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RESEARCH ARTICLE

Phyto-derived surfactants offer vast promise for optimized hydrocarbon extraction: A review and future directions

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ABSTRACT - The escalating global demand for energy, juxtaposed with the dwindling hydrocarbon reserves, necessitates the investigation of innovative recovery methodologies. A substantial fraction, roughly sixty percent, of OIP remains entrapped in reservoir rocks' void spaces post-primary and secondary extraction. Chemical flooding constitutes a promising strategy to recuperate the residual oil. Surfactant facilitates oil recovery augmentation through IFT mitigation and modulating wettability, thereby decreasing the capillary number and improving oil mobilization. Laboratory experiments have validated the efficacy of surfactant-enhanced waterflooding, yet, the implementation of this technique in situ presents several challenges. Fortunately, botanical sources of natural surfactant offer a resource-efficient solution, boasting Inherent eco-compatibility, in stark contrast to their synthetic counterparts. Saponins, a phytochemical constituent of plants, exhibit outstanding surficial dynamics and oil mobilization potential, rendering them a viable alternative for ameliorating energy production. This review presents a definitive and erudite analysis of the cutting-edge advancements in harnessing phyto-derived surfactants to enhance liquid hydrocarbon recovery. The analysis encompasses plant-based surfactant properties, extraction techniques, natural sources, and their role in reducing IFT and rock wettability upturn. Temperature, structure, salinity, and other factors impact surfactant performance. Plant-derived natural surfactants have achieved preeminent IFT reduction, contact angle optimization and substantial oil recuperation in laboratory settings. Phyto-derived surfactants in nanotechnological applications have demonstrated augmented efficacy in laboratory settings, surpassing their non-nanoparticularized counterparts. As such, Future research should explore mechanisms, scale up, and combine natural surfactant nanomaterials for optimal efficiency. This paradigm shift could revolutionize various industries, yielding innovative solutions and transformative outcomes.

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1.0 INTRODUCTION

The desideratum for energy expenditure has proliferated all over and is projected to continue increasing in future years. Consequently, hydrocarbon is acknowledged as the leading transitory energy fountainhead and is envisioned to be a pivotal looming energy contributor. Most major hydrocarbon reserves are running out, despite attempts by companies to postpone the exhaustion phase [1]. As conventional liquid hydrocarbon reserves dwindle and energy demand rises, alternative recovery methods are needed, yet industrial quantity still dominate [2]. As energy requisition continues to grow while resources become scarcer, amplifying oil recoverability from previously untapped reserves are preeminent. These untapped reserves are exploited by conventional reserve techniques which leaves a significant fraction (about 60%) of the initial oil accumulation [3]. The reason for two-thirds OIIP can be attested to two factors: residual oil and bypassed oil. Capillary forces trap residual oil in discrete ganglia formed by fimbriated protrusions of the oleic phase. Gbadamosi *et al.* [4] portrayed that a joint effect of localized hydrostatic disparity and IFT brings forth capillary trapped oil. Conversely, formation heterogeneities or an unpropitious kinematic fluidity disparity between saline aqueous and oleic phases are evident. The aforementioned factors recoverability is the target of unconventional techniques.

Surfactant augmented waterflood interaction with the residual and bypassed oil displays auspicious results in laboratory assessments [4]. The surfactant garnered interest owing to its oil solubilization benefit, which is contingent on its surfactant component. Surfactants are comprised of hydrophilic and hydrophobic segments which portray their polar and nonpolar moieties [5]. This endows the surfactant to autonomously assemble at the liminal region of oil-water juxtaposition and alleviate the IFT to enhance dissolution efficacy [6]. Nevertheless, despite the meticulous evaluation process for selecting an ideal surfactant, achieving consistent field results remains a multifaceted challenge. Azza *et al.* [5] recommended that a top-notch surfactant will theoretically curtail the interfacial tension (IFT) from 10^{-3} mN/m to 10^{-4} mN/m. Frequently, the on-site application necessitates copious amounts of surfactants at a specific level of efficacy. However, adsorption phenomenon causes significant reductions in surfactant concentration on the reservoir surface. Anionic surfactants like sodium dodecyl sulfate (SDS) are commonly used in oil industry for their stable performance

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and low adsorption on sandstone reservoirs [7]. Synthetic surfactants are prone to adsorption on rock surfaces, leading to reduced injection rates and heightened economic costs [8]. Considering the prohibitive expense of synthetic surfactants, efficient resurgence of crude oil counterweights economic outlay. Arising from looming crude oil price decline, artificial surfactant cost surpasses liquid hydrocarbon exploitation expenses [7]. As per the most recent global guidelines, the utilization of harmful and non-degradable substances is advised. Consequently, these specified restrictions prompt researchers to seek a viable substitute for surfactants derived from natural source. Thus, the adoption of natural surfactants is proposed as a substitute for synthetic surfactants [1]. There has been a shift towards the use of natural surfactant (NS) derived from plant sources for EOR applications. Over the past fifteen years, articles have been published in academic literature demonstrating the effectiveness of natural surfactants. This is pinned on eco-friendly characteristics such as biodegradability, low toxicity, and sustainability of these surfactants compared to their synthetic counterparts [9]. Natural surfactants provide a sustainable alternative to enhance oil recovery, offering a valuable eco-friendly solution [10].

A natural or bio-based surfactant is a surfactant that is procured from the biogenic matter of plants or animals. Bio-based surfactants are amphiphilic agents, possessing hydrophilic and hydrophobic moieties, mitigate IFT between oleaginous and aqueous phases [1]. Gbonhinbor *et al*. [11] evaluated characteristic curvature of *Jatropha curcas* and *Dialiumguineense Willd* leaf extracts for cEOR application in Nigeria. The empirical findings revealed computed curvature parameters exhibiting hydrophobicity, spanning 0.116 to 0.194, indicative of pronounced oleophobicity. This implies that bio-based surfactants have a proclivity to form reverse microemulsion as they are allured to the oleic hydrocarbon phase. Additionally, El-Dossoki *et al.* [12] assessed the nonpolar characteristics of natural surfactant formulations: *Jatropha curcas*, *Dialiumguineense*, *Vernonia amygdalina* and *Aspilia africana*. The evaluation revealed CMC ranges of 0.45-0.6% and hydrophobicity spectra of 0.116-0.194, suggesting diminished interfacial tension, albeit requiring further investigation. Their diminutive positive values render them conducive to mitigating interfacial tension and enhancing the mobilization of entrapped petroleum. Bera and Mandal [13] classified natural surfactants used in cEOR similar to chemical surfactants, namely, amphoteric, cationic, non-ionic, and anionic. The plant-derived cationic surfactants comprise a plethora of botanicals, including *Olea europaea*, *Seidlitzia rosmarinus*, *Pistacia lentiscus*, and *Prosopis species*. Additionally, nonionic surfactants, exemplified by *Zizyphus Spina* Christi-derived Saponin and *Glycyrrhiza Glabra*, constitute a subset of botanical-based surfactant agents [14]. Through the examination and study of phytochemicals, Saponin forms natural surfactants [15].

Saponin lacks electrical hydrophilic charges (i.e., non-ionic) and is immanent in vegetal tissues such as flowers, fruits, seeds, roots, and leaves. They are characterized by a sturdy structure composed of polycyclic hydrocarbons conjugated with saccharide molecules [16]. Saponins exhibit properties that make them soluble in both water and oil, which is attributed to their nature. The aglycone part of saponins has lipid characteristics, which enable its attachment to hydrocarbons, whereas the sugar component is water-soluble [17]. Saponins have captured significant attention up-to-the-minute years due to their unique characteristics like elevated surface activity and emulsifying ability. Various inquiries have been undertaken to probe the phase behavior of saponin-based plant extracts in oil-aqueous surfactant systems. Specifically, Li *et al.* [18] scrutinized the effect of saponin pH and concentration on the phase behavior of oil-aqueous systems. Elevating saponin concentrations yielded a concomitant diminution of IFT at the oleaginous-aqueous interface. Furthermore, its stability persists across a broad pH spectrum, suggesting versatility and adaptability in diverse practical applications. Soapnut saponin reduced crude/water IFT from 19 mN/m to 2.5 mN/m, sourced from fruit pericarp shell samples [11]. Similarly, Li *et al*. [19] explored the ramification of saponin-based nanoparticles impacton phase equilibrium of oleaginous-surfactant solutions. The nanoparticles were prepared using a solvent evaporation method and characterized for size and stability. Consequently, the saonin-nanoparticles improved stability and Mitigated IFT at the oleaginous-aqueous interface in the formulated system. Moreover, Obuebite *et al.* [7] used quotidianagro-leafs (*cocos micifera, carica papaya, cocos micifera, vernomia amygdala* e.t.c) extract for surfactant augmented flooding and obtained additional volume of oil. Various types of plant extracts from different plant species, such as *Artemisia judaica* [20], basil [21], and *Vitagnus* plants [22], have been studied for EOR applications.

Saponins are eco-friendly and capable of biodegrading, making them a more sustainable choice for CEOR in contrast to artificial surfactants [23]. Continued research and development in this domain led the continued growth and adoption of natural surfactants in hydrocarbon industry. Despite their encouraging results, the usage of natural surfactants is still confined to laboratory investigations [4]. Challenges subsist in the widespread adoption of natural surfactants for EOR, including scalability, cost-effectiveness, and compatibility with existing production processes. However, ongoing research efforts are aimed at obliterating these challenges and further optimizing natural surfactants usage in exploitation industries. Overall, Natural surface-active agents have the proficiency to advance oil exploitation and minimize ecological ramifications. As such, this research review focuses on the contemporary advancements of natural surfactants for CEOR application.

2.0 NATURAL SURFACTANTS AND CHARACTERIZATION

Natural surfactants are delineated as sustainable, biorenewable amphipathic agents derived from botanicals and biomaterials. Additionally, natural surfactants are organic substances that exhibit both hydrophilic (water-attracting) and hydrophobic (water-repelling) characteristics. These sustainable surfactants are sourced from flora or fauna, specifically polar lipids, leveraging biomolecular resources from the natural kingdom. These surfactants are obtained through direct extraction or chemical synthesis using components from the aforementioned sources. Tension reducibility at the surface and interface of incompatible phase systems led to their application in cEOR. This particular property enables natural surfactants to function as emulsifiers, detergents, wetting agents, foaming agents, and solubilizers [24]. Natural surfactants are considered environmentally friendly due to their lower toxicity and non-biodegradability [9]. Imuetinyan *et al*. [25] categorized natural surfactants into distinct groups based on their origins and chemical compositions. Some of the most prevalent types include:

- Polymeric surfactants: Natural polymers like polysaccharides and proteins (like gelatin) can display surfactant characteristics when dispersed or dissolved in water. These polymeric surfactants offer unique properties and are utilized in various industries.
- Saponins: Saponins, glycosides derived from various plant species, possess a core structure of steroidal or triterpenoid nature with attached sugar molecules. Known for their robust foaming characteristics, saponins are commonly utilized as natural emulsifiers and detergents.
- Phospholipids: Phospholipids represent a significant group of natural surfactants present in cell membranes. Comprising a hydrophilic head group (with a phosphate component) and two hydrophobic fatty acid tails. Phospholipids form lipid bilayers crucial for controlling molecular transport across cell boundaries.
- Proteins: Proteins, macromolecules comprising amino acids linked by peptide bonds, can function as surfactants due to the presence of amphiphilic regions. Certain proteins, such as globular proteins like albumin and casein, feature hydrophobic areas that interact with hydrophobic substances, allowing them to stabilize emulsions and foams.
- Glycolipids: Glycolipids, a lipid class containing a carbohydrate component attached to a hydrophobic lipid tail, are commonly present in cell membranes. Aside from playing critical roles in cell recognition and signaling, glycolipids can also act as surfactants by mitigating IFT between aqueous and oleaginous phases.
- Terpenoids: Terpenoids form a diverse biomolecular ensemble from isoprenoid polymers, include substances like squalene and its derivatives that demonstrate surfactant properties. Their emollient and moisturizing effects make them popular ingredients in cosmetics.

Surfactants derived via synthesis and extraction, analogous to their conventional counterparts. They are taxonomized into four primary categories predicated on their electrochemical properties and solubility characteristics: non-ionic, anionic, cationic, and zwitterionic. Furthermore, scientific investigators have successfully developed novel classifications, including polymeric, Gemini, and viscoelastic surfactants [26, 27]. These surfactants exhibit disparate properties and applications, such as EOR, stabilizing emulsions, foams, and contributors of energy advancement.

3.0 NATURAL SURFACTANTS AND CHARACTERIZATION

Natural surfactants (NS) are also procured from distinguishable botanical components, comprising foliar, roots, flowers, and seeds. Even oil obtained from plants is also plant-derived natural surfactants [28, 29, 30]. Most vegetable oils contain acid (i.e., triglyceride fatty) residue, which can be turned into ethyl ester by reacting with methanol, respectively. This process is called transesterification and is commonly used to produce biodiesel. The resulting esters are excellent surfactants due to their amphiphilic nature [28]. Amino acids constitute an additional font of NS, derivable from both vegetal and animal sources. Their versatility and adaptability in generating diverse surfactant types render them highly sought for eclectic applications. Amino acids are the protein structural component with water-attracting and water-repelling parts. Therefore, they can form different types of surfactants hinging on ionic potency and pH of the formulation [31, 32].

Moreover, eco-friendly surface-active ionic-liquids are being explored as EOR agents owing to their aromatic and ionic characteristics. Ionic liquids are molten salts that are liquid at environmental conditions and have exceptional distinct attributes. They can be designed to have specific properties by differing the cation and anion. For a case in point, imidazolium-based ionic liquids are fabulous surfactants due to their gigantic hydrophobic cation and miniature water-attracting anion [33, 34]. In addition, NS can also be procured from animals and microorganisms and tailored to cEOR by modifying their chemical configuration [35].

Saponins, a diverse group of compounds, reside in various botanical parts such as roots, foliar, fruits, pericarp, seeds and flowers [36]. They are bioactive compounds found in a wide range of vascular plants. Extracting saponins from plants often results in a combination of variegated saponin entities [37]. The composition and concentration of these extracted saponins differ between various plant species and various parts of the same phytotype. Many plants with high saponin content have traditionally been utilized as NS. **Table 1** showcases some of these saponin-rich plants, including other potential plant sources of natural surfactants. Saponins are ubiquitous among vascular flora, spanning numerous phylogenetic lineages.

Dicotyledonous plants, such as Leguminosae, Araliaceae, and Caryophyllaceae, are sources of triterpenoid saponins. While, Monocotyledonous families, notably Agavaceae, Liliaceae and Dioscoreaceae, are esteemed as prolific sources of steroidal saponins, possessing considerable phytochemical significance [38]. These plant families exercise a profound influence in the production and distribution of saponins in the botanical world.

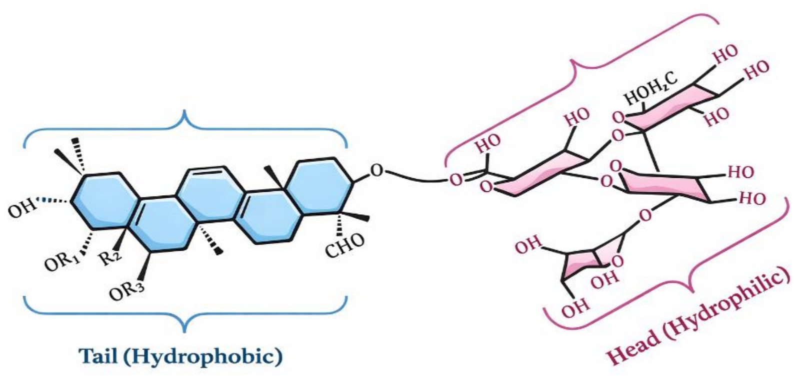

Figure 1. A chemical configuration (structure) of saponin. Redrawn based on work by [1]

Table 1. Plants with high concentration of saponins-based surfactant (a) Leaf (b) Root (c) Stem (d) Fruit (e) Flower (f) Seed

(a) USED PART: LEAF

S/N	REFERENCE	BOTANICAL NAME	LOCAL NAME
1	[39]	*Humulus lupulus*	Hops
2	[39]	*Anethum graveolens*	Dill
3	[40]	*Vernonia Amygdalina*	bitter leaf
4	[11]	*jatropha curca*	lapalapafunfun
5	[11]	*dialium guineense willd*	Velvet-tamarind, Black tamarind, Chaleku, Icheku, Awin, Uge
6	[41]	*Juglans regia*	Common walnut and English walnut
7	[42]	*Myrtus communis*	Myrtle
8	[6]	*Trigonella foenum-graecum*	fenugreek
9	[6]	*Cicer arietinum*	chickpea or chick pea
10	[22]	*Vitex agnus-castus*	vitex, chasteberry, Abraham's balm and monk's pepper
11	[6]	*Beta vulgaris*	sugar beet
12	[7]	*Moringa oleifera*	Drumstick, horseradish and malunggay
13	[43]	*Anabasis Setifera*	Hamd al arnab, shuaairan and salsolasetifera
14	[44]	*Albizia Julibrissin*	Mimosa, silk tree
15	[45]	*Cissus modeccoides*	-
16	[45]	*Garuga pinnata Roxb*	Garuga
17	[45]	*Microcos tomentosa*	Pokok
18	[45]	*Oxalis corniculata*	Creeping wood sorrel
19	[45]	*Acorus gramineus*	Japanese Sweet, Dwarf Sweet Flag
20	[45]	*Aesculus assamica*	Horse Chestnut
21	[46]	*ZyziphusSpinaChristi*	Chrit thorn, sidr, kurna and nabeq
22	[47]	*Agave sislana*	Sisal
23	[48]	*Cordia myxa*	Lasora, gunda, tenti dela and lasura
24	[49]	*Camelia japonica*	Japanese Camellia, Camellia and PillnitzerKamelie
25	[50]	*Eucalyptus*	gum or stringybark
26	[51]	*Allium nigrum*	Ornamental onion
27	[51]	*Beaucarnearecurvata*	Ponytail palm
28	[52]	*Matricaria chamomilla*	chamomile, German chamomile, kamilla, wild chamomile, scented mayweed
39	[53]	*Cordia myxa*	Indian-cherry, Sudan-teak, Clammy-cherry, Sapistan, Sebesten-plum, Selu
30	[53]	*Prosopis africana*	African mesquite, iron tree, gele
31	[53]	*Olea europaea*	Olive
32	[54]	*Morus rubra*	Mulberry
33	[54]	*Lawsonia inermis*	Henna
34	[55]	*Lonicera japonica*	Honeysuckle
35	[55]	*Chlorophytum borivilianum*	Safed musli
36	[55]	*Agave americana*	Agave, Bara Kunwar, Kantala, Ran Ban
37	[36]	*Digitalis purpurea*	Purple foxglove
38	[36]	*Digitalis Ianata*	Woolly foxglove

Table 2. *Continued*

(b) USED PART: ROOT

S/N	REFERENCE	BOTANICAL NAME	LOCAL NAME
1	[51]	*Allium nigrum*	Ornamental onion
2	[51]	*Bupleurum chinense*	Bei Chai Hu
3	[51]	*Chiococca alba*	West Indian milkberry
4	[55]	*Asparagus adscendens*	Sansban, Saunspali
5	[55]	*Asparagus racemosus*	Shatavari
6	[36]	*Glinuslotoides*	Soap Jacob
7	[36]	*Gypsophilla paniculata*	Baby's breath
8	[36]	*Discorea composite*	Yams Rhizomes

(c) USED PART: STEM

S/N	REFERENCE	BOTANICAL NAME	LOCAL NAME
1	[56]	*Linum usitatissimum*	Flax
2	[45]	*Oxalis corniculata*	Creeping wood sorrel
3	[45]	*Cissus modeccoides*	-
4	[45]	*Cissus repen*	-
5	[51]	*Momordica charantia*	Bitter melon
6	[49]	*Camelia japonica*	-
7	[51]	*Caryocar villosum*	Piquia

(d) USED PART: FRUIT

S/N	REFERENCE	BOTANICAL NAME	LOCAL NAME
1	[57]	*SapindusMukorossi*	soapberry, soapnut, washnut, aritha, dodan, and dodani
2	[45]	*Garcinia sp*	Yellow Mangosteen
3	[45]	*Dillenia parviflora*	Molave and Small flower
4	[45]	*Luffa cylindrica*	Sponge Gourd
5	[51]	*Momordica charantia*	Bitter melon
6	[55]	*Asparagus adscendens*	Sansban, Saunspali
7	[57]	*Ilex paraguariensis*	Mate Fruits

(e) USED PART: FLOWER

S/N	REFERENCE	BOTANICAL NAME	LOCAL NAME
1	[37]	*Camellia sinensis*	Tea

(f) USED PART: SEED

S/N	REFERENCE	BOTANICAL NAME	LOCAL NAME
1	[56]	*Linum usitatissimum*	Flaxseed, linseed
2	[59]	*Trigonella foenum-graecum*	Greek hay. Methi and Hulba
3	[38]	*Lens culinaris*	Lentils
4	[38]	*Phaseolus vulgaris*	Haricot bean
5	[49]	*Camelia chekiangoleosa*	Chinese camellia and chekiang camellia
6	[49]	*Camellia reticulata*	-
7	[57]	*Glycine max*	Soya bean Sprouts
8	[36]	*Glinuslotoides*	Soap Jacob
9	[60]	*Camellia oleifera*	Tea
10	[36]	Digitalis purpurea	Purple foxglove

3.1 Techniques for Plant-Based Surfactant Extraction

Environmental factors and extraction process significantly influence saponin composition and content, as discussed by [61, 36]. Rai *et al*. [38] highlighted various extraction techniques currently utilized for saponins, ranging from traditional methods to more modern, environmentally friendly approaches:

- Conventional techniques such as reflux extraction, Soxhlet extraction, and maceration utilize organic solvents, which typically involve the use of organic solvents.
- Green technologies like ultrasound-assisted extraction, and accelerated solvent extraction and microwave-assisted extraction aim to diminish environmental impact.

Different extraction methods have unique pros and cons in efficiency, cost, and environmental impact, chosen based on plant material and saponin needs. Conventional methods have drawbacks: high solvent use, long extraction times, and environmental/health risks. Maceration and soxhlet methods struggle with natural samples, binding analytes strongly [62]. Polar solvents like methanol and ethanol leave unwanted residues, limiting industrial use [40]. Earlier research favored traditional methods, but recent trends show a move towards green synthesis for improved efficiency and eco-compatibility [16]. In contradiction, ultrasonic extraction is versatile, compatible with any solvent, making it the top choice for extracting natural compounds [63]. Green technologies have lower natural impact, but researchers opt for conventional extraction techniques (70%) over green methods (30%), as shown in Figure 2. Ultrasonic extraction optimizes efficacy, antioxidant activity, and preserves polysaccharide structure [64, 65]. Methodological choices are frequently dictated by the particular investigative paradigm and research objectives of the respective scientific inquiry.

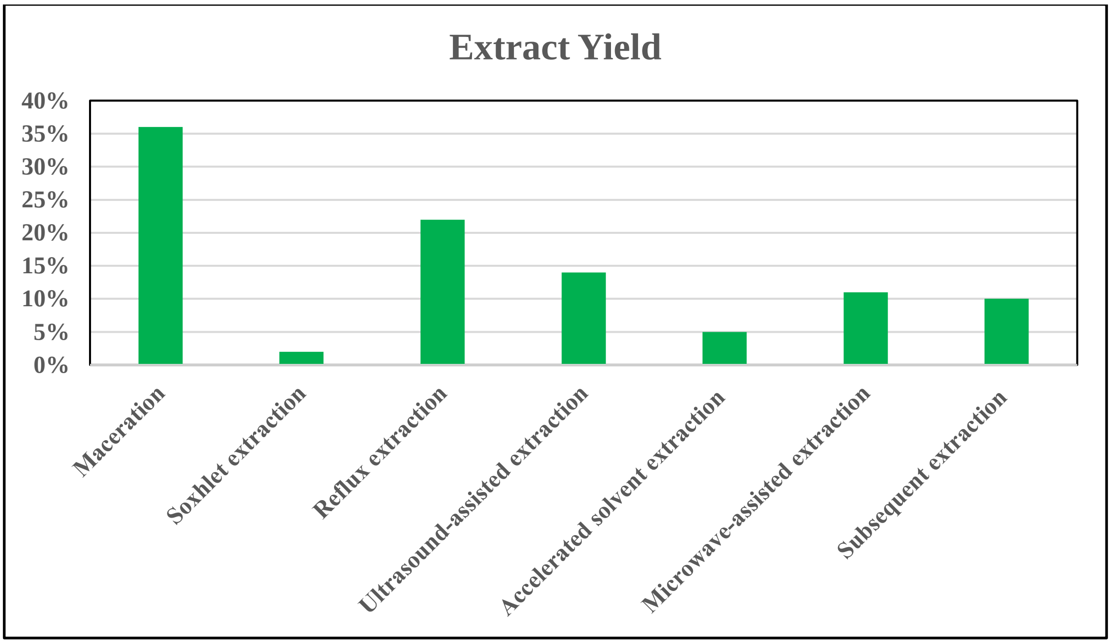

Figure 2. Present techniques used for extraction according to data by [16]

4.0 SCIENTIFIC INQUIRES RELEVANT TO SURFACTANT CEOR APPLICATIONS

Scientific explorations pertinent to surfactant-enhanced hydrocarbon retrieval applications have been broadly dissected in the field of petroleum engineering and chemistry. The scientific discoveries related to plant-based surfactants in CEOR have demonstrated their effectiveness, sustainability, and economic feasibility. Additionally, Plant-based surfactants combined with polymers and nanoparticles produce synergistic benefits for Enhanced Oil Recovery (EOR). Combining plant-based surfactants with other EOR methods enhances oil recovery efficiency, showcasing their versatility and potential. Research advancements will spur innovation, paving the way for sustainable, plant-based surfactants in oil recovery.

In hydrocarbon recuperation, surfactants have a substantial impact by amplifying the extraction process. This is achieved through four principal mechanisms, these include reducing IFT, reservoir wettability modification, foam production, and concocting emulsions [66]. The first mechanism, involves using surfactants for IFT diminution between water and oil, thereby increasing oil mobility and easing extraction. Wettability alteration, on the other hand, the second mechanism refers to changing the surface properties of rocks to enhance oil extraction. Foam generation entails the creation of foam using surfactants to displace oil from rock formations, while emulsification involves creating stable oil-water emulsions to transport oil over long distances. This subdivision presents a succinct exposition of the underlying modalities that are elucidated, highlighting their importance in optimizing the oil recovery process. Pre-screening investigations prior to flooding and flooding scientific discoveries relevant to surfactant CEOR applications are tabulated below.

Investigations into surface-active solutions revealed minor concentration adjustments precipitate profound property alterations [67]. These sudden transmutations in solution characteristics are symptomatic of a fundamental metamorphosis in the behavior of the solute within the solution. Such observations provide cogent evidence substantiating the hypothesis that micelles are indeed generated in surfactant solutions. CMC specifies the limiting concentration for meaningful surfactant utilization. A surface adsorption characteristic can be elucidated through CMC-derived variables [40]. Understanding CMC enables design of effective EOR strategies, optimizing oil recovery and environmental stewardship. The accompanying illustration presents a compilation of currently available, state-of-the-art CMC data pertaining to naturally occurring surfactants. This in turn provides a comprehensive and authoritative repository of relevant information.

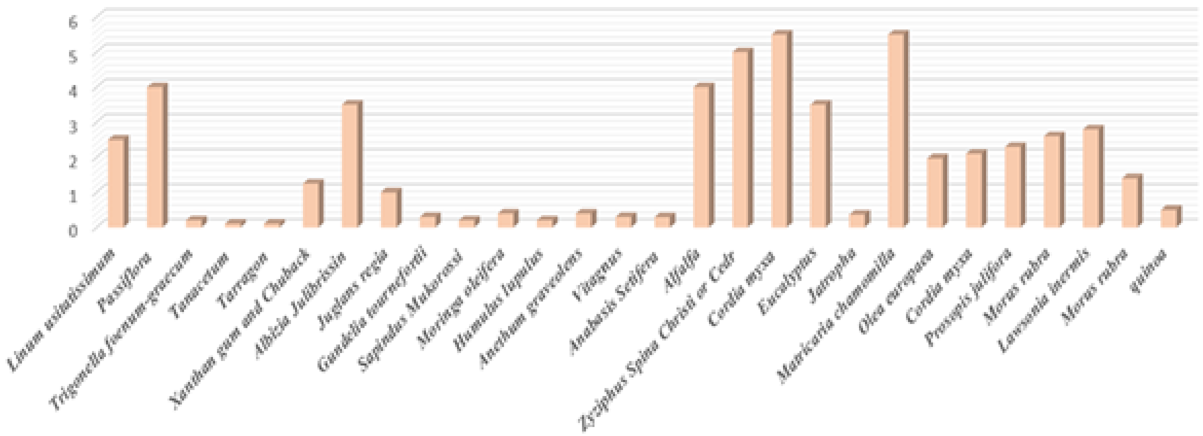

Figure 3. Published CMC values of some plant-derived natural surfactants

Table 3. summary of natural surfactants scientific investigations preeminent to CEOR

Ref.	NS	S. Type	Config.	Result CMC (wt%)	IFT (mN/m)			Contact Angle (°)			IR (%)
					From	To	Opt. (%)	From	To	Opt. (%)	
[57]	*Linum usitatissimum*	Non-ionic	CO, W, NS	2.5	33	7.5	77.3	N/A	N/A	-	11
[39]	*Humulus lupulus*	Anionic	CO, W, NS	0.2	28	5.61	80.0	151	65.18	56.8	8.56
[39]	*Anethum graveolens*	Non-ionic	CO, W, NS	0.4	28	2.44	91.3	151	73.34	51.4	10.11
[68]	*Passiflora*	Non-ionic	CO, W, NS	4	32	13	59.4	122	55	54.9	7.5
[69]	*Trigonella foenum-graecum*	Non-ionic	CO, W, NS	0.2	27	10	63.0	74	48	35.1	10.17
[70]	*Tanacetum*	Non-ionic	CO, W, NS	0.1	29.5	5.12	82.6	100	33	67	13.2
[70]	*Tarragon*	Non-ionic	CO, W, NS	0.1	28	6.57	76.5	100	30.8	69.7	11.7
[40]	*Vernonia Amygdalina*	Non-ionic	CO, W, NS	N/A	18	0.97	94.6	118.5	45.7	61.4	N/A
[71]	Xanthan gum and Chuback	Anionic	CO, W, NS	1.25	N/A	N/A	74	16.71	60.52	-2.6	16
[72]	quinoa	Cationic	CO, W, NS	0.15	N/A	N/A	24.5	146	26.3	82.0	24.1
[44]	*Albizia Julibrissin*	Non-ionic	CO, W, NS	3.5	34	10	70.6	165.02	86.59	47.5	11.6
[41]	*Juglans regia*	Non-ionic	CO, W, NS	1	11.18	2.54	77.3	165	56.7	65.6	N/A
[73]	Gundeliatournefortii	Non-ionic	CO, W, NS	0.3	28	3	89.3	160	20	87.5	19.8
[7]	*Moringa oleifera*	Cationic	CO, W, NS	0.4	N/A	N/A	-	N/A	N/A	-	18.8
[74]	*SapindusMukorossi*	Cationic	CO, W, NS	0.2	23.24	1.59	93.2	N/A	N/A	-	N/A
[22]	*Vitagnus*	Non-ionic	CO, W, NS	0.3	29.5	5.28	82.1	114	29	74.6	10.6
[43]	*Anabasis Setifera*	Cationic	CO, W, NS	0.295	5.797	1.145	80.2	N/A	N/A	-	15.4
[75]	*Alfalfa*	Non-ionic	CO, W, NS	4	N/A	N/A	63.39	N/A	N/A	49.41	19.2
[46]	*Zyziphus Spina Christi* or *Cedr*	Non-ionic	CO, W, NS	5	15.635	3.741	76.1	N/A	N/A	-	15
[48]	Cordia myxa	Cationic	CO, W, NS	5.5	33	16.24	50.8	137.05	130.65	4.7	27
[50]	*Eucalyptus*	Cationic	CO, W, NS	3.5	35.2	10.5	70.2	140.6	60.2	57.2	N/A
[76]	*Jatropha*	Non-ionic	CO, W, NS	0.6	2.74	0.37	86.5	N/A	N/A	-	26
[52]	*Matricaria chamomilla*	Cationic	CO, W, NS	5.5	30.63	12.57	59.0	N/A	N/A	-	N/A
[53]	*Olea europaea*	Non-ionic	K, DW, NS	1.97	36.5	14	61.6	N/A	N/A	-	N/A
[53]	*Cordia myxa*	Non-ionic	K, DW, NS	2.1	36.5	20.15	44.8	N/A	N/A	-	N/A
[53]	*Prosopis julifora*	Non-ionic	K, DW, NS	2.3	36.5	15.11	58.6	N/A	N/A	-	N/A
[54]	*Morus rubra*	Non-ionic	K, DW, NS	2.6	43.9	4.01	90.9	62.5	48.5	22.4	N/A
[54]	*Lawsonia inermis*	Non-ionic	K, DW, NS	2.8	43.9	3.05	93.1	66	37	43.9	N/A
[77]	*Morus rubra*	Non-ionic	K, DW, NS	1.4	42	20	52.4	150	30	80	7

Note: CO Crude oil, W, Water, K Kerosene, DW Distilled water

A descriptive statistical analysis was carried out to throw more light on the CMC published data. From the analysis, the average micelle formation concentration was 1.88 wt%, enabling optimal oil-water solubilization. A standard deviation of 2.47 wt% indicates variability in concentration among surfactants, forming a bell-curve distribution. The mean represents the peak concentration, while the standard deviation indicates the spread of concentrations. Some surfactants are effective at low concentrations, while others require higher concentrations. Most surfactants fall around the mean, with significant variation attributed to chemical structure and molecular weight differences. This information enables optimization of surfactant-based processes, selection of effective surfactants, and strategies to mitigate variability.

3.2 Effect of Blending of OPT and A. mangium on Its Physical Properties

The paramount objective of amphiphilic agent injection into reservoirs lies in modulating fluid-fluid interfaces by attenuating IFT and altering fluid-rock properties via wettability modification of the porous medium. Surfactants or amphiphilic molecular entities, comprise hydrophilic and hydrophobic moieties, facilitating molecular alignment at the oil-brine interface. This strategic alignment diminishes interfacial energy, thereby reducing tension and promoting fluid mobilization [5]. The hydrophobic moiety, typically a protracted hydrocarbon, fluorocarbon, siloxane, or polymer chain, interacts with the oil phase. While, the hydrophilic moiety, often a polyoxyethylene or polysaccharide derivative, engages with the aqueous phase [4]. Upon injection, surfactants self-assemble at the oil-brine interface, reducing IFT and facilitating oil mobilization. Biobased surfactants, derived from renewable resources, offer distinct advantages, including biodegradability and low toxicity. Their molecular configuration optimizes performance, leveraging functional groups to facilitate interactions with aqueous and oil phases. There by enhancing IFT ebb via mechanisms such as hydrogen bonding or van der Waals forces [5]. This augmented IFT mitigation facilitates more efficient oil displacement from reservoir rock surfaces, culminating in improved petroleum extraction efficiency. In systems comprising crude oil and brackish (saline) water, IFT initiates increase in capillary force which is paramount to enmesh hydrocarbon. Therefore, surfactant augmented injection is often employed in IFT reduction [78]. According to Kalantari *et al*. [79] and Cong *et al*. [80] existing attractive force acting at the boundary interface of two non-mixable liquids is commonly known as IFT. Diverse surface-active agents can be employed at insignificant concentrations altering between 500ppm and 2000ppm to achieve10^{-2} dynes/cm or less [81, 82, 83]. The molecular binding force in surfactant-water system is less strong than isolated water molecule, bringing about surface tension (SFT) reduction. In an aqeous-oil-surfactant formulation, when surfactant molecules are added to an oil-aqueous-mixable solution, they displace some oil-aqueous molecules at the original interface. This adsorption phenomenon, stems in a new arrangement where the water-repelling components of the surfactant interact strongly with oil. as such, the water-attractingmoduleinteracts more strongly with water. Therefore, the IFT is incredibly diminuted compared to the base interaction situated at the aqueous-oleaginous interface before the augmentation of surfactant [84, 85]. Figure 4 shows the current IFT percentage reduction of natural surfactant sourced from plant parts.

The ability of surfactants to ebb IFT in oil-brine emulsion is greatly influenced by the ions present in the brine. As previously mentioned, there is a salinity level specifically at which the IFT is minimized. This optimal salinity is typically measured by the quantified grams of dissolved salt. Nevertheless, research has concluded that divalent or multivalent cations incorporation into a surfactant augmented solution decreases the optimal salinity [66].

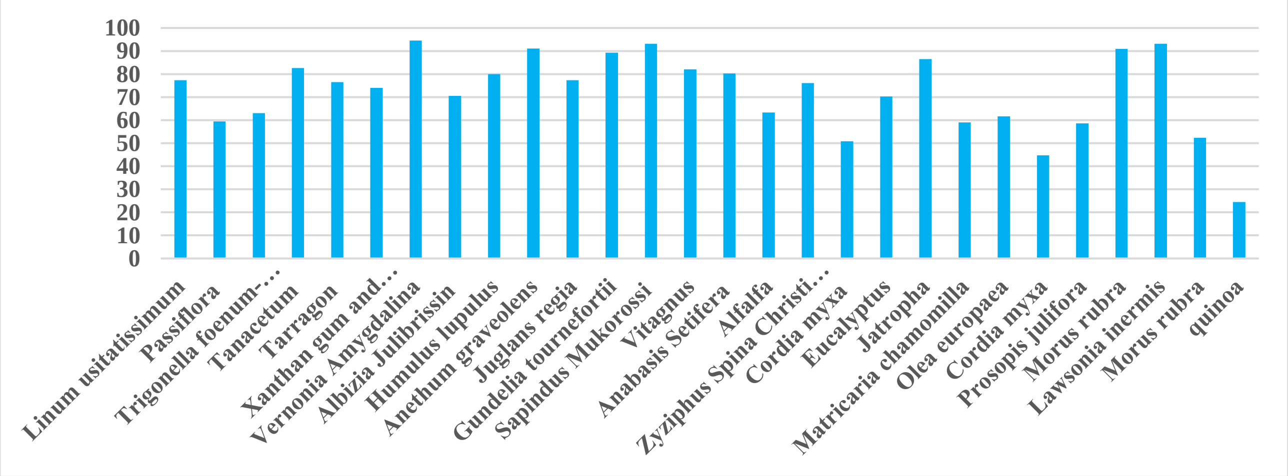

Figure 4. Published IFT percentage reduction of natural surfactants

Here's a comprehensive analysis interpretation of the above tabulated statistical result/findings:

- The natural surfactant's addition profoundly impacted the sample's Interfacial Tension, yielding a remarkable 73.2% reduction.
- The Standard Deviation decreased, indicating a more uniform Interfacial Tension distribution after surfactant addition.
- Confidence level (95%) level narrowed from 4.330698 to 2.441251, indicating a more precise estimate of the population mean IFT.

- Kurtosis shifted from slightly peaked to flatter, signifying a more uniform distribution.
- Skewness transformed from left-skewed to right-skewed, indicating a symmetric distribution shift.
- Median Interfacial Tension decreased substantially, supporting the significant reduction.

Hence, natural surfactant's addition optimized interfacial properties, enhancing the sample's suitability for various applications.

Table 4. Descriptive statistical analysis of extracted IFT data

Initial IFT			Final IFT	
S/N	Main Features	Value	Main Features	Value
1	Mean	28.06623	Mean	7.5181423
2	Standard Error	2.102752	Standard Error	1.185339
3	Median	29.5	Median	5.445
4	Mode	28	Mode	10
5	Standard Deviation	10.72197	Standard Deviation	6.044066
6	Simple Variance	114.9607	Simple Variance	36.53074
7	Kurtosis	0.3272197	Kurtosis	- 0.57574
8	Skewness	- 0.8029	Skewness	0.730919
9	Range	41.16	Range	19.78
10	Minimum	2.74	Minimum	0.37
11	Maximum	43.9	Maximum	20.15
12	Sum	729.722	Sum	195.479
13	Count	26	Count	26
14	Largest	43.9	Largest	20.15
15	Smallest	2.74	Smallest	0.37
16	ConfidenceLevel (95.0%)	4.330698	Confidence Level (95.0%)	2.441251

4.1.1 IFT Influencing Factors

Most surfactants exhibit non-static IFT behavior in oil-water formulation, where IFT initially fluctuate drastically with time [86]. This phenomenon can be used to test for surfactant augmentation in crude oil. If IFT changes over time in the oil-brine emulsion, it indicates the incorporation of slowly diffusing surfactants [87].

4.1.1.1 Surfactant Concentration

Surfactant concentration in oil-aqueous surfactant configuration can have a potent influence on IFT. Studies have shown that stepping up surfactant levels prompts interfacial tension reduction in diverse emulsion configurations [88]. IFT diminution arises from enhanced molecular adsorption of surfactant species at the interface, augmenting surface activity. At diminutive surfactant concentrations, IFT reduction is negligible, with minimal molecular aggregation at the interface occurring. As the surfactant concentration increases, amphipathic molecules aggregate at the interface which in turn triggers IFT diminution. However, this high surfactant concentration may result in maximal formation adsorptive capacity which mars favorable IFT alteration [89]. Different surfactants have different molecular structures and properties, which can affect their sorption at the interface and, therefore, the IFT. The IFT diminution exhibits a more pronounced dependence on anionic surfactant concentration than nonionic counterparts [88]. The surfactant type, concentration levels, and its unavoidable sorption between fluid-rock interaction varies under widespread circumstances. Consequently, the correlation of surfactant level and IFT is non-linear.

4.1.1.2 Addition of Polymer

Polymer and surfactant interaction is intricate and relies on chemical properties of both components. In an oil-aqueous surfactant formulation, Polymer augmentation can influence the IFT in two ways: by affecting Interfacial surfactant adsorptive accrual and by modifying the polymer orientation at the interface. Interfacial amphipathic molecular assimilation is impacted by polymer addition, which is influenced by surfactant level and type. As a result, polymer presence can alter the interfacial energetics of the system and, in turn, impact surfactant adsorption.

Research has indicated that the incorporation of a hydrophilic macromolecule, such as polyvinyl alcohol (PVA), can augment the interfacial adsorptive affinity of nonionic surfactants, exemplified by Tween 80 [90]. This is because the hydrophilic properties of the polymer improve surfactant solubility in the aqueous phase and enhance its ability to adhere to the interface. Conversely, the inclusion of a hydrophobic polymer, such as polyethylene oxide (PEO), can decrease the sorption of un-charge surfactants at the interface [91]. Additionally, the orientation of the polymer at the interface can impact the IFT. The orientation of the polymer chains can influence surfactant molecules assemble and ultimately modify the IFT. The polymer incorporation can bring about IFT mitigation owning to steric hindrance of polymeric chains.

Research has demonstrated that the way PEO is arranged at the interface can impact the IFT in oil-water configuration [92]. When PEO is present at the interface, it reduces interfacial tension by pushing water molecules away from the IFT boundary. While, when a hydrophobic polymer like PVA is present, it can increase interfacial tension by compacting surfactant molecules more tightly at the interface [93]. The incorporation of polymer to oil-aqueous surfactant emulsion leads to IFT alterations depending on the nature of the interface. Water-soluble polymer enhances sorption of un-charge ionic surfactants at the interface, while a hydrophobic polymer can decrease it. The arrangement of the polymer at the IFT boundary can also alter the tension at the boundary. This is because certain polymers can hinder the surface causing a decreasing force, while others can increase IFT by consolidating the surfactant.

4.1.1.3 Presence of Alkali

The acting IFT in oil-aqueous surfactant formulation can be significantly impacted by the presence of an alkali. Alkalis are frequently utilized to elevate the system's pH, which can alter the ionization of surface-active agent molecules and affect their clumps at the interface. Research has confirmed that Alkaline augmentation induce a pronounced diminution of IFT between immiscible oil-water phases [94]. IFT reduction is ascribed to enhanced surfactant ionization, yielding diminished interfacial free energy and augmented molecular affinity. Furthermore, alkali introduction can prompt the formation of surfactant molecules at the IFT boundary, thereby further lowering the IFT.

The type of alkali implemented in oil-aqueous surfactant systems can notably influence interfacial tension. Alkalis possess unique properties that can affect their interaction with surfactant molecules and, in turn, impact interfacial tension. Research has revealed that the use of sodium hydroxide (NaOH) can result in a more substantial decrease in interfacial tension than the use of potassium hydroxide (KOH) [95]. This is attributed to NaOH's stronger alkalinity compared to KOH, which allows it to ionize surfactant molecules more efficiently at the interface.

4.1.1.4 Co-Surfactant

The introduction of co-surfactants into oil-aqueous surfactant systems can have a notable effect on interfacial tension. Co-surfactants are often added to surfactant solutions to improve their capacity to pare IFT. Research has proved that co-surfactants can increase the binding of amphipathic molecules migrate to the interface, precipitating IFT diminution [96]. Moreover, co-surfactants can modify the packing of Interfacial surfactant molecular aggregation occurs, which can further reduce interfacial tension. The type of co-surfactant augmented can also impact the IFT in oil-aqueous surfactant configuration. Different co-surfactants possess varying properties, which can affect their interaction with surfactant molecules and, in turn, influence the interfacial tension. Studies have signified that alcohols as co-surfactants can produce a noteworthy ebb in IFT. Alcohols are able to modify surfactant molecules arrangement at the interface, which can increase their adsorption and ultimately result in a reduction in IFT. Similarly, the use of aromatic compounds as co-surfactants can also lower IFT by modifying the surfactant molecules orientation [97].

Overall, introduction of co-surfactants into oil-aqueous surfactant systems can significantly impact interfacial tension. Co-surfactants are able to enhance clump of Interfacial surfactant molecular aggregation occurs and modify their packing, which leads to a mitigation in interfacial tension. Additionally, the type of co-surfactant utilized can influence IFT in oil-aqueous surfactant formulation.

4.1.1.5 Salinity

The IFT in the oil-aqueous surfactant blend can be enormously affected by the concentration of salt present. The inclusion of salt can alter the ionic strength of the system, ultimately impacting the ionization of the surfactant particles. According to research, salinity increase in the system can lead to a noteworthy elevation of IFT between the oil-water mixtures [98]. This proliferation in IFT occurs due to a reduction in surfactant molecule ionization at the interface. The impact of saline solutions on interfacial tension is surfactant-specific. According to Zhang *et al.* [99], scientific discovery has demonstrated that nonionic surfactants are less affected by variations in salinity compared to anionic surfactants. The reason for this is that anionic surfactants have a stronger inclination to bond with salt ions, which results in a decline in their adherence at the interface and a subsequent rise in interfacial tension. In contrast, nonionic surfactants are less affected by fluctuations in salinity and can uphold their IFT at high salinity. Unlike anionic and nonionic surfactants, cationic surfactants, with their positive charge, exhibit heightened sensitivity to salinity. Deymeh *et al.* [100] introduced an innovative, natural cationic surfactant derived from *Seidlitzia Rosmarinus*, a desert plant native to the Middle East, Western, and Central Asia. This surfactant demonstrated notable efficacy in reducing IFT during enhanced oil recovery (EOR) processes. Below the CMC of 8wt%, IFT showed minimal variation; however, above the CMC, IFT drastically decreased from 32mN/m to 9mN/m, outperforming conventional commercial surfactants. The environmental and economic feasibility of this natural cationic surfactant makes it an appealing option for EOR applications. Moreover, zwitterionic surfactants, characterized by both positive and negative charges, exhibit exceptional performance in saline environments. Oguntade *et al.* [101] demonstrated that zwitterionic surfactants achieve ultralow IFT at concentrations between 0.005 wt% and 0.3 wt%, even with salt concentrations exceeding 20wt%. This remarkable performance proves invaluable in EOR processes where elevated salinity poses challenges. Furthermore, zwitterionic surfactants exhibit strong compatibility with both ionic and nonionic surfactants, enhancing their interfacial properties and salt tolerance. As such, the level of salt in the surfactant system consisting of oil and water can greatly affect the IFT between these two phases. When salinity is increased, the interfacial tension can rise because surfactant molecules become less ionized at the interface. However, it is vital to consider the impact of salinity levels on IFT depends on surfactant type usage.

4.1.1.6 Molecular Structure of Surfactants

The way surfactants are structured at a molecular level have a substantial impact on the IFT in oil-aqueous surfactant configuration. The solubility of amphipathic molecules in both oil and water and their adsorption capacity at the interface are determined by their molecular structure. Hydrophobic tail distance in surfactants affects interfacial tension by influencing their adsorption at the interface. Surfactants with longer hydrophobic tails tend to have greater interfacial activity and are more effective at reducing interfacial tension [102]. Similarly, the incorporation of unsaturation in the hydrophobic tail can also impact IFT. Unsaturated surfactants tend to have higher IFT compared to their saturated counterparts because of their increased flexibility [103]. Surfactant interfacial activity is significantly modulated by head-group dimensions and charge, affecting molecular aggregation and interfacial disposition. Anionic surfactants have intensified electrostatic interactions with the interface, leading to higher interfacial activity compared to nonionic surfactants [104]. Additionally, smaller head-groups tend to pack more efficiently at the interface, resulting in increased interfacial activity. It should be noted that different types of surfactants possess unique molecular structures and properties that can affect their interfacial activity and, consequently, the interfacial tension. Therefore, anionic surfactants, with their stronger electrostatic interaction with the interface, typically exhibit higher interfacial activity than nonionic surfactants. In the same way, positive surfactants typically exhibit greater IFT than negative surfactants due to their Interfacial adsorptive capacity augmentation [103].

4.1.1.7 Temperature

Several studies have investigated temperature impact on IFT in non-mixable oil-water formulation. A study reveals that supplementing the temperature from 25°C to 60°C resulted in IFT ebb in oil-water configuration incorporating nonionic surfactant [104]. The authors gave credit for effect to the enhanced solubility of the surfactant in water at higher temperatures. In addition, Ahmed and EI-Sayed [106] explored the aforementioned research with a cationic surfactant. The authors found that temperature elevation from 25°C to 60°C produces indifferent result, with the most significant reduction occurring at 50°C. The authors signified that these elevated temperatures fostered enhanced surfactant molecular kineticity, yielding increased mobilization and activity. Similarly, Moradi *et al*. [107]investigated the same research with mixed surfactant formulation and ascertained non-distinguishable result and deduction. Furthermore, Yekeen *et al*. [57] investigated a natural surfactant extracted from *Sapindusmukorossi* under elevated temperature (80°C) and pressure (8 MPa). The result publicized a untrivial mitigation in IFT from 23.24 mN/m to 1.59 mN/m. Similarly, Imuetinyan *et al*. [25] evaluated biobased surfactant derived from *Vernonia amygdalina* (VA) leaves under simulated reservoir conditions (100°C and 3000 psi). The results insinuated a considerable diminution in IFT, from 18.0mN/m to 0.97mN/m, under the specified conditions. These results highlight the effectiveness of surfactants in reducing IFT at elevated temperatures. This justifies their potential as surfactants under reservoir conditions and positioning them as viable candidates for EOR. However, further research is crucial to comprehensively understand the behavior and stability of these surfactants under high-temperature, high-pressure reservoir conditions. In summary, temperature plays a noteworthy function in determining the IFT ebb in oil-water surfactant configuration. Increasing temperature generally leads to IFT mitigation, primarily due to the enhanced solubility and mobility of surfactant molecules. These outcomes have critical implications for the development of surfactant systems for use in oil-water applications.

4.2 Reservor Wettability Modification

Wettability refers to how easily a fluid adheres to the surface area in conjunction with another non-mixable fluid. NS has been found to have similar effects to traditional surfactant, effectively altering displacement characteristic of oil-wet state to a water-wet state. This is preferable for optimal recovery efficiency as shown in the figure below. Water-wet falls between 0° and 70° contact angles, 70° and 110°for intermediate wetting, and 110° and 180° as oil-wet [108].By rock substrate displacement property alteration to a water-wet condition, the capillary adhesive force debilitate, initiating the adhered liquid-hydrocarbon mobilization. Wettability condition can be changed due to rock substrate and surfactant interaction, based on surfactant type usage and rock characteristics.

Figure 5. Alteration of lithological surface hydrophilicity in a reservoir. Redrawn based on work by [3]

Researchers have demonstrated that natural surfactants are capable of causing alterations in porous medium hydrophilic properties. Imuetinyan *et al*. [40] noted that NS derived from *Vernonia Amygdalina* was able to alter the wetting characteristic of sandstone substrate to 45.7° from 118.5°. Similarly, Chen *et al*. [27] concocted a naturally occurring surfactant from leftover cooking oil, and they evaluated its potential to change wettability. The contact angle ebb from 96.17° to 30.7° when the NS altered the wetting property of simulated brine. The contact angle dropped even more to just 27.8° when the amphipathic concentration rose to 3.0 g/l. In addition, Zhang *et al*. [99] showed that wetting characteristic decreased with augmented NS procured from castor oil, going from 92.04 to 38.79°. Furthermore, it was shown that soybean oil-derived from NS reduced surface hydrophilicity significantly by 52.08% to 44.1°. Moreover, Kumar *et al.* [109] produced a NS from Jatropha oil and tested its ability to alter the wetting characteristic of oil-wet quartz substrate. Previous publications percentage reduction of contact angles using different plants are presented in **fig 6**. The surfactant was capable to change the quartz surface to a water-wet condition. In contradiction, many of them are not capable of achieving a strongly hydrophilic regime and a contact angle less than 30°. Therefore, upcoming scientific investigations should concentrate on altering the structure of NS to enhance their interaction and effectiveness.

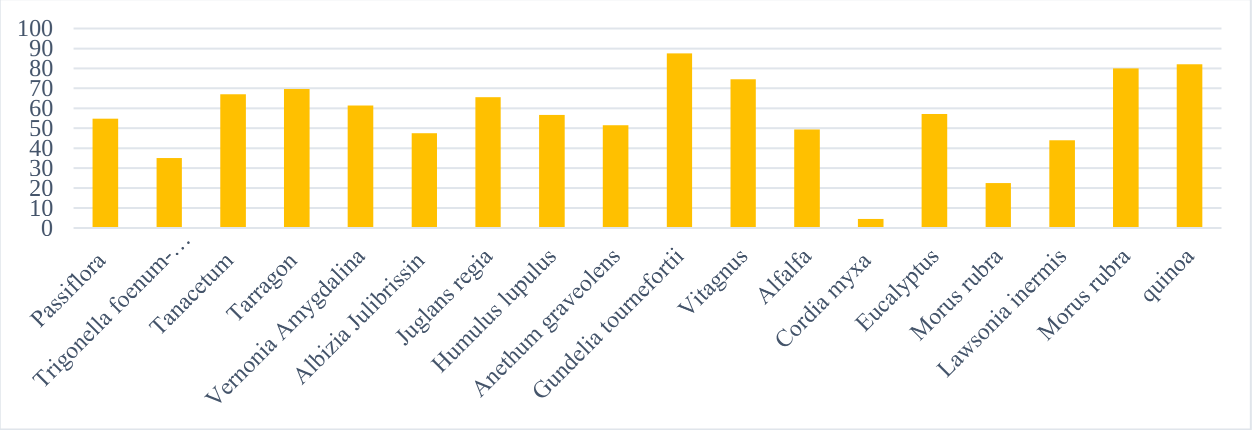

Figure 6. Current contact angle percentage reduction of natural surfactant procured from plant

Here's a comprehensive analysis interpretation of the above tabulated statistical result/findings:

- Natural surfactant addition precipitated a profound 63.6% reduction in mean Contact Angle, from 129.6767° to 47.0525°.
- Standard Deviation decreased from 29.46146 to 20.30692, indicating a more uniform Contact Angle distribution.
- Confidence Level narrowed from 18.71892 to 12.9024, reflecting enhanced precision in population mean estimation.
- Kurtosis shifted from platykurtic to mesokurtic, indicating a more normal distribution of Contact Angle values.
- Skewness transformed from left-skewed to right-skewed, signifying a symmetric distribution shift.
- Median Contact Angle decreased substantially from 131.3° to 46.85°, supporting the significant reduction.

Hence, natural surfactant addition optimized wetting properties, enhancing surface spreading and wetting efficacy.

Table 5. Descriptive statistical analysis of extracted CA data

Initial CA			Final CA	
S/N	Main Features	Value	Main Features	Value
1	Mean	129.6767	Mean	47.0525
2	Standard Error	8.504792	Standard Error	5.862103
3	Median	131.3	Median	46.85
4	Mode	100	Mode	N/A
5	Standard Deviation	29.46146	Standard Deviation	20.30692
6	Simple Variance	867.9778	Simple Variance	412.371
7	Kurtosis	-0.7925	Kurtosis	-0.41967
8	Skewness	-0.42281	Skewness	0.546568
9	Range	91.02	Range	66.59
10	Minimum	74	Minimum	20
11	Maximum	165.02	Maximum	86.59
12	Sum	1556.12	Sum	564.63
13	Count	12	Count	12
14	Largest	165.02	Largest	86.59
15	Smallest	74	Smallest	20
16	ConfidenceLevel (95.0%)	18.71892	Confidence Level (95.0%)	12.9024

4.3 *Natural Surfactant Adsorption*

Adsorption's importance in proving CEOR economic viability is emphasized by Tumba *et al*. [110]. Low chemical retention is cost-effective. Surfactant-porous media interaction is influenced by factors like electrostatics, van der Waals forces, ion exchange, association, π electron polarization, and hydrophobic interaction. Ahmadi *et al*. [111] analyzed ZSC-derived surfactant adsorption on carbonate rocks. No precipitation; salt cations enhanced adsorption via electrostatic attraction. Additionally, Azza *et al*. [5] conducted a comparative evaluation of natural surfactants from botanicals on quartz sand substrate. High salinity reduced adsorption due to compact structure and compressed electrical double layer. Furthermore, Kesarwani *et al*. [112] scrutinized a biodegradable surfactant derived from Karanj, testing its adsorption on sandstone. It had 15% less retention than SDS. Moreover, Yusuf *et al*. [113] studied soapnut fruit surfactant adsorption on carbonate rocks using surface tension methods. Natural surfactant retention was lower than ionic surfactants due to weaker hydrogen bonding. Hence, natural surfactant adsorption on sandstone and carbonates exhibits negligible surface affinity, suggesting suitability for chemical EOR, as highlighted by Kalam *et al*. [114].

4.4 Natural Surfactant Hydrocarbon Recoverability

Natural surfactants boost oil recovery in EOR, outperforming other oleic recovery methods. IFT, CMC, microemulsion, wettability, and adsorption tests assess natural surfactants oil recoverability. Innumerable studies have been conducted to explore the potential of NS in boosting incremental oil recovery (See Table 2). Yermukhan *et al*. [56] analyzed flaxseed oil procured from *Linum usitatissimum*. Through various screening investigations, they found a CMC of 2.5 wt% and 21% reduction in IFT, resulting in 39–50% additional recovery. Similarly, Imuetinyan *et al*. [115] reported a 15% enhancement in petroleum recovery via core flooding with a saponin-derived NS solution under HPHT conditions. Additionally, *Quinoa* surfactant solution (0.15%) increased oil recovery from 60% to 78.8% in carbonate core plugs [72]. *Myrtus communis* derived surfactant increased oil recovery by 14.3% in carbonate core plugs, according to Nowrouzi *et al*. [42]. Moreover, *Alfalfa* extract was utilized in a saline solution core flooding procedure, resulting in an additional recovery of 19.2% [75]. Building on this, mulberry leaf extract, a natural surfactant, boosted oil recovery by 7% in tertiary carbonate/sandstone cores [77]. Furthermore, Saxena *et al*. [116] evaluated palm oil-derived surfactant and revealed 25-27% augmentation of recovery factor via injection in sandpack experiments. Again, Emadi *et al*. [46] developed a formulation using *Zizyphus Spina Christy* leaf extract, resulting in a 15% incremental recovery. Jalali et al. [48] demonstrated *Cordia myxa* leaf extract's efficacy as a natural surfactant, yielding a 27% enhancement in oil recovery. Lastly, Palmnel oil-based green surfactant (0.4 wt.%) achieved 24.3% incremental oil recovery, demonstrating its potential in EOR[117]. The figure below represents the current advancement of natural surfactant oil recoverability in laboratory settings.

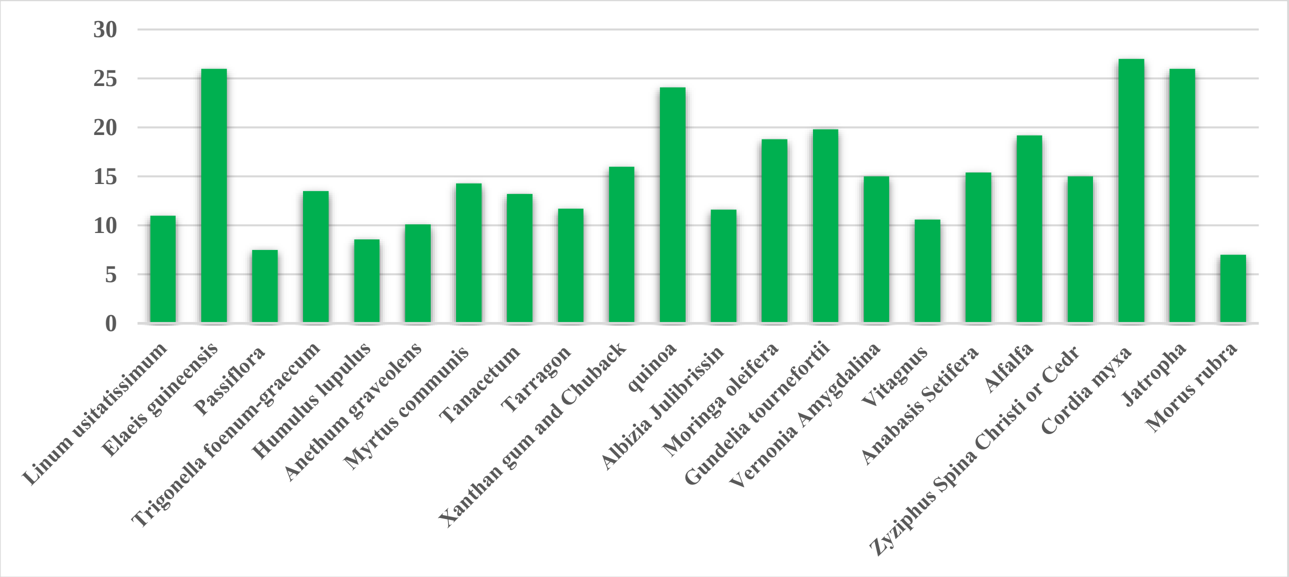

Figure 7. Contemporary advancement of natural surfactant additional oil recoverability

4.5 Natural Surfactant Nanomaterials Application

Plant extracts diminished the IFT between oil and water, promoting oil migration toward production wells and boosting recovery. Various plant extracts were examined for their potential in EOR, as highlighted in Table 2. Researchers noted a significant impact on oil recovery, primarily by lowering IFT and shifting wettability from oil-wet to water-wet. Recent advancements in this biobased surfactant pre-screening evaluations encompass the integration of nanotechnology for enhanced performance and efficiency.

Nanotechnology has revolutionized the hydrocarbon industry, providing innovative solutions to long-standing challenges. From exploration to EOR, nanoparticles have proven to be game-changers [4]. The synergistic interplay between nanoparticles and surfactants enhances performance by optimizing nanoparticle behavior in intricate temperate and untemperate conditions. The combination of nanomaterials and natural surfactants demonstrated synergistic effects, enhancing oil recovery through wettability alteration and IFT ebb [39]. Consequently, the integration of both elements yields a more potent oil-optimized-approach, as they collectively improve fluid dynamics within the reservoir [118]. As such, researchers have focused on nanomaterials, such as nanoparticles (NPs) and nanocomposites (NCs), due to their distinct properties and large surface areas [119, 120]. Advancing research unlocks vast potential for nanomaterials to transform hydrocarbon exploitation, promising a brighter future. Nanomaterials have shown promise in EOR owing to their unique capability to interact with both hydrophilic and water-repelling components. Their hydrophobic nature can alter rock surface wettability, reducing capillary forces [121, 122]. When interacting with surfactants, they generate nanosurfactants with exceptional and intriguing properties, distinct from the original components. The resulting suspension or composite material demonstrates superior characteristics, unlike the individual elements. Nanosurfactants exhibit ultra-low interfacial tension due to the irreversible adsorption of nanoparticles at the interface. Overall, nano-chemicals show reduced adsorption during tests in porous media, making them highly suitable for enhanced oil recovery. These properties enabled them to enhance the effectiveness of EOR processes, leading to improved oil recovery [118, 123, 124]. Consequently, they are considered the next revolutionary advancement in chemical EOR techniques [4].Therefore, a more profound impact can be achieved in reducing IFT and altering wettability using phyto-based and nanomaterials combination [125].

Al-Sabagh *et al.* [126] reported that *A. judaica*extract and silver nanoparticles recovered 33% incremental recovery. Currently, Manshad *et al.* [39] Assess the impact of eco-compatible nanofluid in hydrocarbonrecuperation using natural additives and nanomaterials. *Anethum graveolens* surfactant (i.e., NS) outperformed others, IFT significantly diminished from 22.6 to 2.443 millinewtons per meter and recovered 10.11% more oil. Combining nanocomposites with surfactants ebbs IFT, with a minimum value of 2 mN/m achieved with *Anethum graveolens* surfactant. Nanosurfactants significantly reduced rock surface contact angle, with a minimum of 38.41° achieved with *Humulus lupulus* and NCs. *Anethum graveolens* nanosurfactants extracted an additional 14.10% of OOIP, outperforming the natural surfactant solutions. Similarly, Chen *et al.* [127]found that graphene oxide NCs and soybean extract synergistically enhanced petroleum recovery by 40% in EOR. Mixing nanomaterials with natural surfactants EOR, altering wettability and reducing IFT, showing synergistic effects [128].

The integration of nanotechnology has transformed the industry, offering a more efficient, sustainable, and productive approach to oil and gas operations. Adding nanocomposites to conventional chemical recovery methods has shown potential for optimizing residual petroleum extraction from reservoirs [129, 130]. Additionally, nanoparticles have addressed flow assurance issues, improved drilling and completion operations, and even optimized hydraulic fracturing [4].

Table 6. List of some published nanomaterials utilized with biobased surfactants

Ref.	**Nanocomposite (NC)**	**Nanoparticle (NP)**	**Chemical Formula**
[118]	Magnetite	-	Fe_3O_4
[131]	-	Nanobentonite	-
[131]	Xanthan gum	-	TiO_2
[126]	-	Silver	Ag
[132]	-	Carbon-based	-
[133]	-	Zinc oxide	ZnO
[134]	Graphene oxide	-	GO
[135]	Polymer-coated silica	-	-
[136]	Iron (II,III) oxide@ Chitosan	-	Fe_3O_4
[137]	Metal oxide	-	SiO_2
[120]	Graphene oxide	-	GO
[138]	Polyacrylamide-grafted silica	-	-
[139]	-	Polymer nanofibers	-

Note: Some nanomaterials are part of nanocomposites (materials combining multiple components, at least one being a nanomaterial).

5.0 LIMITATIONS AND OPPORTUNITIES

Utilizing NS sourced from plants for cEOR is a sustainable and eco-friendly method to enhance oil extraction processes. Surfactants obtained from plant parts provide a biodegradable option compared to traditional synthetic surfactants, which may cause harm to the environment. Plant-based NS in EOR can decrease environmental consequences of oil extraction. Surfactants from replenishable sources are biodegradable, reducing oil extraction's harmful effects on ecosystems and water bodies. By substituting synthetic surfactants with plant-based alternatives, oil companies can enhance their sustainability strategies and diminish their overall environmental footprint.

The incorporation of natural surfactants extracted from plant sources has demonstrated efficacy in enhancing the efficiency of oil recovery processes. These surface-active surfactants reduce oil-water tension, enhancing oil mobilization and recovery. By integrating plant-derived surfactants into cEOR techniques, companies can potentially boost their overall oil production and improve extraction efficiency. Furthermore, a beneficial aspect of utilizing natural surfactants from plants is their cost-effectiveness. Plant-based surfactants offer a financially feasible alternative, sourced from readily available plants. Such a strategy has the potential to assist oil companies in trimming production expenses and enhancing their overall financial viability.

Natural surfactants effectiveness in EOR can be impacted by compatibility issues with other chemicals. Additionally, natural surfactants could demonstrate lower stability under extreme thermodynamic and hyperhaline reservoir conditions, compared to synthetic alternatives. Natural surfactants' diverse composition and characteristics impact their capability to reduce IFT and contact angle, affecting oil recoverability efficacy.

When utilizing NS procured from plant in EOR, a potential limitation lies in their performance variability. Plant source, extraction method, and formulation affect plant-based surfactants' effectiveness, leading to varying performance outcomes. Extensive testing and optimization are necessary to determine optimal plant-based surfactants for oil recovery. Additionally, the scalability of production of NS from plant sources presents another challenge. Logistical hurdles arise when scaling up sustainable surfactant production for large oil extraction operations. Partnerships and infrastructure investments are crucial for a reliable supply of plant-based surfactants.

In summary, Plant-based surfactants in chemical enhanced oil recovery offer advantages in sustainability, efficiency, cost-effectiveness, and health and safety. Research and development can overcome challenges, enhancing efficacy and consistency of plant-based surfactants for oil extraction. Plant-derived surfactants enable oil companies to shift towards sustainable, environmentally friendly extraction practices.

6.0 CONCLUSION

The reviewed literatures imply that plant-derived surfactants have the possibility to be effective agents in improving oil recovery. This exposition undertakes scrutiny into the most recent developments and the current state of utilizing NS in EOR). It analyzes plant-based surfactant properties, extraction techniques, natural sources, and their role in Modulating interfacial energetics and substrate hydrophobicity. Reviewing literature expanded our insight, leading to the following key conclusions:

- Leaves are the main source, but other plant parts with saponin offer a reliable alternative for NS extraction.
- Research focus determines the choice of natural surfactant extraction methods, depending on the study's specific goals and objectives.
- Saponin-based plants extract critical Michelle concentrations ranges from 0.1wt% to 5.5wt%.
- Natural surfactant performance is affected by temperature, structure, salinity, co-surfactants, alkali, and polymers; optimizing temperature and salt concentration enhances performance.
- In the last 15 years, natural surfactants from plants have achieved substantial CA and IFT reductions according to the descriptive statistical analysis.
- Azza et al. [6] suggested ideal surfactants should reduce IFT to 10^{-3}-10^{-4}mN/m, but this goal has not been achieved.
- Natural surfactants from plant parts have yielded substantial recovery enhancements in laboratory experiments over the years.

Natural surfactant nanoparticles and composites show promising potential for future Petroleum fluid recuperation. Ongoing research and advancements can overcome limitations, unlocking the full potential of innovative materials to enhance oil recovery efficiency.

7.0 FUTURE INVESTIGATION

- Investigation of various specific mechanisms of action of plant-derived surfactants in EOR processes.
- Simulating NS flow and transport dynamics in porous substrates, upscaled for in situ field investigations
- Investigating the environmental impacts and sustainability aspects of utilizing plant-based surfactants in oil recovery.
- Understanding the long-term effectiveness and feasibility of these NS in real-world oil recuperation scenarios.
- Investigating the interaction between natural surfactants and sandstone and carbonate rocks to assess their adsorption and retention characteristics.
- Investigate the underlying mechanisms of natural surfactant nanoparticle and nanocomposite interactions with oil and rock surfaces to EOR.
- Explore the potential of combining NS nanoparticle and nanocomposite applications with other EOR methods for further EOR.

8.0 CONFLICT OF INTEREST

All authors declare no conflicts of interest in this research work.

9.0 AUTHORS CONTRIBUTION

G.S. Kuradoite (Writing – original draft; Formal analysis)

J.R. Gbonhinbor (Conceptualization; Project administration; Writing – review & editing; Visualisation; Supervision)

S.P. Peletiri (Project administration; Visualisation)

S. Igbani (Project administration; Visualisation)

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