

A censorious appraisal of the oil well acidizing corrosion inhibitors

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ABSTRACT

Well acidizing is a common stimulation technique for maximizing the output of oil reservoirs. It helps to overcome the low permeability of wellbore by creating new flow channels or enlarging old ones. Corrosion challenge is encountered during the process since tubings are metallic. Corrosion inhibitors are the defence mechanism used in mitigating corrosion problem during acidizing. This review has identified and grouped acidizing corrosion inhibitors into organic-, and polymer-based. The performance of these inhibitors at temperatures of ≥ 60 °C and acid concentration of ≥ 15 wt% is considered. It is noted that greater percentage of studies revolve round the 60 °C. Above 100 °C, the number of scientific articles decreased considerably. Four classes of intensifiers for acidizing corrosion inhibitors have been identified: formic acid, potassium iodide, copper iodide, and antimony chloride. Their chemistries have been discussed. The research gaps identified include (i) scanty information on acidizing inhibitors at temperatures ≥ 150 °C, (ii) limited information on natural polymers and plant biomaterials as acidizing inhibitors, (iii) scanty information on the mechanism of inhibition at temperatures ≥ 150 °C, and (v) limited information on the composition of corrosion products under acidizing conditions. Thus, recommendations for future researches have been given.

1. Introduction

Even though alternatives to fossil fuels are now being investigated, mankind's need for them continues to grow and the price of crude oil per barrel is expected to rise to \$178 by 2050 (Amadeo, 2022). Over 60 percent of all global energy demands are met by oil and natural gas.

Most oil wells contain rock formations such as calcium carbonate, dolomite, siderite, etc. That obstruct the flow of oil. Particularly, in carbonate and sandstone reservoirs, well acidizing is a common way for maximizing oil output through either the expansion or dissolution of the formations to enhance flow (Robertson and Chilingarian, 1989). This process, although beneficial usually create a corrosive environment for the metallic components of the wells. Acidizing thus requires the incorporation of effective corrosion inhibitors into the acid solution to safeguard the wellbore from corrosion. Corrosion inhibitors are synthetic or natural chemicals that, when added to a corrosive solution in small doses, reduce the pace of corrosive attack on metals. Corrosion is worth examining as it has been cited as the leading cause of numerous fatalities and the largest single cause of facility failures in the petroleum

industry (Ratnayake, 2012). Fig. 1 shows the economic cost of corrosion (El Ibrahim et al., 2020).

1.1. General background

A decrease in oil production due to flowline blockage presents a reason for oil well stimulation which in most cases involves the introduction of acid to oil well reservoir to dissolve formation rocks and/or soluble components present in the well. Carbonate and sandstone reservoirs are the two types of well reservoirs known (Ehrenberg and Nadeau, 2005). Sandstone oil well acidizing involves the use of a mixture of 3 wt% HF and 12 wt% HCl, followed by 15 wt% HCl pre-flush (Brondel et al., 1994) to percolates the porous media, dispersing and dissolving soluble components present in the matrix, and in effect remove the blockage. Carbonate acidizing entails the use of strong acid solution (usually 15 wt% HCl) to etch rock matrix, forming conductivity channels called wormholes that enhance oil flow. The carbonates interact with the introduced acid solution and produce a chloride salt solution, water, and carbon dioxide as illustrated in Eq. (1).

Abbreviations: BQC, Benzyl quinolinium chloride; AMPC, (E) -5-amino -3-(4-methoxyphenyl)-N'-(1-(4-methoxyphenyl) ethylidene) (-1Hpyrazole-4-carbohydrazide; ACPC, (E) -5-amino-N'-(4-chlorobenzylidene) -3-(4-chlorophenyl)-1Hpyrazole-4-carbohydrazide; NAC, N-acetyl cysteine; CTCH, 1-cinnamylidene-3-thiocarbonylhydrazide; DCTCH, 1,1-dicinnamylidene-3-thiocarbonylhydrazide; NDTHDC, N¹,N¹-diallyl-N⁶,N⁶-tripropylhexane-1,6-diaminium chloride.

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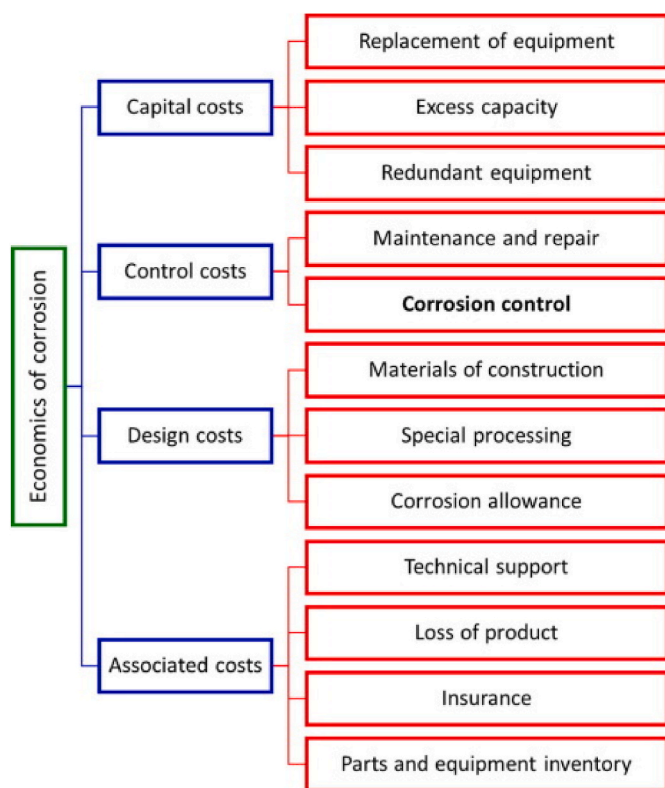
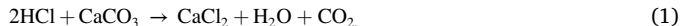


Fig. 1. The Economic cost of corrosion (El Ibrahim et al., 2020). © 2017 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University.



Several factors control the rate at which the acid and the carbonate rocks react: the concentration of the acid, the surface area of the carbonate rock available, and the temperature. Beside HCl, hydrogen fluoride, formic, and acetic acid can also be used in acidizing. Nitric, citric, phosphoric, sulphuric acids can sometimes be combined with the commonly used acidizing acids. HCl is the preferred acid because it forms soluble metal chlorides. HCl has the ability to dissolve formations such as calcium carbonate (CaCO_3), dolomite (CaMgCO_3), siderite (FeCO_3), and iron oxide (Fe_2O_3).

API N80, L80, J55 and Super-13 are types of steel used in the construction of oil wells (Brondel et al., 1994). Acidizing process encourages the corrosion of metallic components of oil wells as well as the acidizing equipment. Several factors control the rate at which the acid affects the metals during corrosion. These factors include the acid contact time, acid concentration, type of acid, and temperature. Though avoiding corrosion is impossible, it can be managed by the application of certain precautions. The application of corrosion inhibitors helps to keep the rate of corrosion during acidizing at a minimum. Hence, the use of an effective inhibitor during acidizing process helps companies to cut cost by the introduction of lower grade carbon steel in well construction. The choice of corrosion inhibitor to be used is dependent on the strength of the acid, the type of steel, the contact time, and the well temperature. Vulnerability to thermal decomposition and loss of integrity of inhibitor effectiveness at elevated temperature possess an important role in selection of inhibitor. This review attempts to give an up-to-date information on corrosion inhibitors designed for acidizing applications. It confines itself to corrosion inhibitors designed under the following conditions: acid concentration $\geq 15\%$; temperatures $\geq 60^\circ\text{C}$.

1.2. A brief history of acidizing

For nearly 120 years, the use of acid treatment and stimulation to improve permeability and increase well production have been utilized in the oil industry. After well acidizing in the late 1940s, other well acidizing methods were introduced. Alchemist Jabir ibn Hayyan discovered hydrochloric acid approximately 800 AD. The pioneer report on acid treatment of oil wells could be traced to the report of Williams et al. (1979) as far as 1895. A year after Williams et al. report, the Standard Oil received a patent for acidifying limestone with HCl in 1896 (Williams et al., 1979). The use of hydrochloric acid (HCl) was introduced by Standard Oil to stimulate wells that were produced from carbonate deposits in Lima, Ohio. Herma Frasch, a Standard Oil chemist is accredited with discovering the acidizing technique. On March 17, 1896, he was granted the first patent on acidizing. In Lima, Ohio wells, the novel acidizing procedure was used with tremendous success. Frasch predicted the necessity for corrosion prevention as well as recommended the use of a latex packer to separate the steel region before pouring the acid into the carbonate formation. Inappropriately, for a diversity of aims, maintaining acidification was not possible. It was not until the late 1920s that oil well stimulation resumed, and not commercially until 1932. The effort of Sylvia Stoesser, reported by The Dow Chemical Company (The Dow Chemical Company, 1925) as The Dow Chemical Company's first female research scientist, marked the second milestone. Sylvia Stoesser's main breakthrough occurred a few years later, when she collaborated with John Grebe, the head of the Dow physics laboratory, to create an acid inhibitor for oil well stimulation. In 1932, The Pure Oil Company which ran oil wells in the Midland zone, had perceived those researchers at the Dow Physics Laboratory were investigating with acidifying brine wells to enhance its yield. Dow was able to eradicate compounds from the deep brine before recurring the residue to the well. Originally, the use of arsenic and copper salts as inhibitors did not yield positive results in reducing the corrosive nature of the acid. Stoesser focused her study on organic compounds in the hopes of developing a material that would build an organic layer on the metal pipe's surface, shielding it from corrosive acid contact. The Pure Oil Company had a vigorous exploration program in Michigan and possessed oil property there. Dow had brine wells in the region that were produced from a sandstone formation. As a result, Pure Oil Company requested that Dow assist them with their operations. Since Dow had no curiosity in oil manufacture, in 1932 both companies worked hand in hand to utilize HCl to stimulate quite several oil wells in Michigan. Nevertheless, the acid fracturing was not recognised and utilized until 1930s and 1940s. Clason and Staudt projected that the centrifugal dissemination of acid would not cause the production increase seen in acidizing treatments in carbonates. He claimed that crevices must exist, and that huge gains in productivity could only be explained by enlarging the fissures and/or removing boring fluid or other deposits from the crevices or cracks. In 1972, Nierode et al. (1972) obtained a kinetic model for the reaction of HCl with limestone which was an unintentional third milestone. This research transformed carbonate acidification from a mystery to a science with some predictability. Nierode et al. (1972) used their prototypical to forecast acid reactions and create acid treatments during operations. Fig. 2 shows a summarized flow diagram of the important events stated.

1.3. Types and procedure of acidizing process

Acid treatments are divided into three categories: acid washing, matrix acidizing, and fracture acidizing.

1.3.1. Acid washing

The main purpose of acid washing is simply tubular and wellbore cleaning. It is not intended to treat the formation but to clear out debris obstructing flow in the well. It is mostly used in carbonate formations. It is the process of cleaning a well at low pressure with a mild hydrochloric

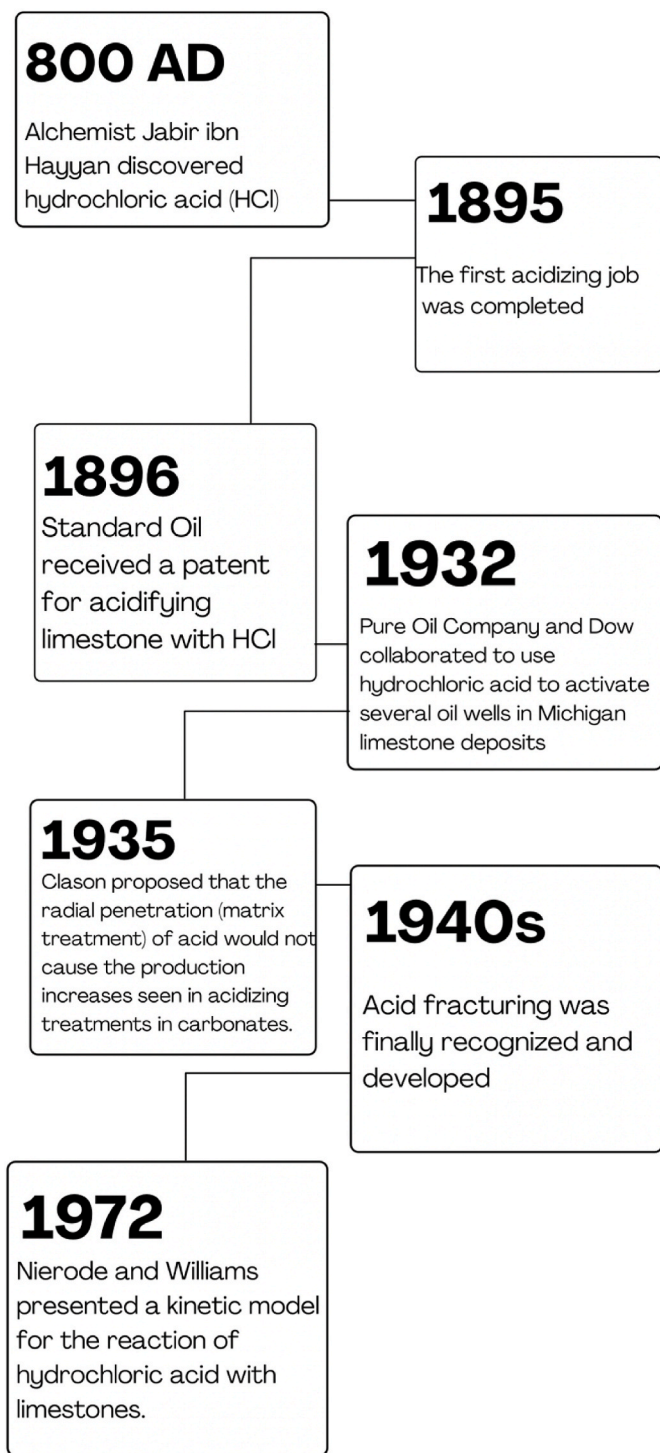


Fig. 2. History of acidizing.

acid solution (usually 7 wt%) (API, 2014) and additives to remove debris, rust, and scale, allowing oil and gas to flow easily into the well.

The acid is pumped directly to the region of geological formation that must be cleaned using steel tubing. Dilute acid is used in a minimal volume. When pumping acid into the well, the pressure should be high enough to balance off the down-hole pressure while also marginally exceeding the pressure of the formation. The pressure imposed on the well allows acid to flow down the well and quickly into the formation. This allows small particles to dissolve.

1.3.2. Matrix acidizing

Matrix acidizing is a stimulation technique whereby acid is pumped into a well to infiltrate rock pores at a pressure that is below the formation-fracturing pressure. The acid dissolves sediments and muds that are hindering flow. This procedure increases the reservoir's innate pores, allowing petroleum to flow without obstruction. It is intended to improve or restore permeability around the wellbore (a radius of 8–24 inches [20.3–61 cm]) without damaging the producing formation. Acid volume of between 15 and 200 gal [0.19 and 2.5 m³] per foot [meter] of producing formation is used for this process (API, 2014) and the acid concentration ranging from 5 to 15 wt% (Williams et al., 1979; API, 2014; Crowe et al., 1981). HCl solution is recommended for the dissolution of carbonate minerals while HCl/HF formulations is for plugging minerals, mainly silicates (clays and feldspars) (Pourabdollah, 2020) (Ahmed et al., 2014). The first matrix acidizing jobs were quite effective in improving carbonate oil production (Williams et al., 1979; Crowe et al., 1981). The stimulation process has been claimed to have a success rate in the range of 50–75% (Rabbani et al., 2018) and the global market for matrix acidizing is expected to be in the region of 75–80% relative to other stimulation techniques (Enelamah et al., 2003).

1.3.3. Fracture acidizing

Compared to matrix acidizing, fracture acidizing involves the injection of acid into a carbonate formation at a pressure above the formation-fracturing pressure (King, 1986). Thus, the flowing acid etches the fracture faces in an unregular pattern, forming conductive channels that remain open even in the absence of a propping agent after the fracture closes. The volume of HCl used for fracture acidizing ranges from 100 to 500 gal [1.24–6.2 m³] per foot [meter] of producing formation. Acid fracturing is recommended for carbonate reservoirs and not for sandstone (Gaurina-Medimurec et al., 2021). Because acid reacts faster with carbonates and is consumed, it is recommended that the acid reaction rate is considerably reduced. This is a major disadvantage in fracture acidizing of carbonate oil wells. The distinction between fracture and matrix acidizing can be shown in Fig. 3.

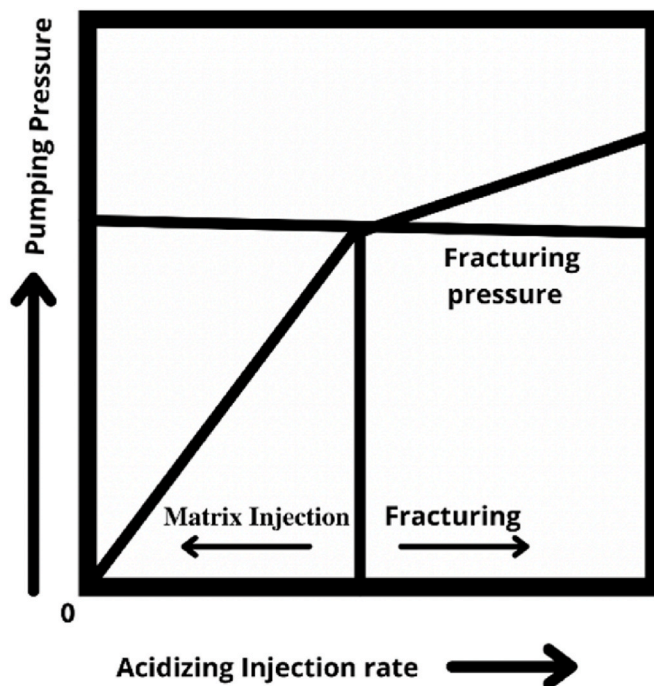
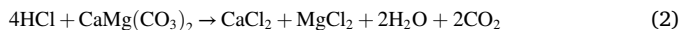


Fig. 3. Difference between fracture and matrix acidizing considering pumping pressure and acidizing injection rate.

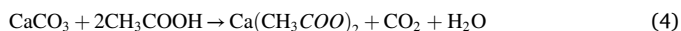
1.4. The chemistry of acidizing process

The two common type of well reservoirs are the carbonate and sandstone. HCl is the frequency used acid during acidizing. The chemical interaction between HCl and limestone in a carbonate oil well reservoir can be depicted as follows:

HCl and dolomite reaction is identical to limestone with additionally magnesium chloride obtained during the process.

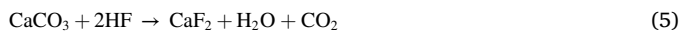


The highest dissolving power is gotten from HCl for carbonate deposits followed by formic acid and acetic acid (Table 1). The products of the reaction are either water-soluble or gaseous. Limestone and dolomite do not completely react with organic acids, therefore less rock is dissolved by a given volume than the chemical formula depicted in Equations (3) and (4) (Williams et al., 1979).



A mixture of HCl and HF are used as treating acids for sandstone oil well reservoirs. The main purpose is to dissolve small particles like clays that clog the formation's flow channels near the wellbore (Abdelmoneim and Nasr-El-Din, 2015; Smith and Hendrickson, 1965). The reactions of HF with various minerals found in sandstone reservoirs are represented by Equations (5)–(9):

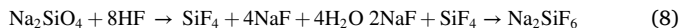
With calcite:



With silica:



With silicates (feldspar or clays):



1.5. Inhibitors: why needed?

Corrosion inhibitors are commonly employed to suppress the rate of corrosion of metals in a range of disciplines, ranging from industrial to construction sectors. Inhibitors are primarily used to safeguard acid pumping/handling equipment as well as well equipment. Therefore, a corrosion inhibitor can be described as a chemical substance that successfully decreases the rate of corrosion. Basically, two parameters are used to measure the effectiveness of an inhibitor: the corrosion rate (v) and the percentage inhibition efficiency ($\% \eta$). The average v can be obtained using Eq. (10) (ASTM International, 1999):

$$v = \frac{K \times W}{A \times T \times D} \quad (10)$$

Table 1

Dissolving power of acids (Williams et al., 1979).

Acid	5% ^a	10% ^a	15% ^a	30% ^a
Limestone (CaCO₃)				
HCl	0.026	0.053	0.082	0.175
HCOOH	0.020	0.041	0.062	0.126
CH ₃ COOH	0.016	0.031	0.047	0.096
Dolomite (CaMg(CO₃)₂)				
HCl	0.023	0.046	0.071	0.152
HCOOH	0.018	0.036	0.054	0.112
CH ₃ COOH	0.014	0.027	0.041	0.083

^a Volume rock dissolved/volume acid solution reacted.

where K is a conversion constant and equals 3.45×10^6 or 8.78×10^4 when the unit of v is mils per year (mpy) or millimetres per year (mm/y). K is equal to 3.45×10^3 , 2.87×10^2 , 8.76×10^7 , and 2.78×10^6 if the unit of v is inches per year (ipy), inches per month (ipm), micrometres per year ($\mu\text{m}/\text{y}$), and picometres per second (pm/s), respectively (ASTM International, 1999). T is the immersion time in hours, A is the exposed surface area in cm^2 , W is the mass loss in grams, and D is the density of the substrate in g/cm^3 .

Faraday's Law can as well be used to calculate the corrosion rate, either in terms of penetration rate (PR) or mass loss rate (MR) (ASTM G102, 2015):

$$PR = K_I \frac{i_{\text{corr}}}{D} EW \quad (11)$$

$$MR = K_2 i_{\text{corr}} EW \quad (12)$$

where: PR is given in mm/yr , i_{corr} is the corrosion current density in $\mu\text{A}/\text{cm}^2$, K_I equals 3.27×10^{-3} , $\text{mm g}/\mu\text{A cm y}$, and EW is the equivalent weight and is dimensionless.

MR is expressed in $\text{g}/\text{m}^2 \text{d}$, and K_2 is equal to 8.954×10^{-3} , $\text{g cm}^2/\mu\text{A m}^2 \text{d}$.

For acid cleaning or washing operations under normal atmospheric conditions, the maximum corrosion rate allowable for carbon steel is ≤ 50 mpy (Umoren and Solomon, 2020).

Another important parameter for the evaluation of inhibitor's performance is the computation of the inhibition efficiency, usually in percentage. When the evaluation is performed using weight or mass loss technique, inhibition efficiency is calculated using Eq. (13). Similarly, Eqs. (14) and (15) are used when inhibitor's performance is examined using the electrochemical impedance spectroscopy and potentiodynamic polarization techniques, respectively. In most cases, an effective corrosion inhibitor is expected to exhibit an inhibition efficiency of greater than 75%.

$$\eta(\%) = \frac{(v_{\text{uninhibited}} - v_{\text{inhibited}})}{v_{\text{uninhibited}}} \times 100 \quad (13)$$

$$\eta(\%) = \left(\frac{R_{\text{ct}}(\text{inhibited}) - R_{\text{ct}}(\text{uninhibited})}{R_{\text{ct}}(\text{inhibited})} \right) \times 100 \quad (14)$$

$$\eta(\%) = \left(\frac{i_{\text{corr}}(\text{uninhibited}) - i_{\text{corr}}(\text{inhibited})}{i_{\text{corr}}(\text{uninhibited})} \right) \times 100 \quad (15)$$

where R_{ct} is the charge transfer resistance in $\Omega \text{ cm}^2$.

Corrosion control is critical in acidizing procedures because of the detrimental effect of the process on metallic structures. The acidizing solution must be fortified with an effective corrosion inhibitor to keep the rate of corrosion of metallic components within the acceptable limit (Subramania et al., 2008; Panossian et al., 2012).

2. Corrosion inhibitor for acidizing process

As earlier mentioned, metals corrosion during acidizing procedures is a serious challenge, hence, the use of effective inhibitor is sacrosanct for the success of the process. However, the task of selecting and application of the right chemical is a complex one. It is not uncommon for a corrosion inhibitor that works in one well to fail in another (Khodyrev et al., 2011). Nevertheless, the general requirements for an ideal acidizing corrosion inhibitor include:

- (i) it should be capable of multi-inhibition. That is, it should be effective in different acid media (HCl, H₂SO₄, H₃PO₄, HClO₄, HNO₃, H₂CO₃, and H₂S);
- (ii) it should be highly thermally stable retaining its outstanding inhibition performance with temperature fluctuation;

- (iii) it should be cheap and at low concentration be capable of maintaining its efficiency in the face of extreme operating conditions (high temperature and velocity);
- (iv) it should be resistant to hydrolysis by bases and acids. In other word, it should be chemically stable;
- (v) it should not wash off easily and capable of protecting against all forms of corrosion.
- (vi) it should be odourless and have low viscosity;
- (vii) it needs to be eco-friendly (green, not toxic).

2.1. Organic-based acidizing inhibitors

Organic corrosion inhibitors, mostly the acetylenic alcohols, aromatic aldehydes, alkenylphenones (Jasinski and Frenier, 1992; Growcock, 1989; Frenier et al., 1991), amines (Walker, 1994), amides, nitrogen-containing heterocycles (e.g., imidazoline-based (Singh and Quraishi, 2015; Solomon et al., 2019; Solomon et al., 2020), nitriles, imminium salts, triazoles, pyridine and its derivatives or salts (Williams et al., 1992, 1993a, 1993b)), quinoline derivatives, thiourea derivatives, thiosemicarbazide, thiocyanates, quaternary salts (Williams et al., 1992, 1993a, 1993b), and condensation products of carbonyls and amines (Quraishi and Jamal, 2000a, 2000b) are used during acidizing procedures. They inhibit majorly by adsorption mechanism (Khodyrev et al., 2011; Quraishi and Jamal, 2000a, 2000b). Table 2 summarizes the corrosion inhibition performance of some organic acidizing inhibitors.

In some formulations, organic compounds work in synergy with propargyl alcohol (de Queiroz Baddini et al., 2007; Perry et al., 1990). For instance, propargyl alcohol-formaldehyde mixture, propargyl alcohol-propylene mixture (de Queiroz Baddini et al., 2007; Perry et al., 1990) as well as propargyl alcohol-benzyl quinolinium chloride (BQC) formulation are highly effective acidizing inhibitors. Nevertheless, the high toxicity of propargyl alcohol is of serious concern as it is capable of posing serious negative effect on the environment and on human lives (Thakur et al., 2013). The current research drive is to have effective inhibitor devoid of propargyl alcohol. Wang et al. (2019) reported a new class of indolizine compound as green acidizing inhibitor capable of providing excellent protection at a much lower dose than BQC-propargyl alcohol mixture. Scheme 1 shows the synthesis of the indolizine derivative Di-BQC and MDi-BQC. Di-BQC, a dimer of BQC was synthesized by heating a mixture of triethylamine and BQC through 1,3-dipolar cycloaddition. MDi-BQC, in the other hand was synthesized through the intermolecular 1,3-dipolar cycloaddition reaction between BQC and acetoxyl quinolinium chloride. In 15 wt% HCl solution at 90 °C and after 4 h of immersion, the presence of 1.0 wt% Di-BQC and MDi-BQC caused a decrease in the corrosion rate of N80 steel from 1243.5 g m⁻² h⁻¹ to 2.01 g m⁻² h⁻¹ and 3.15 g m⁻² h⁻¹ corresponding to inhibition efficiency of 99.84% and 99.75%, respectively. In 20 wt% HCl solution at 90 °C, the addition of 1.0 wt% Di-BQC and MDi-BQC protected the metal surface by 99.3% and 99.26%, respectively reducing the corrosion rate of N80 steel from 1647.89 g m⁻² h⁻¹ to 10.57 g m⁻² h⁻¹ and 12.17 g m⁻² h⁻¹. Di-BQC and MDi-BQC also performed effectively in 12 wt% HCl + 3 wt% HF mixture at 90 °C. After 4 h of immersion, corrosion rate was reduced from 1104.98 g m⁻² h⁻¹ to 2.10 g m⁻² h⁻¹ and 2.07 g m⁻² h⁻¹, respectively and the N80 steel surface was protected by 99.81%.

Paul et al. (2020) investigated the effectiveness of synthesized (E)-5-amino-3-(4-methoxyphenyl)-N'-(1-(4-methoxyphenyl) ethylidene) (-1Hpyrazole-4-carbohydrazide (AMPC) and (E)-5-amino-N'-(4-chlorobenzylidene)-3-(4-chlorophenyl)-1Hpyrazole-4-carbohydrazide (ACPC) on mild steel corrosion prevention in a 15 wt% HCl solution. The synthesis scheme is given in Scheme 2. The inhibitors (AMPC and ACPC) exhibited a high capability for inhibiting corrosion of metal steel in a 15 wt% HCl giving inhibition efficiency of 91.06% and 86.61% at 60 °C for AMPC and ACPC, respectively.

The thiocarbohydrazide derivatives, namely (1-cinnamylidene-3-thiocarbohydrazide) (CTCH) and (1,1-dicinnamylidene-3-

thiocarbohydrazide) (DCTCH) (their structures and some properties are given in Table 3) are another highly effective inhibitor for carbon steel corrosion in 15 wt% HCl solution (Subramania et al., 2008). They are very effective even up to 110 °C. Sathiya et al. (Subramania et al., 2008) investigated the inhibitory action of CTCH and DCTCH on carbon steel corrosion in 15 wt% HCl solution. At 90 °C and 110 °C, the corrosion rate of carbon steel in the studied corrosive medium was found to be 6309.57 mmpy and 14,417.00 mmpy, respectively. However, in the presence of 1500 ppm CTCH, the corrosion rate was lowered to 112.11 mmpy and 255.96 mmpy at 90 °C and 110 °C, respectively with the inhibitor protecting the metal surface by 98.2%. The DCTCH exhibited slightly better inhibitory property than CTCH. The presence of 1500 ppm in 15 wt % HCl solution at 90 °C and 110 °C protected carbon steel surface by 99.0% reducing the corrosion rate from 6309.57 mmpy and 14,417.00 mmpy, respectively to 62.01 mmpy and 140.71 mmpy. The high inhibition efficacy was associated with effective adsorption on the metal surface due to the presence of N and S atoms, -C = N group, and aromatic rings in DCTCH and CTCH (Subramania et al., 2008). The higher inhibiting effect by DCTCH relative to CTCH was linked to the influence of the substituted terminal hydrogen on both sides of the hydrazino group on efficiency due to the increase of π -electron density on the ligating sulfur atom leading to an easier electron transfer from the functional group (C = S) to the metal, producing greater coordinate bonding and, hence, greater adsorption and higher inhibition efficiency of DCTCH.

The amino acids are one of the target compounds to serve as replacement in the nearest future for the toxic corrosion inhibitors. They are biodegradable, harmless to both humans and the natural environment, and easy to produce with very high purity. The natural amino acids are mostly the α -amino acids and contain carboxyl and amino functionalities bonded to the same carbon atom (Fig. 4) that qualify them as potential corrosion inhibitors. However, the corrosion inhibiting property of amino acids is influenced by the nature of the -R group. According to Hluchan et al. (1988), the corrosion inhibiting property of the amino acids increase as the hydrocarbon chain gets longer or as the number of additional amino groups increased. Researchers have therefore subjected amino acids to modification in order to enhance their performance and make them suitable for application in harsh environments like acidizing.

Ituen et al. (Ituen et al., 2017) studied the performance of N-acetyl cysteine (NAC) and its formulations mild steel, J55, and X80 corrosion in 15 wt% HCl solution at various temperatures and compared their inhibition performance with that of a commercial corrosion inhibitor. The formulations were designated as NACGK (1 mM NAC + 10⁻⁵ M glutathione + 10⁻⁵ M KI), NACPK (1 mM NAC + 10⁻⁵ M polyethylene glycol (Molecular weight 4000 g/mol) + 10⁻⁵ M KI), and NACHK (1 mM NAC + 10⁻⁵ M 5-hydroxytryptophan + 10⁻⁵ M KI). It was found that the steels corroded in the order J55 > mild steel > X80 steel after 5 h of immersion. At 90 °C, 1 mM NAC was found to lost its inhibition efficacy while the formulations NACGK, NACPK, and NACHK protected X80 steel by 91.4%, 88.9%, and 81.5% which was comparable to 95.6% being the inhibition efficiency of a commercial inhibitor. The team also reported an inhibition efficiency of 89.2% for L-theanine + PEG + KI formulation deployed as inhibitor for X80 steel in 15 wt% HCl solution at 90 °C after 5 h of immersion Ituen et al. (Ituen et al., 2019).

2.2. Polymeric-based inhibitors

Polymers are very large molecules that are made up of many tiny molecules called monomers. The repeating unit(s) in polymer chain confers multiple adsorption centers characteristic on polymers – one of the properties that evoke the research interest on polymers as metals corrosion inhibitors. They can form complexes with metal ions, cover a large surface area on metal surfaces, and shield them from corrosive species in solution (Umoren et al., 2020). Polymers can be utilized as corrosion inhibitors as well as protective coatings. Deoxyribonucleic

Table 2
Some examples of organic-based acidizing corrosion inhibitors.

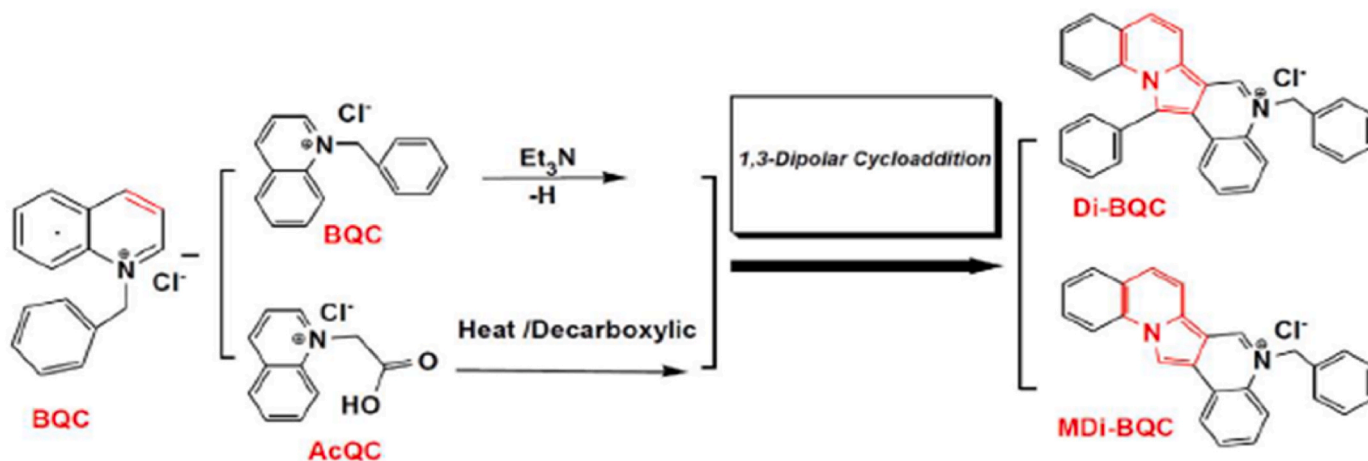
Inhibitor	Medium	Substrate	Inh. Conc.	Experimental conditions	IE (%)	Ref.
Octyl alcohol	15 wt% HCl	MS	1%	Method: WL Temp.: 105 °C IT.: 6 h	82%	Jayaperumal (2010)
Propargyl alcohol	15 wt% HCl	MS	1%	Method: WL Temp.: 105 °C IT.: 6 h	99%	Jayaperumal (2010)
Formaldehyde:phenol (1:2 mixture)	15 wt% HCl	N80 steel	0.8%	Method: WL Temp.: 90 °C IT.: 24 h	71%	Kumar and Vishwanatham Emranuzzaman (2008)
Formaldehyde:o-cresol (1:2 mixture)	15 wt% HCl	N80 steel	0.8%	Method: WL Temp.: 115 °C IT.: 24 h	93%	Kumar and Vishwanatham Emranuzzaman (2008)
Formaldehyde:p-cresol (1:2 mixture)	15 wt% HCl	N80 steel	0.8%	Method: WL Temp.: 115 °C IT.: 24 h	90%	Kumar and Vishwanatham Emranuzzaman (2008)
Tributylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	98%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Aniline + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	97%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
n-Octylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	92%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Diphenylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	92%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Dodecylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	91%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
di-n-Butylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	91%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Cyclohexylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	90%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
n-Butylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	84%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Triethylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	81%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Hexylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	76%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
sec-Butylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	76%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Diethylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	75%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Propylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	74%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Isopropylamine + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	72%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
1,3-Dibutyl-2-thiourea + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	96%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
1,3-Diethyl-2-thiourea + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	88%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
1,3-Dimethyl-2-thiourea + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	71%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Propargyl alcohol + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	98%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
2-Pentyn-1-ol + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	97%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
3-Butyn-1-ol + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Temp.: 60 °C IT.: 3 h	97%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)

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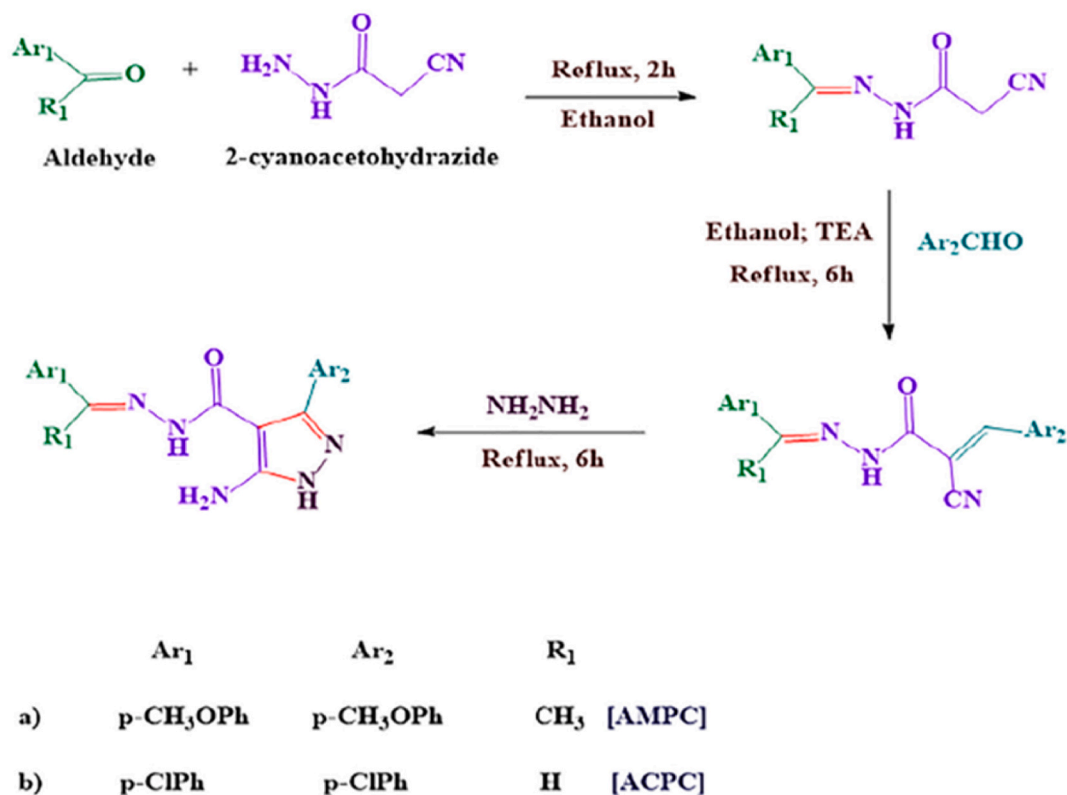
Table 2 (continued)

Inhibitor	Medium	Substrate	Inh. Conc.	Experimental conditions	IE (%)	Ref.
2-Butyn-1-ol + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Tempt.: 60 °C IT.: 3 h	96%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
2-Butyne-1,4-diol + 0.6% (w/v) formaldehyde	15 wt% HCl	CS UNS-G4130	2% (w/v)	Method: WL Tempt.: 60 °C IT.: 3 h	94%	(Finšgar and Jackson, 2014) (Cardoso et al., 2007; de Queiroz Baddini et al., 2007)
Furfuryl alcohol	15 wt% HCl	N80	80 mmol/L	Method: WL Tempt.: 110 °C IT.: 24 h	90%	Vishwanatham and Haldar (2008)
3-Undecane-4-aryl-5-mercapto-1,2,4-triazole	15 wt% HCl	MS	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	83%	Quraishi and Jamal (2000a)
3-(Heptadeca-8-ene)-4-aryl-5-mercapto-1,2,4-triazole	15 wt% HCl	MS	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	95%	Quraishi and Jamal (2000a)
3-(Deca-9-ene)-4-aryl-5-mercapto-1,2,4-triazole	15 wt% HCl	MS	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	99%	Quraishi and Jamal (2000a)
3-(Deca-9-ene)-4-aryl-5-mercapto-1,2,4-triazole	15 wt% HCl	MS	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 6.0 h	96%	Quraishi and Jamal (2000a)
Dicinnamylidene acetone	15 wt% HCl	N-80	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	96%	Sardar and Ali (2002)
Dicinnamylidene acetone + 1000 mg/L KI	15 wt% HCl	N-80	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	93%	Sardar and Ali (2002)
Disalicylidene acetone	15 wt% HCl	N-80	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	99%	Sardar and Ali (2002)
Disalicylidene acetone + 1000 mg/L KI	15 wt% HCl	N-80	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	98%	Sardar and Ali (2002)
Divanillidene acetone	15 wt% HCl	N-80	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	30%	Sardar and Ali (2002)
Divanillidene acetone + 1000 mg/L KI	15 wt% HCl	N-80	5000 mg/L	Method: WL Tempt.: 105 °C IT.: 24 h	22%	Sardar and Ali (2002)
2-Benzoyl-3-hydroxy-1-propene	15 wt% HCl	J55	2 g/L	Method: WL Tempt.: 65 °C IT.: 24 h	92%	Frenier et al. (1991)
2-Benzoyl-3-hydroxy-1-propene + adduct of trimethyl-1-heptanol with 7 mol of ethylene oxide (THEO)	15–28 wt % HCl	J55	4 g/L + 1.0 g/L THEO	Method: WL Tempt.: 65 °C IT.: 24 h	99%	Frenier et al. (1991)
2-Benzoyl-3-methoxy-1-propene + DDPB	15–28 wt % HCl	J55	4 g/L + 1.0 g/L DDPB	Method: WL Tempt.: 65 °C IT.: 24 h	98%	Frenier et al. (1991)
2-Benzoyl-3-hydroxy-1-propene + Ndodecylpyridinium bromide (DDPB)	15–28 wt % HCl	J55	4 g/L + 1.0 g/L DDPB	Method: WL Tempt.: 65 °C IT.: 24 h	99%	Frenier et al. (1991)
2-Benzoyl-1,3-dimethoxypropane + DDPB	15–28 wt % HCl	J55	4 g/L + 1.0 g/L DDPB	Method: WL Tempt.: 65 °C IT.: 24 h	99%	Frenier et al. (1991)
2-Benzoyl-1,3-dimethoxypropane + THEO	15–28 wt % HCl	J55	4 g/L + 1.0 g/L THEO	Method: WL Tempt.: 65 °C IT.: 24 h	99%	Frenier et al. (1991)

IT = immersion time; WL = weight loss; EIS = electrochemical impedance spectroscopy; MS = mild steel; IE = inhibition efficiency.



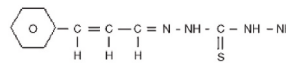
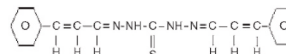
Scheme 1. Synthesis of the indolizine derivative Di-BQC and MDI-BQC from quaternary quinolinium salts BQC and AcQC (Wang et al., 2019). Reproduced with permission from Wang et al. (2019). © 2019 Society of Petroleum Engineers.



Scheme 2. Reaction scheme for AMPC and ACPC (Paul et al., 2020). Reproduced with permission from Paul et al. (2020). © 2020 The Authors. Production and hosting by Elsevier B.V. on behalf of Indian Institute of Technology (ISM) Dhanbad, India.

Table 3

Molecular formula, molecular weight, structure, and melting point of CTCH and DCTCH (Subramania et al., 2008). Reproduced with permission from Subramania et al. (2008). © 2008 The Authors. Production and hosting by Corrosion journal Vol. 64, No. 8.

Name of compound	Molecular formula	Molecular weight	Structure	Melting point (°C)
1-cinnamylidene-3-thiocarbohydrazide (CTCH)	C ₁₀ H ₁₂ N ₄ S	220.20		163
1,1'-dicinnamylidene-3-thiocarbohydrazide (DCTCH)	C ₁₉ H ₁₈ N ₄ S	334.29		165

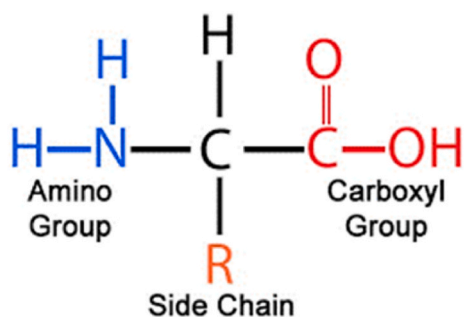


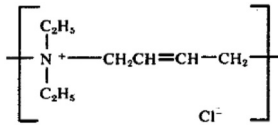
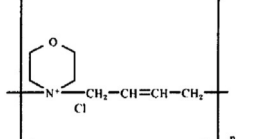
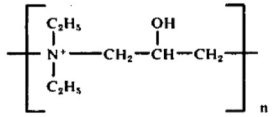
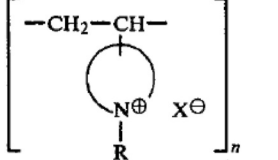
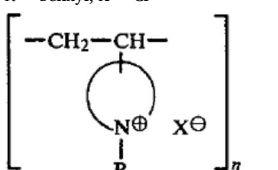
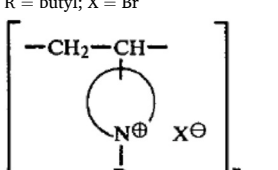
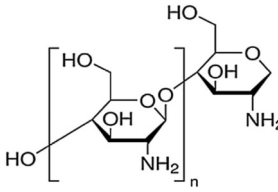
Fig. 4. The basic structure of amino acids.

acid, for example, is a biopolymer that has a high inhibitory efficacy against steel reinforcement (Jiang et al., 2017). Similarly, chitosan, a natural polymer, is utilized as a corrosion inhibitor in hydrochloric acid (Wang et al., 2021; Chauhan et al., 2020). Beside the presence of multiple adsorption centers, polymers are environmentally friendly, non-toxic, and cost-effective. Despite the attractive features of polymers, not many polymers are useable under acidizing conditions. This is

because, common polymeric materials are unstable at high temperature required for acidizing process. At very high temperature, polymers decompose and could clog the flow channels. In fact, their applications are in acid pickling/cleaning environments where the temperature is less than 60 °C (Umoren and Solomon, 2019).

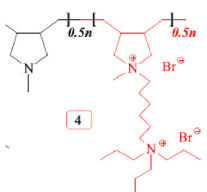
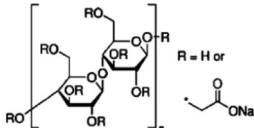
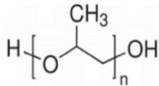
Nevertheless, some polymeric materials still gain application in acidizing process but mostly in combination with synergists. In Table 4 is summarized some polymeric compounds/formulations evaluated as corrosion inhibitors under acidizing conditions. The polyquaternary compounds are among the most studied polymeric materials for acidizing applications (Annand and Woodson, 1976). They have a broad liquid range (appro. 300 °C) (Kärnä et al., 2010) and are effective as inhibitor in acidizing process (Table 4). They can ensure over 90% protection of carbon steel surface protection in acidizing environment. Polyquaternary amines, for example formed by reacting diethylamine with 1,4-dichlorobutene or diethylamine with epichlorohydrin, at 0.25% concentration protected low carbon steel surface in acidizing medium by over 90% at 93.3 °C (Annand and Woodson, 1976). Quinlan (1980) showed that quaternary polymers exhibit superior inhibitory effect than non-quaternary polymers in acidizing medium. The author reported that while quaternary polymers could offer inhibition efficiency of over 90%, the inhibition efficiency of the non-quaternary

Table 4
Some effective polymeric inhibitors for acidizing condition.

Inhibitor	Structure of repeat unit	Inhibition performance	Ref.
The reaction product of diethylamine and 1,4- dichlorobutene		<ul style="list-style-type: none"> - Conc.: 0.25% - IE: 70–90% - Tempt.: 93.3 °C - Medium: 280 g/L H₂SO₄ 	Annand and Woodson (1976)
The reaction product of morpholine and 1,4- dichlorobutene		<ul style="list-style-type: none"> - Conc.: 0.25% - IE: 70–85.0% - Tempt.: 93.3 °C - Medium: 280 g/L H₂SO₄ 	Annand and Woodson (1976)
The reaction product of diethylamine and epichlorohydrin		<ul style="list-style-type: none"> - Conc.: 0.25% - IE: 70–90% - Tempt.: 93.3 °C - Medium: 280 g/L H₂SO₄ 	Annand and Woodson (1976)
The reaction product of 4-vinyl pyridine and benzyl chloride	 R = benzyl; X = Cl	<ul style="list-style-type: none"> - Conc.: 20,090 mg/L - IE: 93% - Tempt.: 93.3 °C - Medium: 15 wt% HCl - IT: 4 h 	Quinlan (1980)
The reaction product of 4-vinyl pyridine and butyl bromide	 R = butyl; X = Br	<ul style="list-style-type: none"> - Conc.: 2500 mg/L - IE: 99% - Tempt.: 93.3 °C - Medium: 15 wt% HCl - IT: 4 h 	Quinlan (1980)
The reaction product of 4-vinyl pyridine and ethyl iodide	 R = ethyl; X = I	<ul style="list-style-type: none"> - Conc.: 2500 mg/L - IE: 99% - Tempt.: 93.3 °C - Medium: 15 wt% HCl - IT: 4 h 	Quinlan (1980)
The reaction product of para-vinylpyridine and benzoyl peroxide quaternized with methyl iodide	-	<ul style="list-style-type: none"> - Conc.: 0.1% - CR: 0.17 mpy - IE: 91% - Tempt.: 82.2 °C - Medium: 15 wt% HCl - IT: 24 h 	Muzyczko et al. (1970)
The reaction product of para-vinylpyridine and benzoyl peroxide mixed with propargyl alcohol	-	<ul style="list-style-type: none"> - Conc.: 0.1% - CR: 0.06 mpy - IE: 97% - Tempt.: 82.2 °C - Medium: 15 wt% HCl - IT: 24 h 	Muzyczko et al. (1970)
Chitosan/silver nanoparticles composites		<ul style="list-style-type: none"> - Conc.: 1000 mg/L - CR: 0.06 mpy - IE: 94% - Tempt.: 60 °C - Medium: 15 wt% H₂SO₄ - IT: 10 h 	Solomon et al. (2017a)
Biopolymer dextrin-based graft copolymer	-	<ul style="list-style-type: none"> - Conc.: 0.15 g/L - IE: 98% - Tempt.: 60 °C - Medium: 15 wt% HCl 	Biswas et al. (2019)
Random copolymer, containing diallylmethylamine and N ¹ ,N ¹ -diallyl-N ¹ -methyl-N ⁶ ,N ⁶ ,N ⁶ -tripropylhexane-1,6-diammonium dibromide units + KI	-	<ul style="list-style-type: none"> - Conc.: 100 mg/L - CR: 43.4 mm/yr - IE: 88% - Tempt.: 90 °C 	Odegunmi et al. (2020)

(continued on next page)

Table 4 (continued)

Inhibitor	Structure of repeat unit	Inhibition performance	Ref.
		- IT: 6 h	
Carboxymethyl cellulose/silver nanocomposites		- Conc.: 1000 mg/L CR: 7.54 mpy - IE: 96% - Temp.: 60 °C - Medium: 15 wt% H ₂ SO ₄ - IT: 10 h	Solomon et al. (2017b)
Polypropylene glycol		- Conc.: 1000 ppm CR: 31.63 × 10 ⁻⁴ g cm ⁻² h ⁻¹ - IE: 88% - Medium: 15 wt% HCl - IT: 24 h - Temp.: 60 °C	Umoren (2016)

CR = corrosion rate; IE = inhibition efficiency; IT = Immersion time.

counterpart is less than 80%.

Polyquaternary polymers effective as acidizing inhibitors are commonly synthesized from polyamines, namely diethylene triamine, dipropylene triamine, triethylene tetramine, tripropylene tetramine, tetraethylene pentamine, tetrapropylene pentamine, etc. (Annand and Woodson, 1976) and also from polyalkyleneimines, i. E the higher molecular weight amines derived from alkyleneimine such as polyethyleneimines, polypropyleneimines, etc. (Annand and Woodson, 1976). They can also be synthesized from vinyl heterocyclics, such as vinyl pyridine, vinyl pyrazine, vinyl piperidine, vinyl quinoline, alkylated vinyl pyridine, alkylated pyrazine, alkylated vinyl piperidine, alkylated vinyl quinoline, etc. (Singh and Quraishi, 2015) and other nitrogen-containing compounds. To effectively function as metals corrosion inhibitors, polyquaternary polymers are expected to be soluble in an aqueous solution, hence they are usually synthesized with sufficient cationic group to ensure a long adsorptive life, i.e., each atom adheres to the metal for an extended period (Annand and Woodson, 1976) (Quinlan, 1980).

The polymer of N¹,N¹-diallyl-N⁶,N⁶,N⁶-tripropylhexane-1,6-diaminium chloride (NDTHDC), poly (N¹,N¹-diallyl-N⁶,N⁶,N⁶-tripropylhexane-1,6-diaminium chloride) (poly-NDTHDC) is reported to be a highly promising inhibitor for API X60 carbon steel corrosion in 15 wt% HCl solution with good thermal and chemical stability (Fig. 5) (Odegunmi et al., 2020). The polymer is stable in 15 wt% HCl solution and thermally stable up to 214 °C (Fig. 5(a)) (Odegunmi et al., 2020) and the FTIR spectra reveals that the polymer is chemically stable as the bands are intact after heating in the acid solution (Fig. 5(b)).

It was shown that 100 mg/L of poly-NDTHDC afforded inhibition efficiency of 87.5% at 90 °C after 6 h of immersion and that the inhibition performance improves under hydrodynamic condition up to 1500 rpm (Odegunmi et al., 2020). Fig. 6 shows the highly protected steel surface in 15 wt% HCl solution by 100 mg/L poly-NDTHDC for 6 h at 90 °C (Fig. 6(d)) relative to the unprotected (Fig. 6(b)) and NDTHDC protected (Fig. 6(b)) surfaces. The poly-NDTHDC protected surface is in close resemblance with the uncorroded surface in Fig. 6(a). The inhibition efficacy of poly-NDTHDC is due to its ability to form poly-NDTHDC + Fe²⁺ ion complex that substantially cover the metal surface and shield it from corrosive species in the acid solution.

The modification of polymers via nanocompositing is reported to improve the stability and inhibition effectiveness of polymers. The basis is that, metals nanoparticles, because of their active properties have the tendency to interact chemically with carbon steel surface (Solomon et al., 2017b, 2017c; Umoren and Madhankumar, 2016) which in turns causes the recharging of the metal surface. When nanoparticles interact

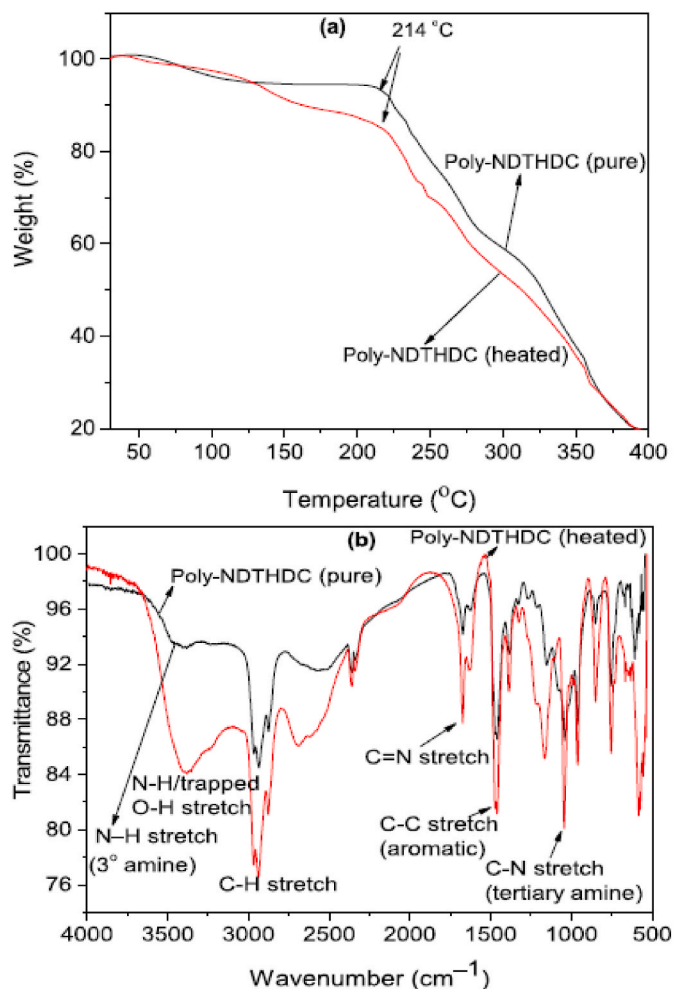


Fig. 5. Comparative (a) TGA and (b) FTIR spectra of pure poly-NDTHDC and poly-NDTHDC recovered from 15 wt% HCl solution after being heated at 90 °C for 12 h (Odegunmi et al., 2020). Reproduced with permission from Odegunmi et al. (2020). © 2020 The Authors. Production and hosting by American Chemical Society.

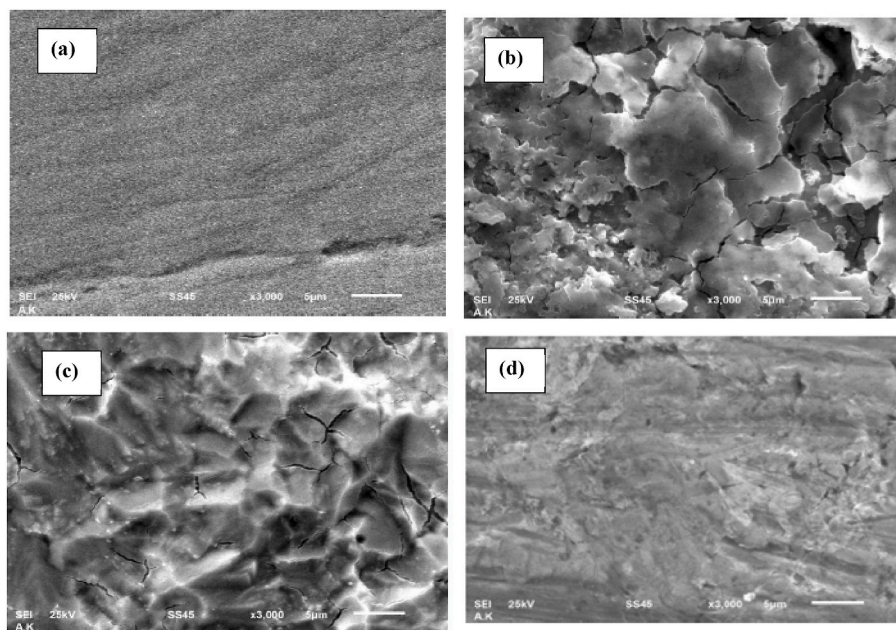


Fig. 6. SEM images showing the surface morphology of the API X60 steel sample surface (a) before immersion and after immersing in 15 wt % HCl solution containing (b) no inhibitor, (c) 1000 mg/L NDTHDC, and (d) 100 mg/L poly- NDTHDC for 6 h at 90 °C (Odewunmi et al., 2020). Reproduced with permission from Odewunmi et al. (2020). © 2020 The Authors. Production and hosting by American Chemical Society.

with a metal surface, extra electrons on the metal surface are transferred from the d-orbital to the anti π orbital of the inhibitor molecules and the retro-donation favours the adsorption of inhibitor molecules (Solomon et al., 2017b, 2017c; Umoren and Madhankumar, 2016). Solomon et al. (2017b) reported that the inhibition efficiency of carboxymethyl cellulose/silver nanoparticles composite increased with increase in temperature and that 1000 mg/L of the nanocomposite protected the surface of low carbon steel in 15 wt% H_2SO_4 solution by 96.37% at 60 °C after 10 h of immersion. Also, the corrosion rate of low carbon steel after 24 h of exposure to 15 wt.% H_2SO_4 and 15 wt.% HCl solutions was reported to be reduced from 494.84 mm/y and 520.55 mm/y to 178.95 mm/y and 111.96 mm/y, respectively by 1000 mg/L of Gum Arabic-silver nanoparticles composite (Solomon et al., 2018a). Other reports have equally highlighted the effectiveness of polymer-metal nanocomposites as inhibitor in acidizing environments (Umoren and Madhankumar, 2016; Badr et al., 2020).

2.3. Intensifiers in acidizing process

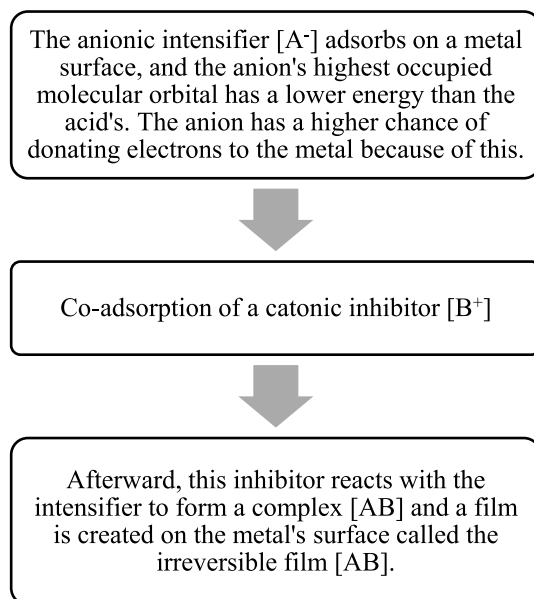
The corrosion inhibitor intensifiers are chemicals that enhance the effectiveness of corrosion inhibitors. In the other word, they are used to increase the corrosion inhibitor performance range. Summarily, corrosion inhibitor intensifiers are used to.

- (i) elongate the inhibitor time and provide safe contact time for acidizing treatment,
- (ii) allow the inhibitor to perform effectively in strong and highly concentrated acids,
- (iii) allow the inhibitor to still function at downhole temperatures (Brezinski, 1999; Hill and DeMott, 1977).

There are four main types of intensifiers for acidizing corrosion inhibitors (Al-Mutairi et al., 2005):

- (i) formic acid,
- (ii) potassium iodide,
- (iii) antimony chloride, and
- (iv) copper iodide

The selection of an intensifier for a particular inhibitor package and application is a very essential task as intensifiers are not compatible with all corrosion inhibitors, and many have restrictions governing their temperature, duration, and environmental conditions. For example, in 15 wt% HCl, formic acid acts effectively as intensifier within the temperature range of 120–160 °C (Cassidy et al., 2013). Antimony-based intensifiers are compatible with 15 wt% HCl, but not with stronger acids like 28 wt% HCl (Cassidy et al., 2013). In fact, the antimony-based intensifiers are limited to acid concentrations of less than 17 wt% (Al-Mutairi et al., 2005). An intensifier has to be screened for compatibility before selecting for a particular corrosion inhibitor. Scheme 3 illustrates the general mechanistic steps at which intensifiers function.



Scheme 3. Mechanism by which intensifiers function.

2.3.1. Formic acid

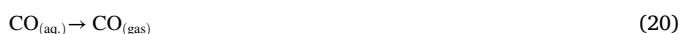
Formic acid has a long history of being used in the oil and gas industry to aid the inhibition performance of corrosion inhibitors (Cassidy et al., 2007; Al-Katheeri et al., 2002). Al-Katheeri et al. (2002), for instance noted that at Saudi Aramco, the use of formic and acetic acids is of major importance in well stimulation. Formic acid is thought to function as intensifier by undergoing a dehydration reaction that produces water and carbon monoxide (CO), a known corrosion inhibitor according to Eq. (16) (Cassidy et al., 2007; Al-Katheeri et al., 2002). Formic acid could therefore be accurately described as a precursor to CO, the inhibiting molecule.



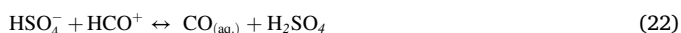
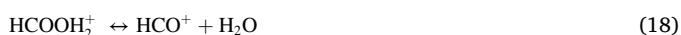
Formic acid does not undergo spontaneous dehydration in any condition. Two requirements must be made for formic acid to decompose and serves as an intensifier:

1. A strong acid concentration is required (normally, it is used in acid concentration of up to 15 wt%);
2. A high temperature is required (works well at 120–160 °C).

In HCl under the above stipulated conditions, formic acid dehydrates according to the following mechanisms (Cassidy et al., 2007):



Equation (17), that is the formic acid protonation is expected to occur rapidly while the formation of the acylium cation in Eq. (18) is regarded as the rate-determining step (Cassidy et al., 2007). Similarly, the dehydration mechanism in H₂SO₄ solution is as follows (Cassidy et al., 2007):



Al-Taq et al. (2012) investigated the effect of formic acid on the inhibition performance of a monodiamine (*N-N*-diallyl-*N*-propargyl-1-dodecyl ammonium chloride) and diamine (*N-N*-diallyl-*N*-propargyl-*N*¹-formyl-1, 12-diaminododecane) compounds on coiled tubing steel in 28 wt% HCl solution at 60 °C, 70 °C, and 80 °C. It was found that the addition of formic acid to the studied compounds enhance their inhibition efficiency. The addition of 0.9 M formic acid to 400 mg/L diamine and 400 mg/L monoamine improved the efficiency from 89.24% to 92.84%–90.77% and 93.34%, respectively after 4 h of immersion at 80 °C. Umoren et al. (2021a) reported an increase in the inhibition efficiency of 200 mg/L of butanolic extract of date palm leaves in 15 wt% HCl solution at 60 °C from 45% to 85.3% upon the addition of 3 mM formic acid.

Although formic acid has been utilized as a corrosion inhibitor intensifier for acidizing process, its effectiveness is however affected by temperature and contact time. As previously stated, formic acid works better as intensifier between in 15 wt% HCl and at 120–160 °C. According to Brezinski (1999), CO gas production for 28% HCl/formic acid mixtures ceased after 3 h at 300 °F (149 °C); in 20% HCl, CO production slowed at about 7 h and inhibition of corrosion failed in the same time frame as when gas production stopped. Motivated by these observations Al-Katheeri et al. (2002) undertook a study to determine the fate of

formic acid at temperatures up to 250 °F (121 °C) in deep gas wells. It was found that in concentrated HCl at 250 °F, the amount of formic acid present in corrosion inhibitors and intensifiers decreased with time. The initial concentration of formic acid was found to decrease by 60% after 8 h. The authors recommended that long shut-in times should be avoided when formic acid is used as intensifier at temperature up to 250 °F as the corrosion of the substrate could be promoted since the corrosion inhibitor concentration is significantly reduced.

2.3.2. Potassium iodide

Potassium iodide (KI) has been proven to be a very effective intensifier for high temperature acidizing inhibitors (Solomon et al., 2020; Umoren et al., 2021a). They have strong tendency to adsorb chemically on a metal surface replenish than other halide ions (Solomon et al., 2020; Umoren et al., 2021a). This is due to the higher ionic radius of iodide ions compared to other halide ions. According to authors (Solomon et al., 2018b), in the acid solution, dissolved oxygen oxidized iodide ions to triiodide and pentaiodide ions. The triiodide and pentaiodide ions preferentially adsorb chemically on the metal surface and satisfactorily replenish the surface such that sufficient amount of the protonated inhibitor molecules can cooperatively adsorb on top of the triiodide and pentaiodide ions layers, the so-called synergistic effect. It was shown that the addition of 1 mM KI to 400 mg/L of 2-heptadecyl-1-[2-(octadecanoylamino)ethyl]-2-imidazoleline upgraded the inhibition efficiency from 49.0% to 87.6% for low carbon steel in 15 wt% HCl solution at 60 °C after 24 h of immersion (Solomon et al., 2020).

A blend of potassium iodide with formic acid exhibits a strong synergistic effect that could in turn significantly enhance the corrosion protection ability of acid corrosion inhibitors. For instance, Al-Taq et al. (2012) studied the combined effect of potassium iodide and formic acid on the corrosion inhibition performances of *N-N*-diallyl-*N*-propargyl-1-dodecyl ammonium chloride and *N-N*-diallyl-*N*-propargyl-*N*¹-formyl-1, 12-diaminododecane on coiled tubing steel in 28 wt% HCl solution at 80 °C after 4 h of soaking time. The results indicated that the addition of KI at 4 g/L of 28 wt% HCl solution in combination with 0.9 M formic acid to 400 mg/L of *N-N*-diallyl-*N*-propargyl-1-dodecyl ammonium chloride and *N-N*-diallyl-*N*-propargyl-*N*¹-formyl-1, 12-diaminododecane, respectively increased the inhibition efficiency of *N-N*-diallyl-*N*-propargyl-1-dodecyl ammonium chloride from 93.3% to nearly 99.9% while that of *N-N*-diallyl-*N*-propargyl-*N*¹-formyl-1, 12-diaminododecane was increased from 90.77% to 98.3% (Al-Taq et al., 2012). The corrosion rate of the coiled tubing steel significantly reduced from the non-acceptable level of >0.05 lb/ft² to acceptable limit of 0.0048 lb/ft². Similar findings was reported by Brezinski (1999).

2.3.3. Copper iodide

Copper iodide is also a component of many commercial acid corrosion inhibitors. It is capable of improving the inhibition performance of organic inhibitor. It is effective up to about 160 °C, but has limited solubility in acid solutions (Fink, 2021). Beside the solubility issue, the use of corrosion inhibitors containing copper iodide as intensifier for the protection of carbon steel is problematic due to the deposition of copper metal on the steel surface under certain conditions. It has been shown experimentally that some of the cuprous ions are effectively reduced to metallic copper by metallic iron under typical bottomhole acid stimulation treatment conditions (Marques and Mainier, 1994):



The Cu²⁺ species can be generated by the Cu⁺ disproportionation reaction that could occur in the hydrochloric acid medium (Marques and Mainier, 1994):



Since the metallic copper is more cathodic than low carbon steel commonly used in the oilfield, its deposition on the steel surface induces galvanic-type corrosion (Marques and Mainier, 1994). Carlos do Carmo Marques and Mainier (1994) investigated the corrosion problems associated with the use of copper-based corrosion inhibitor intensifier in acid stimulation treatments. The investigation which was performed using several techniques including the Scanning Electronic Microscopy and X-rays Fluorescence analysis revealed that, although the performance of the tested propargyl-alcohol and alcoholamine-based corrosion inhibitors in 15 wt% HCl solution at 100 °C was enhanced by the addition of copper iodide, galvanic corrosion was promoted occasioned by copper deposition on steel. They noted that copper deposition on steel was due to the reduction of both Cu^+ and Cu^{2+} cations promoted by the metallic iron in the acidic medium and that the deposited copper behaves like a micro cathode on the steel surface causing the remaining uncovered steel surface to act as the anodic (corroded) region.

2.3.4. Antimony chloride

Antimony chloride can be used as intensifier for acid corrosion inhibitors in acid stimulation treatments. However, as earlier mentioned, antimony-based intensifiers are compatible with HCl of concentration less than 17 wt% (Al-Mutairi et al., 2005). Antimony-based intensifiers like copper iodide are capable of causing bi-metallic corrosion (Cassidy et al., 2013). Environmental concerns on heavy metals also limit the usage of copper iodide and antimony chloride.

2.3.5. Acetic acid

Acetic acid is not expected to function as an inhibitor intensifier; however, it is found in many intensifier formulations especially in conjunction with formic acid (Salgaonkar and Belakshe, 2015; Boles et al., 2009). It is believed that acetic acid has a higher stability relative to formic acid (Benziger and Madix, 1980), hence would contribute to the technical and economic success of the downhole acid treatment. The adsorption and decomposition pattern are similar to those of formic acid but at a higher temperature. For example, Benziger and Madix (1980) noted that formic acid adsorbed on steel surface through the loss of the acidic hydrogen to form a stable formate at a temperature of 171 °F, then it decomposed at 423 °F to produce CO_2 , CO and H_2 . Acetic acid, in the other hand was found to follow the same path, but at a higher temperature of 504 °F (Benziger and Madix, 1980). Al-Katheeri et al. (2002) observed that in 28 wt% HCl at 250 °F, after 8 h of contact time, the corrosion inhibitors and intensifiers contained approximately 60% of the initial formic acid concentration but the concentration of acetic acid remained almost the unchanged.

2.4. Research gaps and recommendations

1. The recent depletion of shallower oil wells is pushing the offshore oil and gas drilling activities to move further offshore and deeper underwater so as to find sources of production in low-risk areas. Meanwhile, this is posing a severe challenge to the industry because higher temperature and pressure. The implication is that most effective inhibitors for acidizing process are losing their potency. There is therefore high demand for corrosion inhibitors that can perform effectively at temperatures as high as 350 °C. The review report identified that bulk of the research works done under acidizing conditions revolves round temperatures less than 100 °C (Tables 2 and 3). Information on acidizing inhibitors becomes scanty at temperatures ≥ 150 °C. Future researches should target high temperatures acidizing inhibitors.
2. There is a clarion call for all to ensure the preservation on our natural environment. Various countries have put plans in place to phase out toxic chemicals. The European countries, for instance announced plan to phase out PFAs chemicals by 2030 (Lerner, 2030). The review rather observes that information on natural polymers and plant biomaterials as acidizing inhibitors is limited. Umoren et al. (2021b)

in their study on butanolic extract of Date palm leaves as corrosion inhibitor for carbon steel in 15 wt% HCl solution observed that the inhibition efficiency of the extract at optimum concentration of 1000 ppm decreased from 97% at 25 °C to 86% at 60 °C after 24 h of immersion. The authors attributed the downward trend in inhibition efficiency to the decomposition of the extract. The instability plant extracts and natural polymers under acidizing conditions might be the reason behind the less work done on them. Nevertheless, these classes of compounds should be the focus future research areas. Modification could help to improve their performance under harsh conditions.

3. There is a complete lack of information on the mechanism of inhibition as well as the corrosion product composition at temperatures ≥ 150 °C. Such information is important for the designing on highly thermally stable corrosion inhibitors. Scientists working in this area should consider the mechanism of inhibition at high temperatures as a priority.

3. Summary and conclusions

The review article delves into the science of metal corrosion inhibition under acidizing conditions. The focus is on acid solutions, percentage of concentration, and temperatures typically seen in well acidizing (i.e., $\geq 15\%$ acid concentration; ≥ 60 °C). Carbon steel is the most prevalent material used in the construction of oil and gas wells. These steel products are exposed to extremely corrosive conditions during the acidizing process and must be protected with a corrosion inhibitor. Inhibitors used during acidizing process are organic- and polymer-based. Individual components, however, are ineffective in well acidizing procedure and are often compounded with appropriate intensifiers to protect metal in acidizing settings. The commonly used intensifiers are formic acid, potassium iodide, copper iodide, and antimony chloride. The intensifiers have their own strength and weakness. Copper iodide and antimony chloride have the tendency of inducing galvanic corrosion. Their continuous usage is also limited by environmental concerns.

The knowledge gaps identified in the review article include: (i) scanty information on acidizing inhibitors at acidizing temperatures ≥ 150 °C, (ii) limited information on natural polymers and plant biomaterials as acidizing inhibitors, (iii) scanty information on the mechanism of inhibition at temperatures higher than 150 °C, and (v) limited information on the composition of corrosion products under acidizing conditions. Based on the identified knowledge gaps, the following recommendations are made:

- 1) Future researches should be geared toward the development of inhibitors for practical applications as oil wells are getting deeper. The acidizing temperature of ≥ 150 °C and the acid concentration of $\geq 15\%$ should be taken into consideration when investigating a compound for application as acidizing inhibitor.
- 2) To ensure the preservation of the environment, research activities on acidizing inhibitors should target animal and plant-based sources like the natural polymers and the plant extracts.
- 3) Future studies should also be devoted to understanding the mechanism of inhibition under acidizing conditions. Information on this area is very scanty presently.
- 4) More so, more studies should be carried out to understand the composition of the corrosion products at acidizing conditions as this will help in the development of models for such corrosion process.

Declaration of competing interest

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

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