydraulic fracturing has a chemical concentration of 0.5% in 99.5% of water. It was also reported that, according to the data from California Department of Conservation's Division of Oil, Gas, and Geothermal Resources (DOGGR), matrix acidizing holds the highest concentration of up to 18.3% chemicals, of which 15% is acid. Hydrochloric acid used for carbonate acidizing is producing damage dermatologically and orally due to long-term exposure and is hazardous for flowlines, equipment, and the local water supply.

Following these reported concerns, a study conducted by Stringfellow¹³⁰ found a majority of the chemicals used in the oil and gas operations to be environmentally hazardous and unregulated, especially the ones used in acidizing operations

Table 4. Emulsifiers Used for Synthesizing Emulsified Acids and Their Limitations

emulsifier	type	limitation
cetylpyridinium chloride ⁸⁴	cationic surfactant	low stability under high temperature, pH, and salinity; toxicity potential
petronate HH (sodium sulfonate) ⁵⁰	anionic surfactant	
IPE101 ⁵⁰	nonionic surfactant	high concentration; low stability under high temperature, pH, and salinity
tallow amine acetate ³³	cationic surfactant	low stability under high temperature, pH, and salinity; toxicity potential
aliphatic ethoxylate alcohol ²⁷	nonionic surfactant	low stability under high temperature, pH, and salinity
cetyltrimethylammonium ammonium chloride ²⁷	cationic surfactant	low stability under high temperature, pH, and salinity; toxicity potential
ALK90 (alkyl alcohol ethoxylate/ethoxylation grade 9) ²⁸	nonionic surfactant	high concentration; low stability under high temperature, pH, and salinity
RNX110 (alkylphenol ethoxylate/ethoxylation grade 11) ²⁸	nonionic surfactant	high concentration; low stability under high temperature, pH, and salinity
nanoclays ⁸⁸	pickering agent	limited availability
Ultral L10, L20, L70, and L100 ⁸⁶	nonionic surfactant	high concentration
Span80 (sorbitan monooleate) ⁸³	nonionic surfactant	high concentration; low stability under high temperature, pH, and salinity; requires addition of a hydrophilic surfactant for a stable emulsion
Tween 80 (polyoxyethylene sorbitan ester)	nonionic surfactant	high concentration; low stability under high temperature, pH, and salinity; requires addition of an oleophilic surfactant for a stable emulsion
biosoft N25-9 (ethoxylation grade 9) ⁸³	nonionic surfactant	significant concentration, requires addition of an oleophilic surfactant for a stable emulsion.
Claytone-SF ⁹⁰	pickering agent	costly, toxicity potential
cetyltrimethylammonium bromide (CTAB) ⁹¹	cationic surfactant	high concentration is required, limited stability

that are used in larger volumes than other routine operations. Chemicals such as hydrochloric acid, hydrofluoric acid, and xylene are to be classified under categories 1 (highly toxic even in low concentrations) and 2 (toxic in high concentrations) of the United Nations Globally Harmonized System (GHS) for acute mammalian toxicity and ecotoxicity.

Matrix stimulation currently occurs at depths of 2000–11000 feet which is close by the aquifers. The flowback of acidizing fluids has a pH of 0.2 to 5 during the initial flowback.¹²⁴ Up to 50–60% of fluid returns, while the rest remains inside. Hence, the groundwater can be contaminated, as it is present in many cases near the induced wormholes or close to naturally fractured zones where acidizing fluid gets lost. Similarly, the surface water cannot be safe as the produced water even after treatment is not suitable to be introduced into the local water supply. Acidizing disposal wells and abandoning wells are also root causes of wastewater contamination to aquifers.

The composition of emulsified acids mostly consists of the above-mentioned hazardous chemicals. For example, diesel and xylene are conventionally used as the oil phase, and hydrochloric acid is used as the aqueous phase. Also, the surfactants used are normally ionic surfactants, which are known to be toxic and nonbiodegradable.^{130,131} These chemicals need to be properly analyzed and regulated for suitable utilization in stimulation operations, especially with the major threats posed by their heavy usage. Moreover, environmentally friendly and cost-effective alternatives need to be employed as much as possible. For instance, waste oil can replace diesel, and nonionic surfactants as well as pickering particles can replace ionic emulsifiers, as can be seen in the studies conducted by various researchers.^{82,83,87–90} The use of emulsified acids tends to reduce the amount of hydrochloric acid utilized during an acidizing operation. However, there is a need for an ecofriendly

acidizing medium that is economical and technically on par with the performance of hydrochloric acid.

8. SUMMARY AND LIMITATIONS

As per the literature reviewed, 27 out of 32 studies presented in this paper preferred macroemulsions for field applications, with merely 5 research studies conducted on microemulsion synthesis; some studies claimed the lack of feasibility of microemulsions for field applications due to the high amount of surfactant usage to keep it stabilized. These studies, therefore, favored the application of coarse emulsions over microemulsions for field applications. The retardation and wormholing at low injections can be done by both coarse emulsions and microemulsions. Previous research has come up with reliable observations on the effect of some parameters on the stability and efficiency of emulsified acid systems. The points below deserve to be pointed out:

- (i) Coarse emulsions have until now been considered more cost efficient in matrix acidizing operations due to having low amount of surfactants and the ability to hold large volume of acid compared to microemulsions.
- (ii) Water in oil emulsions provide better retardation than oil in water-based emulsified acids due to having oil in the external phase, which reduces the contact rate of the acid with the rock surface.
- (iii) A small droplet size for the emulsion yields high viscosity and stability.
- (iv) The increase of emulsifier concentration will increase the stability of the emulsion by decreasing the droplet size. However, after a certain optimum value the emulsion stability will be independent of the emulsifier concentration.

- (v) The increase of acid volume will increase the droplet size, allowing the emulsion to contain a larger volume of the acid fraction.
- (vi) The compositional balance between the main constituents and additives is a crucial part of emulsion performance. Screening for adequate balance in composition and positioning of the chemicals during the design phase can provide sufficient degree of improvement during the field execution.

Furthermore, from the chronological development it can be observed that diesel has been the conventional oil phase for laboratory and field-based utilization, followed by a few attempts of substituting it with waste oil and plant (triglyceride)-based oil. Constant progress has been seen in emulsifier selection, as can be seen in Table 4. Mostly surfactant-based emulsifiers have been used, with a vast percentage making use of cationic-based surfactants, followed by nonionic surfactants; this is due to the greater affinity of amines to electrostatically interact with acidic medium in the case of cationic surfactants and the strong hydrogen bonding of the nonionic surfactants. There have been very few trials considering anionic surfactants because of their low efficiency in emulsifying acids, as sulfates and phosphates tend to have a weak interaction with acidic solutions due to the lack of lone electrons contrary to amines; the other reason is that anionic surfactants possess a low dielectric constant in comparison to the cationic surfactants, which solubilize the ions more effectively. Zwitterionic surfactants are rarely used this might be because of their tendency to destabilize at high temperatures above 80 and 100 °C as seen in other oil and gas production operations.¹³² However, as mentioned previously in the type of emulsifiers section, there are certain concerns related to the use of surfactants as emulsifiers, especially ionic surfactants, which precipitate under the presence of multivalent ions (Ca^{2+} and Mg^{2+}) that are the reactant products. These also are not compatible with one another, have toxicity potential, and are not biodegradable. Almost all surfactants require a large concentration to maintain stability. These reasons have recently increased the adaptability of solid particles as emulsifiers, which provide robust emulsion stability at minimum concentration comparatively and mostly have low to negligible toxicity potential. Improvement in upholding reservoir integrity during and after a stimulation process by acting proppants has recently been reported.¹³³ However, the pickering particles currently in use for the synthesis of completion fluids are expansive and have limited availability; particularly in well acidizing, their utilization is still rare. Therefore, solutions such as the use of hybrid emulsifiers (combination of polymer, nonionic surfactant, or solid particles) and functionalizing organic pickering agents to create a more effective emulsifier hold promise against thermal and shear conditions.

9. FUTURE RECOMMENDATIONS

Emulsified acids have been frequently used to generate successful matrix acidizing operations due to their beneficial traits of having a slow reaction with the formation, inhibiting corrosion against the well equipment, catering to low permeable zones, etc. In general, the following issues are highly recommended to be considered during acid stimulation processes: tracking methods for acid leakage, improved treatment of wastewater to guarantee that it is environmentally friendly when dispersing into the local water supply, and

implementing alternatives for replacing toxic chemicals or minimizing their toxic effect.

To some extent, this issues have been looked into by utilizing some alternatives, such as the use of alkyl alcohol, waste oil, and proposed use of triglyceride oil instead of diesel, or by coming up with and adapting substitutes or ways of minimizing the toxicity level of hydrochloric acid,²² as well as use of nonionic surfactants and pickering agents instead of ionic surfactants.^{134,83,89} These developmental endeavors can make the emulsified acid technically, economically, and environmentally feasible for implementation during the current scenario, which demands the deployment of inexpensive and ecofriendly solutions.

10. CONCLUSION

Upon review of the various studies conducted by researchers, emulsified acids have been used to perform matrix acidizing operations for improving production as well as achieving marginal purposes such as acidizing sour gas wells and disposal wells, asphaltene treatment along with acidizing, and using an emulsified acid as a diverting agent for the stimulation of low-permeation zones. Previously conducted research results present emulsified acid as an innovative multipurpose solution to deal with such challenges. Water in oil-based coarse emulsions have until now considered more cost efficient in matrix acidizing operations due to having low amount of surfactants, the ability to hold a large volume of acid compared to microemulsions, and having oil as the external phase, which reduces the contact rate of acid with the rock surface. The compositional balance and positioning between the main constituents and additives during the design phase is a crucial part of emulsion performance, and environmental screening of the fluid can provide a sufficient degree of improvement during the field execution.

AUTHOR INFORMATION

Corresponding Author

Muhammad Mohsin Yousufi – Department of Petroleum Engineering, Universiti Teknologi Petronas, Seri Iskandar 32610, Malaysia; orcid.org/0000-0001-9170-6807; Email: muhammad_22008195@utp.edu.my

Authors

Mysara Eissa Mohyaldinn Elhaj – Department of Petroleum Engineering, Universiti Teknologi Petronas, Seri Iskandar 32610, Malaysia; Institute of Hydrocarbon Recovery, Universiti Teknologi Petronas, Seri Iskandar 32610, Malaysia; orcid.org/0000-0001-5200-8491

Iskandar Bin Dzulkarnain – Department of Petroleum Engineering, Universiti Teknologi Petronas, Seri Iskandar 32610, Malaysia; Institute of Hydrocarbon Recovery, Universiti Teknologi Petronas, Seri Iskandar 32610, Malaysia

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.3c07132>

Funding

This research was funded by the following grant: PETRONAS PRF YUTP-FRG 01SLC0-422

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the support provided by the Institute of Hydrocarbon Recovery at Universiti Teknologi Petronas.

REFERENCES

- (1) *Carbonate Reservoirs: Meeting Unique Challenges to Maximize Recovery*. Schlumberger: Houston, TX, 2007.
- (2) Chacon, O. G.; Pournik, M. Matrix Acidizing in Carbonate Formations. *Processes* **2022**, *10* (1), 174.
- (3) Frasch, H.. Increasing the Flow Of Oil Wells. US 556669 A, 1896.
- (4) Putnam, S. W. Development of Acid Treatment of Oil Wells Involves Careful Study of Problems of Each. *Oil Gas J.* **1933**, *8*, 6–13.
- (5) Nierode; Williams. SPE 3101 Characteristics of Acid Reaction in Limestone Formations. *Soc. Pet. Eng. J.* **1971**, *11* (4), 406–418.
- (6) Williams, B. B.; Gidley, J. L.; Schechter, R. S. History of Acidizing. In *Acidizing Fundamentals*; Society of Petroleum Engineers: Richardson, TX, 1979; pp 1–4.
- (7) Chemical Company Forms Company To Treat Wells. *Oil Weekly* **1932**, 59.
- (8) *Dow Chemical Co. v. Halliburton Oil Well Cementing Co.*, 324 U.S. 320 (1945).
- (9) Pitzer, P. W.; West, C. K. Acid Treatment of Lime Wells Explained and Methods Described. *Oil Gas J.* **1934**, 38.
- (10) Williams, B. B.; Gidley, J.L. S. Chapter 10: Matrix Acidizing of Carbonates. In *Acidizing Fundamentals*; Society of Petroleum Engineers: Richardson, TX, 1979; pp 86–91.
- (11) Lund, K.; Fogler, H. S.; McCune, C.C. Acidization-I. The Dissolution of Dolomite in Hydrochloric Acid. *Chem. Eng. Sci.* **1973**, *28*, 691–700.
- (12) Lund, K.; Fogler, H.S.; McCune, C.C.; Ault, J.W. Acidization- II: The Dissolution Of Calcite In Hydrochloric Acid. *Chem. Eng. Sci.* **1975**, *30*, 825–835.
- (13) Williams, B. B.; Gidley, J.L. S. Acid Types and the Chemistry of Their Reactions. In *Acidizing Fundamentals*; Society of Petroleum Engineers: Richardson, TX, 1979; pp 10–17.
- (14) Cholet, H. *Well Production Practical Handbook*; Editions TECHNIP: Paris, France, 2000.
- (15) Garrouch, A. A.; Jennings, A. R., Jr A Contemporary Approach to Carbonate Matrix Acidizing. *J. Pet. Sci. Eng.* **2017**, *158*, 129–143.
- (16) Hoefner, M. L.; Fogler, H. S. Fluid Velocity and Reaction Rate Effects During Carbonate Acidizing : Application of Network Model. *SPE Prod. Eng.* **1989**, *4*, 56–62.
- (17) Li, Y.; Sullivan, R. B.; Rozieres, J. de; Gaz, G. L.; Hinkel, J. J. An Overview of Current Acid Fracturing Technology With Recent Implications for Emulsified Acids. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Houston, TX, October 3–6, 1993; OnePetro: Richardson, TX, 1993; pp 709–724. DOI: 10.2118/26581-MS.
- (18) Navarrete, R. C.; Holms, B. A.; McConnell, S. B.; Linton, D. E. Laboratory, Theoretical, and Field Studies of Emulsified Acid Treatments in High-Temperature Carbonate Formations. *SPE Prod. Facil.* **2000**, *15* (2), 96–106.
- (19) Frick, T. P.; Kurmayr, M.; Economides, M. J. Modeling of Fractal Patterns in Matrix Acidizing and Their Impact on Well Performance. *SPE Prod. Facil.* **1994**, *9*, 61–68.
- (20) Samuel, M.; Sengul, M. Stimulate the Flow. *Middle East Asia Reserv. Rev.* **2003**, 42–53.
- (21) Portier, S.; André, L.; Vuataz, F.-D. *Review on Chemical Stimulation Techniques in Oil Industry and Applications to Geothermal Systems*; Centre for Geothermal Research, Neuchâtel, Switzerland, 2007.
- (22) Markey, F.; Betz, T.; Gutaples, J.; Ackwith, D.; Taylor, K.; Barati, R. Examining Innovative Techniques for Matrix Acidizing in Tight Carbonate Formations to Minimize Damage to Equipment and Environment. *SEG Global Meeting Abstr.* **2014**, 1445–1455.
- (23) Ebnasajjad, S. Characteristics of Adhesive Materials. In *Handbook of Adhesives and Surface Preparation*; William Andrew Publishing: Oxford, UK, 2011; pp 137–183. DOI: 10.1016/B978-1-4377-4461-3.10008-2.
- (24) Gadhav, A. D.; Waghmare, J. T. A Short Review On Microemulsion And Its Application In Extraction Of Vegetable Oil. *IJRET Int. J. Res. Eng. Technol.* **2014**, *03* (9), 147–158.
- (25) Al-Mutairi, S. H.; Nasr-El-Din, H. A.; Hill, A. D. Droplet Size Analysis of Emulsified Acid. In *Proceedings of the SPE Saudi Arabia Section Technical Symposium*, Al-Khobar, Saudi Arabia, May 9–11, 2009; OnePetro: Richardson, TX, 2009; SPE-126155-MS.
- (26) Hoefner, M. L.; Fogler, H. S. Effective Matrix Acidizing in Carbonates Using Microemulsions. *Chem. Eng. Prog.* **1985**, 40–44.
- (27) Zhang, S.; Wang, F.; Chen, Y.; Fang, B.; Lu, Y. Preparation and Properties of Diesel Oil Microemulsified Acid. *Chin. J. Chem. Eng.* **2008**, *16* (2), 287–291.
- (28) Tupã, P.; Aum, P.; Souza, T. N.; Aum, Y. K. P. G.; de Castro Dantas, T. N.; Dantas Neto, A. A. New Acid O/W Microemulsion Systems for Application in Carbonate Acidizing. *Int. J. Adv. Sci. Technol. Res.* **2016**, *1* (6), 182–196.
- (29) Guidry, G. S.; Ruiz, G. A.; Saxon, A.. SXE/N2Matrix Acidizing. In *Proceedings of the SPE Middle East Oil Technical Conference and Exhibition*, Manama, Bahrain, March 11–14, 1989; OnePetro: Richardson, TX, 1989; SPE-17951-MS. DOI: 10.2118/17951-MS.
- (30) Nasr-El-Din, H. A.; Solares, J. R.; Al-Mutairi, S. H.; Mahoney, M. D. Field Application of Emulsified Acid-Based System to Stimulate Deep, Sour Gas Reservoirs in Saudi Arabia. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, New Orleans, LA, September 30–October 3, 2001; OnePetro: Richardson, TX, 2001; SPE-71693-MS. DOI: 10.2118/71693-MS.
- (31) Kasza, P.; Dziadkiewicz, M.; Czupski, M. From Laboratory Research to Successful Practice : A Case Study of Carbonate Formation Emulsified Acid Treatments. In *Proceedings of the SPE International Symposium and Exhibition on Formation Damage Control*, Lafayette, LA, February 15–17, 2006; OnePetro: Richardson, TX, 2006; SPE-98261-MS. DOI: 10.2118/98261-MS.
- (32) Sarma, D. K.; Agarwal, P.; Rao, E.; Kumar, P. Development of a Deep-Penetrating Emulsified Acid and Its Application in a Carbonate Reservoir. In *Proceedings of the 15th SPE Middle East Oil and Gas Show and Conference*, Manama, Bahrain, March 11–14, 2007; OnePetro: Richardson, TX, 2007; SPE-05502-MS. DOI: 10.2118/105502-MS.
- (33) Nasr-El-Din, H. A.; Al-Dirweesh, S.; Samuel, M. Development and Field Application of a New, Highly Stable Emulsified Acid. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Denver, CO, September 21–24, 2008; OnePetro: Richardson, TX, 2008; SPE -115926-MS. DOI: 10.2118/115926-MS.
- (34) Xiong, C.; Zhou, F.; Liu, Y.; Yang, X.; Liu, X.; Shi, Y.; Tan, Y.; Zhang, F.; Ji, X.; Qin, S.; Huang, S.; Wang, X. Application and Study of Acid Technique Using Novel Selective Emulsified Acid System. In *Proceedings of the International Oil and Gas Conference and Exhibition*, Beijing, China, June 8–10, 2010; OnePetro: Richardson, TX, 2010; SPE-131216-MS. DOI: 10.2118/131216-MS.
- (35) Fatah, W. A.; Nasr-El-Din, H. A. Acid Emulsified in Xylene : A Cost-Effective Treatment To Remove Asphaltene Deposition and Enhance Well Productivity. In *SPE Easter Regional/AAPG Eastern Section Joint Meeting*, Pittsburgh, PA, October 11–15, 2008; OnePetro: Richardson, TX, 2010; SPE-117251-MS.
- (36) Appicciutoli, D.; Maier, R. W.; Strippoli, P.; Tiani, A.; Mauri, L. Novel Emulsified Acid Boosts Production in a Major Carbonate Oil Field with Asphaltene Problems. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Florence, Italy, September 19–22, 2010; OnePetro: Richardson, TX, 2010; SPE-135076-MS.
- (37) Sabhapondit, A.; Guillen, J. R. V.; Prakash, C. Laboratory Optimization of an Emulsified Acid Blend for Stimulation of High-Temperature Carbonate Reservoirs. In *Proceedings of the North Africa Technical Conference and Exhibition*, Cairo, Egypt, February 20–22, 2012; OnePetro: Richardson, TX, 2012; SPE-150337-MS. DOI: 10.2118/150337-MS.
- (38) Huang, T.; Crews, J. B.; Willingham, J. R.; Mitchell, R. A.; Seth, K. Stabilize Emulsified Acids for Carbonate Acidizing. US 8551926 B2, 2013.
- (39) Sayed, M. A.; Zakaria, A.; Nasr-El-Din, H. A.; Holt, S.; Al-Malki, H. Core Flood Study of a New Emulsified Acid with Reservoir Cores. In *Proceedings of the SPE International Production and Operations Conference & Exhibition*, Doha, Qatar, May 14–16, 2012; OnePetro: Richardson, TX, 2012; SPE-157310-MS.

- (40) Gardner, T. R.; Dill, W. R.; Ford, W. G. F.; King, K. L. Well Acidizing Compositions and Method. US 5034140 A, 1991.
- (41) Pandya, N.; Wadekar, S.; Cassidy, J. An Optimized Emulsified Acid System For High-Temperature Applications. In *Proceedings of the Offshore Mediterranean Conference and Exhibition*, Ravenna, Italy, March 20–22, 2013; OnePetro: Richardson, TX, 2013; OMC-2013-107.
- (42) Pandya, N.; Wadekar, S. A Novel Emulsified Acid System for Stimulation of Very High-Temperature Carbonate Reservoirs. In *Proceedings of the International Petroleum Technology Conference*, Beijing, China, March 26–28, 2013; OnePetro: Richardson, TX, 2013; IPTC-16452-MS. DOI: 10.2523/IPTC-16452-MS.
- (43) Al-Zahrani, A. A. Innovative Method to Mix Corrosion Inhibitor in Emulsified Acids. In *Proceedings of the International Petroleum Technology Conference*, Beijing, China, March 26–28, 2013; OnePetro: Richardson, TX, 2013; IPTC-16946-MS. DOI: 10.2523/IPTC-16946-MS.
- (44) Zakaria, A. S.; Nasr-El-Din, H. A. Application of Novel Polymer Assisted Emulsified Acid System Improves the Efficiency of Carbonate Acidizing. *SPE International Symposium on Oilfield Chemistry* 2015, D021S005R008.
- (45) Sidaoui, Z.; Sultan, A. S. Formulating a Stable Emulsified Acid at High Temperatures: Stability and Rheology Study. In *Proceedings of the International Petroleum Technology Conference*, Bangkok, Thailand, November 14–16, 2016; OnePetro: Richardson, TX, 2016; IPTC-19012-MS. DOI: 10.2523/IPTC-19012-MS.
- (46) Bazin, B. From Matrix Acidizing to Acid Fracturing: A Laboratory Evaluation of Acid/Rock Interactions. In *Proceedings of the Abu Dhabi International Petroleum Exhibition and Conference*, Abu Dhabi, United Arab Emirates, November 11–14, 1998; OnePetro: Richardson, TX, 1998; SPE-49491-MS. DOI: 10.2118/49491-MS.
- (47) Al-Anazi, H. A.; Nasr-El-Din, H. A.; Mohamed, S. K. Stimulation of Tight Carbonate Reservoirs Using Acid-in-Diesel Emulsions: Field Application. In *Proceedings of the SPE International Symposium on Formation Damage Control*, Lafayette, LA, February 18–19, 1998; OnePetro: Richardson, TX, 1998; SPE-39418-MS. DOI: 10.2118/39418-MS.
- (48) JPT Staff. Emulsified Acid Enhances Well Production in High-Temperature Carbonate Formations. *J. Pet. Technol.* 1999, 51, 47–48.
- (49) Buijse, M. A.; van Domelen, M. S. Novel Application of Emulsified Acids to Matrix Stimulation of Heterogeneous Formations. *SPE Prod. Fac.* 2000, 15, 208–213.
- (50) Bazin, B.; Abdulahad, G. Experimental Investigation of Some Properties of Emulsified Acid Systems for Stimulation of Carbonate Formations. In *Proceedings of the Middle East Oil Show*, Bahrain, February 20–23, 1999; OnePetro: Richardson, TX, 1999; SPE-53237-MS. DOI: 10.2118/53237-MS.
- (51) Nasr-El-Din, H. A.; Al-Anazi, H. A.; Mohamed, S. K. Stimulation of Water Disposal Wells Using Acid-In-Diesel Emulsion: Case Histories. In *SPE International Symposium on Oilfield Chemistry*, Houston, TX, February 16–19, 1999; OnePetro: Richardson, TX, 1999; SPE-50739-MS. DOI: 10.2118/50739-MS.
- (52) Kaabi, A. Al. Active Partnership. *Middle East Asia Reserv. Rev.* 2003, 54–55.
- (53) Hoefner, M. L.; Fogler, H. S. Role of Acid Diffusion in Matrix Acidizing of Carbonates. *J. Pet. Technol.* 1987, 39, 203–208.
- (54) A. Ali, S.; Hinkel, J. J. Additives in Acidizing Fluids. In *Reservoir Stimulation*, 3rd ed.; Nolte, K. G., Economides, M. J., Eds.; John Wiley & Sons Ltd, 2000; pp 15-5–15-16.
- (55) Kim, I.; Worthen, A. J.; Lotfollahi, M.; Johnston, K. P.; Dicarolo, D. A.; Huh, C. Nanoparticle-Stabilized Emulsions for Improved Mobility Control for Adverse-Mobility Waterflooding. *IOR Norw.* 2017 - 19th Eur. Symp. Improv. Oil Recover. 2017, 1–13.
- (56) Nasr-el-din, H. A. Surfactant Use in Acid Stimulation. In *Surfactants*; Cambridge University Press: Cambridge, UK, 2000; p 329.
- (57) Al-Ghamdi, A. M.; Nasr-El-Din, H. A. Effect of Oilfield Chemicals on the Cloud Point of Nonionic Surfactants. *Colloids Surfaces A Physicochem. Eng. Asp.* 1997, 125 (1), 5–18.
- (58) Denoyel, R.; Giordano, F.; Rouquerol, J. Thermodynamic Study of Non-Ionic-Anionic Surfactant Mixtures: Micellization and Adsorption on Silica. *Colloids Surfaces A Physicochem. Eng. Asp.* 1993, 76 (C), 141–148.
- (59) Sadaghiana, A. S.; Khan, A. Clouding of a Nonionic Surfactant: The Effect of Added Surfactants on the Cloud Point. *J. Colloid Interface Sci.* 1991, 144 (1), 191–200.
- (60) Ivanova, N. I.; Shchukin, E. D. Mixed Adsorption of Ionic and Non-Ionic Surfactants on Calcium Carbonate. *Colloids Surfaces A Physicochem. Eng. Asp.* 1993, 76 (C), 109–113.
- (61) Marszall, L. The Effect of Electrolytes on the Cloud Point of Ionic-Nonionic Surfactant Solutions. *Colloids Surf.* 1987, 25 (2–4), 279–285.
- (62) Manohar, C.; Kelkar, V. K. Model for the Cloud Point of Mixed Surfactant Systems. *J. Colloid Interface Sci.* 1990, 137, 604–606.
- (63) Griffin, W. C. Classification of Surface-Active Agents by “HLB”. *J. Soc. Cosmet. Chem.* 1949, 1 (5), 311–326.
- (64) *Colloidal Particles at Liquid Interfaces*; Binks, B. P., Horozov, T. S., Eds.; Cambridge University Press: Cambridge, UK, 2006.
- (65) du Sorbier, Q. M.; Aimable, A.; Pagnoux, C. Influence of the Electrostatic Interactions in a Pickering Emulsion Polymerization for the Synthesis of Silica-Polystyrene Hybrid Nanoparticles. *J. Colloid Interface Sci.* 2015, 448, 306–314.
- (66) He, X. D.; Ge, X. W.; Wang, M. Z.; Zhang, Z. C. The Preparation of Composite Microsphere with Hollow Core/Porous Shell Structure by Self-Assembling of Latex Particles at Emulsion Droplet Interface. *J. Colloid Interface Sci.* 2006, 299 (2), 791–796.
- (67) Velikov, K. P.; Velev, O. D. Stabilization of Thin Films, Foams, Emulsions and Bifluid Gels with Surface-Active Solid Particles. In *Colloid stability and application in pharmacy*; Tadros, T. F., Ed.; Wiley, 2007; pp 277–306.
- (68) Zhai, X.; Efrima, S. Chemical and Physical Aspects of Macroemulsions Stabilized by Interfacial Colloids. *J. Phys. Chem.* 1996, 100 (26), 11019–11028.
- (69) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions Stabilised Solely by Colloidal Particles. *Adv. Colloid Interface Sci.* 2003, 100–102, 503–546.
- (70) Dickinson, E. Use of Nanoparticles and Microparticles in the Formation and Stabilization of Food Emulsions. *Trends Food Sci. Technol.* 2012, 24 (1), 4–12.
- (71) Binks, B. P. Particles as Surfactants—Similarities and Differences. *Curr. Opin. Colloid Interface Sci.* 2002, 7 (1), 21–41.
- (72) Sarkar, A.; Zhang, S.; Holmes, M.; Ettelaie, R. Colloidal Aspects of Digestion of Pickering Emulsions: Experiments and Theoretical Models of Lipid Digestion Kinetics. *Adv. Colloid Interface Sci.* 2019, 263, 195–211.
- (73) Xu, K.; Zhu, P.; Colon, T.; Huh, C.; Balhoff, M. A. Microfluidic Investigation of the Synergistic Effect of Nanoparticles and Surfactants in Macro-Emulsion-Based Enhanced Oil Recovery. *SPE J.* 2017, 22 (2), 459–469.
- (74) Binks, B. P.; Desforges, A.; Duff, D. G. Synergistic Stabilization of Emulsions by a Mixture of Surface-Active Nanoparticles and Surfactant. *Langmuir* 2007, 23 (3), 1098–1106.
- (75) Chevalier, Y.; Bolzinger, M. A. Emulsions Stabilized with Solid Nanoparticles: Pickering Emulsions. *Colloids Surfaces A Physicochem. Eng. Asp.* 2013, 439, 23–34.
- (76) Tadros, T. F. Fundamental Principles of Emulsion Rheology and Their Applications. *Colloids Surfaces A Physicochem. Eng. Asp.* 1994, 91, 39–55.
- (77) de Groote, M. Process for Increasing the Output of Oil Wells. US 1922154 A, 1933.
- (78) Harris, F. N. Applications of Acetic Acid to Well Completion, Stimulation and Reconditioning. *J. Pet. Technol.* 1961, 13, 637–639.
- (79) Davis, J. J.; Mancillas, G.; Melnyk, J. D. Improved Acid Treatments By Use Of The Spearhead Film Technique. *SPE Rocky Mountain Regional Meeting* 1965, DOI: 10.2118/1164-MS.
- (80) Nierode; Kruk. An Evaluation of Acid Fluid Loss Additives, Retarded Acids, and Acidized Fracture Conductivity. *Fall Meeting of the Society of Petroleum Engineers of AIME* 1973, 1–12.
- (81) Appicciutoli, D.; Maier, R. W.; Strippoli, D. P.; Tiani, A.; Mauri, L. Novel Emulsified Acid Boosts Production in a Major Carbonate Oil

- Field with Asphaltene Problems. In *Proceedings of SPE Annual Technical Conference and Exhibition*, Florence, Italy, September 19–22, 2010; OnePetro: Richardson, TX, 2010; SPE-135076-MS. DOI: 10.2118/135076-MS.
- (82) Sidaoui, Z.; Sultan, A. S.; Qiu, X. Viscoelastic Properties of Novel Emulsified Acid Using Waste Oil: Effect of Emulsifier Concentration, Mixing Speed and Temperature. In *Proceedings of the SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition*, Dammam, Saudi Arabia, April 25–28, 2016; OnePetro: Richardson, TX, 2016; SPE-182845-MS. DOI: 10.2118/182845-MS.
- (83) Yousufi, M. M.; Elhaj, M. E. M.; Moniruzzaman, M.; Ayoub, M. A.; Nazri, A. B. M.; Husin, H.; Saaid, I. M. Synthesis and Evaluation of Jatropa Oil-Based Emulsified Acids for Matrix Acidizing of Carbonate Rocks. *J. Pet. Explor. Prod. Technol.* **2019**, *9* (2), 1119.
- (84) Hoefner, M. L.; Fogler, H. S. Role of Acid Diffusion in Matrix Acidizing of Carbonates. *J. Pet. Technol.* **1987**, *39* (2), 203–208.
- (85) Zhao, R. B.; Yue, X. A.; Hou, J. R. The Corrosion Inhibition Behavior of Microemulsified Acid and Its Acidizing Effect in Core. *Chin. J. Appl. Chem.* **2006**, *23* (2), 149–152.
- (86) Carvalho, R. T. R.; Oliveira, P. F.; Palermo, L. C. M.; Ferreira, A. A. G.; Mansur, C. R. E. Prospective Acid Microemulsions Development for Matrix Acidizing Petroleum Reservoirs. *Fuel* **2019**, *238*, 75–85.
- (87) Huang, T.; Crews, J. B.; Willingham, J. R.; Mitchell, R. A.; Seth, K. Stabilizing Emulsified Acids For Carbonate Acidizing. US 8403051 B2, 2012.
- (88) Ahmed, M.; Sultan, A.; Qiu, X.; Sidaoui, Z.; Ali, A. A. A Novel Emulsified Acid for Deep Wells Stimulation: Rheology, Stability, and Coreflood Study. *Soc. Pet. Eng. - SPE Kingdom Saudi Arab. Annu. Technol. Symp. Exhib. 2018, SATS 2018 2018*, DOI: 10.2118/192312-ms.
- (89) Aly, M.; Aidagulov, G.; Sultan, A.; Gwaba, D.; Abbad, M. Carbonate Matrix Stimulation with Pickering Emulsified Acid Studied by Large-Scale Radial Flow Experiments. In *Proceedings of the Middle East Oil, Gas and Geosciences Show*, Manama, Bahrain, February 19–21, 2023; OnePetro: Richardson, TX, 2023; SPE-213460-MS. DOI: 10.2118/213460-ms.
- (90) Mahmoud, A. A.; AL-Dogail, A. S.; Gajbiye, R. N.; AlSultan, A. S. Development of Emulsified Acid System Using Organoclays. In *Proceedings of the Gas & Oil Technology Showcase and Conference*, Dubai, UAE, March 13–15, 2023; OnePetro: Richardson, TX, 2023; SPE-214149-MS. DOI: 10.2118/214149-ms.
- (91) Mohyaldinn, M. E.; Alakbari, F. S.; Bin Azman Nor, A. N. A.; Hassan, A. M. Stability, Rheological Behavior, and PH Responsiveness of CTAB/HCl Acidic Emulsion: Experimental Investigation. *ACS Omega* **2023**, *8* (25), 22428–22439.
- (92) O'Driscoll, A. Deciding between a Stirrer and a Homogenizer. *Stirrers.net*, May 23, 2018. <https://stirrers.net/blogs/blog/stirrer-or-homogenizer>.
- (93) Al-Mutairi, S. H.; Nasr-El-Din, H. A.; Hill, A. D. Droplet Size Analysis of Emulsified Acid. In *Proceedings of the Saudi Arabia Section Technical Symposium*, Al-Khobar, Saudi Arabia, May 9–11, 2009; OnePetro: Richardson, TX, 2009; SPE-126155-MS.
- (94) Yousufi, M. M.; Elhaj, M. E. M.; Moniruzzaman, M. Comparative Analysis of Corrosion Inhibition: Between Jatrophacurcas, Palm and Diesel Oil Based Emulsified Acids for Acid Stimulation Operations. *IOP Conf. Ser.: Earth Environ. Sci.* **2018**, *164*, No. 012006.
- (95) Kumar, N.; Gaur, T.; Mandal, A. Characterization of SPN Pickering Emulsions for Application in Enhanced Oil Recovery. *J. Ind. Eng. Chem.* **2017**, *54*, 304–315.
- (96) Frelichowska, J.; Bolzinger, M.-A.; Chevalier, Y. Effects of Solid Particle Content on Properties of o/w Pickering Emulsions. *J. Colloid Interface Sci.* **2010**, *351* (2), 348–356.
- (97) Chen, Z.; Dong, M.; Husein, M.; Bryant, S. Effects of Oil Viscosity on the Plugging Performance of Oil-in-Water Emulsion in Porous Media. *Ind. Eng. Chem. Res.* **2018**, *57* (21), 7301–7309.
- (98) Abdulameer, A.; Turzo, Z.; Alameedy, U. Carbonate Rock Matrix Acidizing: A Review of Acid Systems and Reaction Mechanisms. In *Proceedings of XXV. Tavaszi Szél Konferencia*, Budapest, Hungary; Association of Hungarian PhD and DLA Candidates, 2022; pp 303–313.
- (99) Williams, B. B.; Gidley, J. L.; Schechter, R. S. *Acidizing Fundamentals*; Society of Petroleum Engineers: Richardson, TX, 1979.
- (100) Güzey, D.; McClements, D. J. Influence of Environmental Stresses on O/W Emulsions Stabilized by β -Lactoglobulin-Pectin and β -Lactoglobulin-Pectin-Chitosan Membranes Produced by the Electrostatic Layer-by-Layer Deposition Technique. *Food Biophys.* **2006**, *1* (1), 30–40.
- (101) Saikia, T.; Sultan, A.; Barri, A. A.; Khamidy, N. I.; Shamsan, A. A.; Almohsin, A.; Bataweel, M. Development of Pickering Emulsified Polymeric Gel System for Conformance Control in High Temperature Reservoirs. *J. Pet. Sci. Eng.* **2020**, *184*, 106596.
- (102) Hu, Y. T.; Ting, Y.; Hu, J. Y.; Hsieh, S. C. Techniques and Methods to Study Functional Characteristics of Emulsion Systems. *J. Food Drug Anal.* **2017**, *25* (1), 16–26.
- (103) Aryee, A. N. A.; Agyei, D.; Udenigwe, C. C. Impact of Processing on the Chemistry and Functionality of Food Proteins. In *Proteins in Food Processing*, 2nd ed.; Yada, R. Y., Ed.; Woodhead Publishing: Sawston, UK, 2018; pp 27–45. DOI: 10.1016/B978-0-08-100722-8.00003-6.
- (104) Russ, J. C. *Image Analysis of Food Microstructure*; CRC: Boca Raton, FL, 2004.
- (105) AfzaliTabar, M.; Alaei, M.; Ranjineh Khojasteh, R.; Motiee, F.; Rashidi, A. M. Preference of Multi-Walled Carbon Nanotube (MWCNT) to Single-Walled Carbon Nanotube (SWCNT) and Activated Carbon for Preparing Silica Nanohybrid Pickering Emulsion for Chemical Enhanced Oil Recovery (C-EOR). *J. Solid State Chem.* **2017**, *245*, 164–173.
- (106) Laben, A. B.; Al-Kayiem, H. H.; Alameen, M. A.; Khan, J. A.; Belhaj, A. F.; Elraies, K. A. Experimental Study on the Performance of Emulsions Produced during ASP Flooding. *J. Pet. Explor. Prod. Technol.* **2022**, *12* (7), 1797–1809.
- (107) Sayed, M. A.; Nasr-El-Din, H. A.; Nasrabadi, H. Reaction of Emulsified Acids with Dolomite. *J. Can. Pet. Technol.* **2013**, *52* (3), 164–175.
- (108) Bunker, K. L.; McAllister, D.; Allison, K. A.; Wagner, K.; Rickabaugh, K.; Levine, A. M.; Strohmeier, B. R.; Lee, R. J. TEM and FESEM: The Right Combination for Enhanced Particle Characterization. *Microsc. Microanal.* **2008**, *14* (S2), 580–581.
- (109) Mitbumrung, W.; Jain, S.; Winuprasith, T. Properties and Stability of Pickering Emulsions Stabilized by Nanofibrillated Mangosteen Cellulose: Impact of Oil Type and Emulsifier Concentration. *Songklanakarin J. Sci. Technol.* **2020**, *42* (2), 468–476.
- (110) Chu, B. *Laser Light Scattering: Basic Principles and Practice*, 2nd ed.; Dover Publications: Mineola, NY, 2007.
- (111) *A Guidebook To Particle Size Analysis*. Horiba Instruments Incorporated: Irvine, CA, n.d. https://static.horiba.com/fileadmin/Horiba/Products/Scientific/Particle_Characterization/Particle_Guidebook_2022.pdf (accessed 2017-08-20).
- (112) Wriedt, T. Mie Theory: A Review. In *The Mie Theory: Basics and Applications*; Hergert, W.; Wriedt, T., Eds.; Springer, 2012; pp 53–71. DOI: 10.1007/978-3-642-28738-1_2.
- (113) *Zeta Potential: An Introduction in 30 minutes*; Technical Note MRK654-01; Malvern Instruments Limited: Worcestershire, UK, 2015.
- (114) Tadros, T. Application of Rheology for Assessment and Prediction of the Long-Term Physical Stability of Emulsions. *Adv. Colloid Interface Sci.* **2004**, *108–109*, 227–258.
- (115) American Petroleum Institute. *Recommended Practices for Core Analysis*, 2nd ed.; RP-40; API Publishing Services: Washington, D.C., 1998.
- (116) Yousufi, M. M.; Elhaj, M. E. M.; Moniruzzaman, M.; Ayoub, M. A.; Nazri, A. B. M.; Husin, H. b.; Saaid, I. b. M. Synthesis and Evaluation of Jatropa Oil-Based Emulsified Acids for Matrix Acidizing of Carbonate Rocks. *J. Pet. Explor. Prod. Technol.* **2019**, *9* (2), 1119–1133.
- (117) Cairns, A. J.; Al-Muntasheri, G. A.; Sayed, M.; Fu, L.; Giannelis, E. P. Targeting Enhanced Production through Deep Carbonate Stimulation: Stabilized Acid Emulsions. In *Proceedings of the SPE International Conference and Exhibition on Formation Damage Control*,

Lafayette, LA, February 24–26, 2016; OnePetro: Richardson, TX, 2016; SPE-178967-MS. DOI: 10.2118/178967-MS.

(118) Zhang, W.; Li, M.; Lin, M.; Luo, T.; Yao, C. Electrical Conductivity and Stability of O/W Emulsions. *Acta Pet. Sin.* **2008**, *24* (5), 592.

(119) Metal Samples Company. Corrosion Coupons and Weight Loss Analysis: Introduction. *Alabama Specialty Products, Inc.*, n.d. [https://www.alspi.com/coupons\(intro\).pdf](https://www.alspi.com/coupons(intro).pdf)

(120) Afigo, O. S. *Assessment of Corrosion Rate of Dissimilar Welded Metals : Gravimetric Analysis*. **2015**.

(121) ASTM International. Standard Practice for Evaluating and Qualifying Oil Field and Refinery Corrosion Inhibitors Using Rotating Cage; G185-06; West Conshohocken, PA, 2012.

(122) Mohadyaldinn, M. E.; Azad, N. A. A. K. Evaluation of Jatropa Curcas Oil as Corrosion Inhibitor of CO₂ Corrosion in Petroleum Production Environment. *J. Appl. Environ. Biol. Sci.* **2017**, *7*, 28–34.

(123) George E. King Engineering. Acid Backflow HCl Acid Byproducts. *Yumpu*, 2009. <https://www.yumpu.com/en/document/view/49149153/acid-backflow-george-e-king-petroleum-engineering-oil-and-gas->

(124) Taylor, K. C.; Nasr-El-Din, H. A.; Dajani, R. B. Analysis of Acid Returns Improves Efficiency of Acid Stimulation: A Case History. *J. Pet. Sci. Eng.* **2000**, *28* (1–2), 33–53.

(125) Abdullah, K.; Malloy, T.; Stenstrom, M. K.; Suffet, I. H. Toxicity of Acidization Fluids Used in California Oil Exploration. *Toxicol. Environ. Chem.* **2017**, *99*, 78–94.

(126) Daeffler, C. S.; Del Valle, J. F.; Kariampally, J.; Elkhoury, J. E.; Max, N.; Panga, M. Improving Wormholing Efficiency in Carbonates with a Novel System Based on Hydrochloric Acid. *Proceedings of the SPE International Conference and Exhibition on Formation Damage Control*, Lafayette, LA, February 7–9, 2018; OnePetro: Richardson, TX, **2018**; SPE-189540-MS. DOI: 10.2118/189540-ms.

(127) Olajire, A. A. The Petroleum Industry and Environmental Challenges. *J. Pet. Environ. Biotechnol.* **2014**, *5* (4), 186.

(128) ENERGY POLICY ACT OF 2005 U.S.C. §109-58 (2005).

(129) EPA Letter to California State Water Resources Control Board and California Department of Conservation. *United States Environmental Protection Agency*, 2014. <https://www.epa.gov/sites/default/files/2015-07/documents/ca-class-ii-uic-letter-2014-12-22.pdf>

(130) Stringfellow, W. T.; Camarillo, M. K.; Domen, J. K.; Shonkoff, S. B. C. Comparison of Chemical-Use between Hydraulic Fracturing, Acidizing, and Routine Oil and Gas Development. *PLoS One* **2017**, *12* (4), e0175344.

(131) Hossain, K. M. Z.; Deeming, L.; Edler, K. J. Recent Progress in Pickering Emulsions Stabilised by Bioderived Particles. *RSC Advances*. **2021**, *11*, 39027–39044.

(132) Fink, J. Enhanced Oil Recovery. In *Petroleum Engineer's Guide to Oil Field Chemicals and Fluids*, 3rd ed.; Gulf Professional Publishing: Houston, TX, 2021; pp 643–731. DOI: 10.1016/B978-0-323-85438-2.00016-5.

(133) Liu, D.; Yan, Y.; Bai, G.; Yuan, Y.; Zhu, T.; Zhang, F.; Shao, M.; Tian, X. Mechanisms for Stabilizing and Supporting Shale Fractures with Nanoparticles in Pickering Emulsion. *J. Pet. Sci. Eng.* **2018**, *164*, 103–109.

(134) Sidaoui, Z.; Sultan, A. S.; Brady, D. A Novel Approach to Formulation of Emulsified Acid Using Waste Oil. In *Proceedings of the SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition*, Dammam, Saudi Arabia, April 24–27, 2017; OnePetro: Richardson, TX, 2017; SPE-188116-MS.