Review article

A Review of the Mechanism and Role of Wax Inhibitors in the Wax Deposition and Precipitation

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ABSTRACT

The continuous depletion of global oil reserves with the propensity for light distillates propels the oil and gas industry to explore heavier fractions of crude oils with significant amount of paraffin waxes. However, the precipitation and deposition of waxes during the transportation of these waxy crude oils in the pipelines contribute to several issues, such as the flowability reduction, excessive pumping cost, and wax gel formation, that adversely affect the supposedly steady offshore oil production. As a result, substantial resources are expended to resolve these flow assurance problems. The wax inhibitors and pour point depressants are developed and modified to meet the wax remediation criteria. Essentially, the wax crystals are formed through the nucleation, growth, and agglomeration processes, while the deposition of these waxes occurs via molecular diffusion and shear dispersion. The wax inhibitors are able to control the growth of wax crystals through nucleation, co-crystallization, adsorption, and dispersion interactions. This paper particularly assessed the following compounds: (1) polymeric wax inhibitors, (2) nano-hybrid pour point depressants, (3) organic solvents, and (4) surfactants. Given the significance of these compounds in the deposition and precipitation of waxes, it is imperative to comprehensively explore the types and nature of these compounds and their recent applications as well as to critically assess their strengths and drawbacks, which were addressed in this paper. Furthermore, the challenges of using these compounds and

the factors that govern their efficiencies were also discussed. Accordingly, the carbon length and the molecular weight of both paraffin waxes and wax inhibitors are among the most influential factors.

INTRODUCTION

Following the continuous depletion of conventional oil reserves, the production of unconventional oils, such as waxy crude oils and heavy crude oils, increases (Li et al., 2015). In fact, approximately 20% of the global oil reserves are of waxy crude oils, while heavy crude oils constitute about half of the recoverable oil reserves (Ghannam et al., 2012; Kumar et al., 2015). These oil reserves are often produced in the deepwater region with the ambient seawater of extremely low temperature (Shafquet et al., 2015). However, the presence of paraffin waxes in a substantial amount significantly impedes the exploration and production of these unconventional oils, which lead to the gelation of waxy crude oils and eventually, the shutdown of these production pipelines (Lira-Galeana & Hammami, 2000). As the temperature of bulk oil hits below its wax appearance temperature (WAT), the wax molecules precipitate and subsequently transform into wax gel with high yield strength, which surrounds the cross-sectional area of the production pipelines (if there are no remediation steps taken) (Chala et al., 2014). The continuous deposition of the precipitated waxes on the surface of these pipelines subsequently lead to gelation, wherein at this point, the liquid waxy crude oil undergoes three stages of phase transformation (Chala et al., 2018). Firstly, the wax particles aggregate in the oil clusters with the changing temperature and pressure and then precipitate when these oil clusters become large enough. Following that, the gelation of wax layer (wax molecules form a net-like or cage-like structure) takes shape, which is the main cause to the poor fluidity of waxy crude oils (Na et al., 2017). The gel-like wax structure continuously deposits layer-wise, resulting in clogged gel. At this point, the production pipelines have to be brought to a halt. In brief, the oil and gas industry experiences significant challenge in dealing with the deposition and precipitation of these waxes.

Considering that the paraffin wax is the primary cause to the poor flowability of waxy crude oils at low temperature, it is pivotal to consider the nature of hydrocarbons to effectively remediate this issue. Essentially, the paraffin wax consists of long, saturated hydrocarbon chains, with at least 15 or more carbon atoms per molecule (Yang et al., 2013; Ganeeva et al., 2016). The paraffin waxes are generally divided into (1) macrocrystalline wax and (2) microcrystalline wax, which are naturally found in unconventional oils (Japper-Jaafar et al., 2016; Mohamed et al., 2017). The macrocrystalline wax is characterized by low molecular weight and straight chain paraffin (n-alkanes) with varying carbon chain length (between C_{16} and C_{40}). It predominantly crystallizes in the shape of either a platelet-like or

a needle-like. Meanwhile, the microcrystalline wax, which is also known as "amorphous" wax, contains high percentage of isoparaffinic hydrocarbons and naphthenic rings with carbon chain length of between C_{30} and C_{60}. Both types of paraffin wax precipitate and deposit in the production pipelines when the temperature drops below their WAT (Paso et al., 2009; Yang et al., 2015).

Various methods to address the deposition and precipitation of waxes are theoretically proposed and applied in practice with the purpose of improving the flowability of waxy crude oils. After all, the prevention methods are undoubtedly more economical compared to what the remediation methods offer. Fundamentally, these prevention methods are broadly categorized as (1) thermal, (2) mechanical, and (3) chemical (Al-Yaari, 2011). A blend of chemicals or a combination of methods is typically applied to attain the optimum effectiveness in improving the flowability of these waxy crude oils. Some of the most widely used conventional thermal methods to enhance the fluidity are the dilution with light ends method and heating method, but they come with an economic drawback (considering the long-term operation costs these methods require). Apart from these methods, the mechanical pigging method, is also widely recognized to remove paraffin waxes, but it requires periodic production shutdowns; thus, resulting in substantial economic predicament. Therefore, the pigging frequency must be greatly reduced in order to attain higher economic returns. Consequently, the chemical methods, such as wax inhibitors (WIs) and pour point depressants (PPDs), are preferred (Wei, 2015).

The significance of WIs and PPDs have gained growing interest among academicians and industrial practitioners over the past decades. These chemical methods serve as a preventive measure, which forms a "kinetic barrier" and subsequently delays the precipitation of these waxes and the formation of hardened wax. These methods also aid in the removal of deposited wax. With that, the chemical methods are considered as significant practical applications to improve the flowability of waxy crude oils; thus, reducing the maintenance cost of these pipeline facilities. These widely used chemicals include ethylene vinyl acetate (EVA) copolymers, comb-type copolymers, nano-hybrid compounds, organic solvents, and surfactants, which were particularly explored in this paper. Accordingly, this paper explored several categories of WIs and PPDs as well as their purpose to prevent the formation of wax crystals and high pour point (PP). In addition, the mechanisms of WIs and PPDs in waxy crude oils, the factors that govern their efficiencies, and the summary of recent applications and challenges of using these compounds were also critically assessed.

THEORY OF WAX FORMATION

Principally, the wax formation is conceptually similar to the crystallization process. Considering that the wax crystals are exothermic in nature, they emit small amount of heat. Likewise, these crystals require certain amount of heat to dissolve (endothermic process)

(Bhat & Mehrotra, 2004). The crystallization process involves the production of solid ordinate structure from a disordered phase, which typically occurs in thermodynamically unstable solutions. The concentration of solute (or strictly, its chemical potential) in excess of its equilibrium or saturation value serves as the driving force for the formation of these wax particles (Lashkarbolooki et al., 2011).

Firstly, the formation of tiny solid aggregates initiates the nucleation process. Basically, these atoms in the liquid state are prompted to bond and form solids. The subsequent stage is the growth of crystals, which mass transports the solute in the nuclei direction that is formed in the nucleation process. These crystals increase in size with the progressive addition of atoms. The final stage involves the agglomeration process, wherein the size of crystals increases in conjunction with the growing crystals. The cooling surface may experience extremely high supersaturation, which leads to the extensive formation of small crystals by nucleation. When these crystals are not dragged by the system agitation and turbulent flow, they stick to one another as well as to the cooling surface; thus, causing deposition. As a result, the deposition on the surface then behaves as thermal insulation for the flow system (dos Santos et al., 2004).

The deposition of wax occurs via two primary mechanisms (Kelland, 2014). If the pipe wall has lower temperature than the WAT, the wax forms and deposits on the surface of the pipe wall. This scenario is possible even if the temperature of the bulk fluid is above the WAT. In this case, the mechanism is known as molecular diffusion (Yang et al., 2018). Secondly, the shear dispersion potentially shifts the molecules of precipitated wax (that are near to the surface of the pipe wall) and deposits the wax at the lower velocity region in the production pipeline.

MECHANISMS OF WAX INHIBITORS

The mechanisms of WIs and the influence of WIs on the morphology of wax crystals using actual crude oils were extensively explored in various studies. In fact, the inclusion of WIs is widely recognized for delaying the agglomeration of wax crystals by modifying their shape and size (Li et al., 2010). Despite being extensively studied, the mechanisms of WIs are not adequately grasped and can be rather controversial to a certain degree. The present section briefly describes the core theories and mechanisms of WIs. Table 1 summarizes the mechanisms of different WIs and PPDs.

The molecules of both wax and WI undergo the nucleation process. The wax molecules precipitate out from the oil phase of below WAT, which form crystalline nucleus (of a critical size); thus, prompting the formation of a larger compound, specifically the wax crystal. Meanwhile, the high molecular weight of WI propels the crystalline nucleus to self-assemble into a micelle-like aggregate. This eventually forms more subcritical nuclei, which reduce supersaturation and prompt the formation of smaller wax crystals (Yang et

Table 1

Summary of wax inhibitors and pour point depressants and their corresponding mechanisms

Crude oil	WI/PPD	Mechanism	References
Iranian	Ethylene Vinyl Acetate copolymers	Co-crystallization Nucleation Adsorption	Taraneh et al. (2008)
Brazilian	Ethylene Vinyl Acetate copolymers	Co-crystallization	Machado et al. (2001)
Egyptian	Octadecyl Maleate-Vinyl Acetate copolymers	Co-crystallization Wax dispersion	Atta et al. (2015)
Indian	Non-ionic Phenyl-Polyethylene Glycol surfactant	Emulsification	Kumar & Mahto (2017)
Malaysian	Ethylene Vinyl Acetate co-Diethanolamine	Co-crystallization	Anisuzzaman et al. (2017)
China	Polyhedral Oligomeric Silesesquioxane nanocomposites	Co-crystallization Aggregation	Yao et al. (2017)
Indian	Polyhexyl Oleate-co-Hexadecyl Maleimide-co-Alkyl Oleate	Co-crystallization	Patel et al. (2017)
China	Polyoctadecyl Acrylate nanocomposites	Co-crystallization	Yao et al. (2016)
Nigerian	Trichloroethylene-Xylene	Dilution Wax dispersion	Bello et al. (2005)
Model sample	Polyethylene-butene	Co-crystallization	Ashbaugh et al. (2002)
China	Cetyl Trimethyl Ammonium Chloride	Co-crystallization	Gu et al. (2018)
Malaysian	3-2-Methoxyethoxy Propyl-Methyl-bis Trimethylsilyloxy Silane nanohybrid	Wax dispersion Adsorption	Lim et al. (2018)
Indian	Tri-Triethanolamine Monosunflower Ester	Emulsification	Kumar & Mahto (2017)
Egyptian	Ethoxylated fatty alcohols	Wax dispersion Co-crystallization	Khidr & Mahmoud (2007)

al., 2015). As a result, these smaller wax crystals remain stable in the oil phase, which suggests improved flowability (Marie et al., 2005; Naiya et al., 2015).

Another mechanism involves the co-crystallization process when the WI molecules disrupt the crystallization process and modify the growth of wax crystals (Jin et al., 2014). The paraffin wax molecules adsorb on the surface of inhibitors with similar chemical structure, which are then bound together and subsequently form a wax crystal lattice structure (Figure 2e) in the crude oil. This alters the morphology of growing wax crystals and delays the formation of three-dimensional crystals. Tiny spherical-like crystals (altered in shape from large plate-like crystals) are expected to increase the flowability (Soni et al., 2010; Jafari Ansaroudi et al., 2013).

Meanwhile, the adsorption of wax molecules on the surface of the WI inhibits the growth of crystals and alters the formation pattern of crystals through the formation of micelle core (El Mehbad, 2017). In general, the WI serves as a "wrapper" that envelopes

the wax molecules and prevents their growth with the reduced crystal-crystal adhesion (Wei, 2015). Following the co-crystallization process of the WI, tiny spherical-like crystals appear in the solubilization process, which improves the dispersion of tiny wax crystals and eventually reduces the WAT (Cao et al., 2013). Besides that, the interaction of van der Waals forces between the wax crystals and the long alkyl chain of WI also increases the solubility of wax in the crude oil (Yang et al., 2015).

TYPES OF WAX INHIBITORS AND POUR POINT DEPRESSANTS

The previous section briefly described the examples and mechanisms of WIs. The current section discusses the types and the nature of WIs and PPDs, their mechanisms, their recent applications, and the factors that govern their efficiencies. This section explores the following chemicals, which included EVA copolymers, comb-type copolymers, crystalline-amorphous polymers, nano-hybrid PPDs, organic solvents, and surfactants. Table 2 provides recent applications on the reduction of PP using different WIs and PPDs.

Table 2
Reduction of pour point using different wax inhibitors and pour point depressants

Crude oil	PP (°C)	Resulted PP (°C)	WI/PPD	References
Indian	42	1	Non-ionic Phenyl-Polyethylene Glycol surfactant	Kumar & Mahto (2016)
Nigerian	2	-8	Trichloroethylene-Xylene	Bello et al. (2005)
Russian	21	14	Alkyl Acrylates-Dodecylammonium Acrylate-Dodecylammonium Sulfate	Litvinets et al. (2016)
Egyptian	24	3	Gemini surfactant	Ahmed et al. (2017)
China	19	7	Polyoctadecyl Acrylate nanocomposites	Yao et al. (2016)
Egyptian	24	6	Polyalkyl Linoleate–co–Succinic Anhydride	Soliman et al. (2018)
Egyptian	24	-3	Styrene Maleic Anhydride copolymers-Aniline- Triethanolamine with Oleic acid blend	Al-Sabagh et al. (2017)
Egyptian	27	6	Modified Maleic Anhydride-co-Octadecane copolymers	El-Ghazawy et al. (2014)
Iranian	8	-10	Ethylene Vinyl Acetate copolymers	Taraneh et al. (2008)
Brazilian	18	-17	Ethylene Vinyl Acetate copolymers	Machado et al. (2001)
Indian	22	16	Polyhexyl Oleate-co-Hexadecyl Maleimide-co-Alkyl Oleate	Patel et al. (2017)
Malaysian	35	10	Ethylene Vinyl Acetate co-Diethanolamine	Anisuzzaman et al. (2017)
China	15	7.5	Cetyl Trimethyl Ammonium Chloride	Gu et al. (2018)

Ethylene Vinyl Acetate Copolymers

The copolymerization of ethylene and vinyl acetate (VA) forms EVA copolymer. VA, which is a polar compound, consists of methyl and methylene groups with two active oxygen atoms ($C_4H_6O_2$). The simulation of the molecular dynamics (Figure 1) displays strong van der Waals interaction that EVA copolymer exhibits via oxygen atom (in the VA functional group) and hydrogen atom (in n-octacosane wax); thus, contributing to higher probability value of inhibition. As propounded by Al-Sabagh et al. (2007) and Taiwo et al. (2012), the oxygen-containing groups in the WIs inhibit the growth of these waxes. In other words, the oxygen atoms in the EVA copolymers, which reflect intermolecular interaction, increase the solubility of wax and subsequently prevent the wax solid formation.
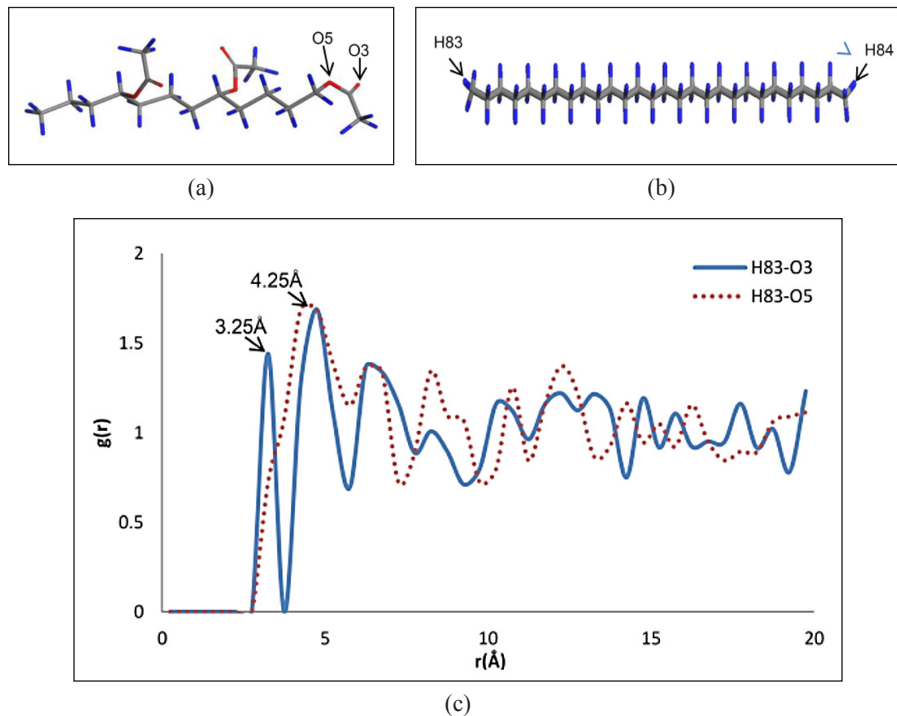

Figure 1. Structure properties defining the active atom of (a) ethylene vinyl acetate (EVA) copolymer, (b) n-octacosane, and (c) Rdf pattern H83 of n-octacosane in EVA inhibitor
(*Source:* Ridzuan et al., 2014) Copyright 2014 by the Society of Petroleum Engineers. Reprinted with permission.

The polymeric WIs are able to optimally interact with the soluble wax in crude oil when the temperature is slightly above WAT. This is due to the interaction between the non-polar long alkyl moieties of WIs and the long-chain paraffin waxes (Yang et al., 2015). The presence of VA functional groups along with the side chains potentially impede the crystallization process of wax and reduce the PP, which eventually improve the overall

flowability (Kelland, 2014; Ridzuan et al., 2014). These side chains co-crystalize into long-chain paraffin, which leaves the polar moiety end tail and creates steric hindrance that interferes with the alignment of new incoming wax molecules. Moreover, the favorable interaction of van der Waals forces between the wax particles and the functional groups in EVA copolymer reduces the gel strength of the wax, which subsequently weakens the tendency of wax deposition. Besides that, the increase in the solubility of wax in crude oil, which is mainly caused by these van der Waals forces, contributes to the reduction of WAT (Ridzuan et al., 2015; Yang et al., 2015)

Various studies on EVA copolymer, as WI, demonstrated significant relevance in the varying VA contents (between 10 wt% and 40 wt%). The optimum VA content for the reduction of PP was reported at 30 wt% under similar conditions (Ashbaugh et al., 2005; Machado et al., 2001). Machado et al. (2001) specifically assessed the influence of EVA copolymer on the viscosity and the PP of Brazilian crude oil with varying VA contents (20 wt%, 30 wt%, 40 wt%, and 80 wt%), which reaffirmed the significant role of EVA copolymer in lowering the viscosity optimally, but only when the temperature was set higher than WAT. The study further reported that there was significant relevance between the VA content and the PP of crude oil.

Meanwhile, Jafari Ansaroudi et al. (2013) examined the influence of EVA copolymer on the viscosity of five Iranian waxy crude oils with different molecular weights. The results of viscosity reduction showed that EVA copolymer with high molecular weight (80) exhibited good influence for the crude oil with relatively low asphaltene content (0.3%), while EVA copolymer with lower molecular weight (32) demonstrated the best efficiency for the crude oil with relatively high asphaltene content (7.8%) under similar conditions. In terms of the PP, the performance of EVA copolymer with different molecular weights exhibited similar regularity.

In addition, Wu et al. (2005) and Ridzuan et al. (2014) performed the simulation of molecular dynamics on EVA copolymer to explore the interaction between EVA copolymer and wax crystals. Due to the high polarity of EVA copolymer (as compared to the wax molecules), the addition of EVA copolymer in the crude oil was found to modify the shape and growth of wax crystals on the surface in the axial direction. Moreover, the concentration of EVA copolymer was also found to govern the morphology of wax crystals to grow in different directions (x-axis, y-axis, and z-axis).

Comb-Type Copolymers

The comb-type polymer consists of polyvinyl backbone with different pendant chains. This type of polymeric WIs fulfilled the statement made by Soni & Bharambe (2008) that emphasized the significance of a good influencer to possess certain characteristics. The length of pendant chains is considered the most crucial feature, considering that the WI

and the long-chain paraffin should exhibit similar length to achieve optimum inhibition. Moreover, the polyvinyl backbone has minimal influence on the performance of WI. However, changing the regularity of this backbone, which serves as the structure for the pendant chains to suspend from, significantly influences the structure of the polymer, which reduces both PP and the degree of crystallinity. Apart from that, the comb-type polymers are widely accepted as WIs and PPDs due to the flexibility these polymers possess. The comb-type polymers are typically divided into two different polymer classes, namely (1) maleic anhydride copolymers (MACs) and (2) poly-acrylate or methacrylate (PA or PMA) ester polymers.

Xu et al. (2009) examined a series of MACs in waxy crude oil, which revealed that the MAC with the longest chain length (C_{18})—as compared to C_{12}—had the best performance in significantly reducing the size of wax crystals. Essentially, the length of alkyl side chain plays a significant role in affecting the performance of these comb-type polymers (Wang et al., 2003a; Soldi et al., 2007). In other words, the longer the length of alkyl chain, the higher the solubility of copolymer in the structure of paraffin wax. Thus, it is assumed that the increased interaction and solubility of wax impede the wax formation and contribute to the reduction of PP (Al-Sabagh et al., 2009). Moreover, the addition of the polyvinyl backbone to the alkyl side chain improves the resistance to the formation of wax crystals. Apart from the improvement of PP, the MACs were found to contribute to the reduction of both deposition rate of wax and yield stress of wax gel, which eventually ease the wax removal process due to lower gel strength (Li et al., 2012). Nonetheless, it remains a challenge to develop a specific type of WI that is universally applicable for diverse fields, which emphasizes the need to have a wide range of comb-type polymers for different compositions of crude oils.

Another important polymer class, which contains the PA and PMA, are also widely used as WIs and PPDs. As previously discussed, the compatibility between the alkyl chains and the structure of paraffin wax in crude oil influences the degree of flowability. The length on the alkyl side chain is also suggested to be longer than C_{18} to match with the long paraffin wax chain, which is usually longer than C_{15}. The discussion on the optimal alkyl side chain length ($> C_{18}$) is further strengthened by a recent study by Jafari Behbahani et al. (2017). Essentially, the specific series of comb polymers and the paraffin chain length must be compatible to hinder the formation of interlocking crystals, as demonstrated in Figure 2. The specific main criteria are aligned with those results of other comb-type polymers (Wang et al., 2003b; Soldi et al., 2007; Al-Sabagh et al., 2013). Nevertheless, the resultant outcomes are highly dependent on the composition of crude oil and the paraffin chain length in specific crude oil.

Apart from the composition of crude oil and the molecular structure of these comb-type polymers, the depressive effect on the waxy crude oil was found to rely on the average molecular weight of these polymers (Borthakur et al., 1996; Yang et al., 2009; Zhang et
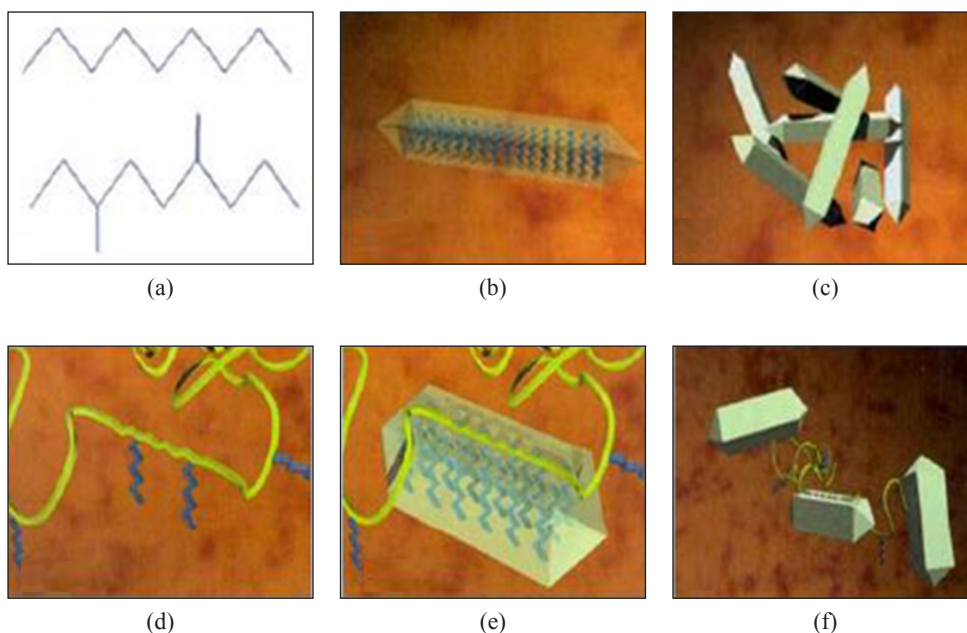
Figure 2. Modification process of the paraffin crystal with the polymeric wax inhibitor, (a) chemical structure of wax, (b) crystal shape of wax structure, (c) crystal structure of growing wax lattice, (d) polymeric wax inhibitor with wax-like components, (e) co-crystallization of wax and wax inhibitor, and (f) sterically hindered wax structure
(*Source:* Al-Sabagh et al., 2016) Copyright 2016 by the American Chemical Society. Reprinted with permission.

al., 2014). This implies that the average molecular weight holds the key to influence the depressive effect of polymeric WIs (the reduction of PP). Furthermore, the influence of molecular weight on the wax inhibition is significantly related to the carbon number range of the paraffin wax in crude oil. Crude oils with wide range of normal paraffin and lower mean carbon number are recommended to be treated by high molecular weight copolymers whereas low molecular weight copolymers are recommended for crude oils with narrow range of normal paraffin and higher mean carbon number (Borthakur et al., 1996). Apart from that, El-Gamal et al. (1994) revealed that the increase in the polydispersity index (broadened distribution of the molecular weight) enhances the inhibition capability of wax; thus, indicating that the polymers with the highest polydispersity index attain the best PP depression. However, Chanda et al. (1998) and Ahmed et al. (2012) revealed contradictory findings on the molecular weight—which is possibly due to the different structure of WIs, the composition of crude oil, and the composition of asphaltene (El-Gamal et al., 1992;

Borthakur et al., 1996; Taraneh et al., 2008). Thus, it can be concluded that the average molecular weight of the comb-type polymers potentially influences the wax inhibition in waxy crude oil. Nonetheless, future studies should consider the composition of crude oil as well as the molecular weight of WIs in the selection of appropriate WI for the specific oil field.

Crystalline-amorphous Copolymers

Polyethylene-polyethylenepropylene (PE-PEP) and polyethylenebutene (PEB) are few examples of crystalline-amorphous diblock copolymers, which contain polyethylene (PE) groups (as crystalline groups) and polybutene (PB) or polyethylenepropylene (PEP) (as amorphous moieties) (Ashbaugh et al., 2002). The presence of two non-polar groups (crystalline non-polar group and amorphous non-polar group) presents an exception case to the standard structural character (Yang et al., 2015).

Previous studies demonstrated that the utilization of PE-PEP controls the size and rheological properties of wax crystals in the middle distillate fuel and crude oils (Leube et al., 2000; Monkenbusch et al., 2000; Ashbaugh et al., 2002). Figure 3 illustrates the difference in the size of these crystals. Meanwhile, Figure 4 reveals that PEP, which has the appearance of brush hairs, envelops the large surface area of PE crystalline core and is likely to self-assemble due to the presence of van der Waals force. On the other hand, the PE crystalline core in the oil phase serves as the nucleation platform for more wax fractions to nucleate at the PE surface. At this point, the PEP simultaneously maintains the micelles in the solution. These diblock copolymers are considered as appropriate wax crystal modifiers and PPDs, given their capability, even at lower concentration.

Apart from the PE-PEP, PEB is another example of diblock copolymers, which were explored in several studies (Guo et al., 2006; Radulescu et al., 2006). The ethylene side chains of PEB are able to self-assemble into the structure of a needle shape or co-crystallize with long-chain n-paraffin, which creates small, thin sheets of paraffin layer in the decane solvent (Radulescu et al., 2006). Meanwhile, Guo et al. (2006) specifically examined the model waxy crude oil with the addition of PEB (into the long-chain wax solution) in the decane solvent, which revealed heterogeneous nucleation upon cooling. Furthermore, the wax was found to crystallize into the structure of a rod shape or a shuttle shape, which demonstrated enhanced yield stress of crude oil (as compared to the structure of a plate shape without the addition of PEB). Generally, these crystalline-amorphous copolymers were shown to manipulate the morphology of wax crystals in either the model waxy crude oil or the distillate fuel; however, the applications and mechanisms of PE-PEP and PEB in actual crude oil are rarely presented over the recent years.
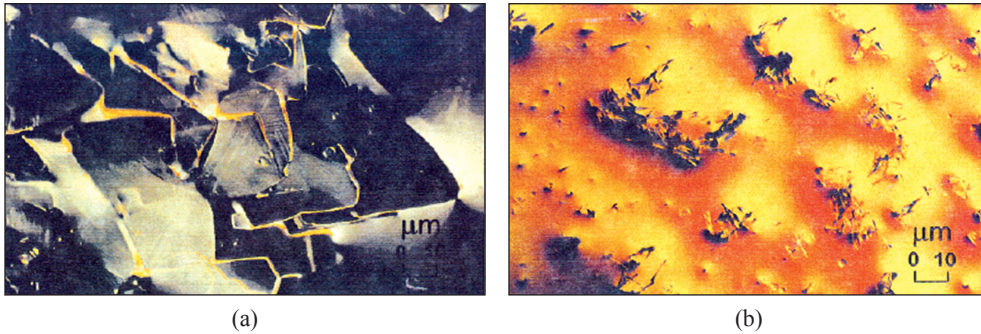
(a)   (b)

Figure 3. Micrographs of untreated polyethylene-polyethylenepropylene (PE-PEP) (left) and treated PE-PEP (right) for diesel fuel at -13°C
(*Source*: Leube et al., 2000) Copyright 2000 by the American Chemical Society. Reprinted with permission.
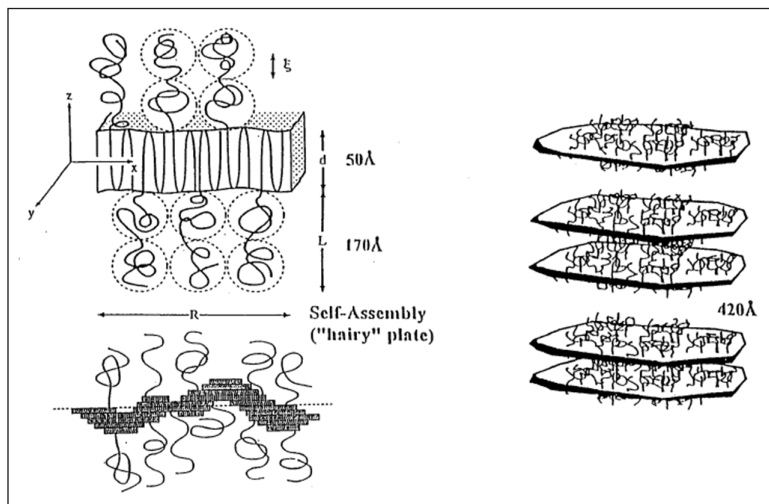

Figure 4. Generic structure of the polyethylene-polyethylenepropylene (PE-PEP) aggregates. The crystallization of polyethylene (PE) forms extended (R) platelets, while the polyethylenepropylene (PEP) hairs form brushes on both sides
(Source: Leube et al., 2000) Copyright 2000 by the American Chemical Society. Reprinted with permission.

Nano-hybrid Pour Point Depressants

The conventional polymeric WIs or PPDs are typically applied for the transportation system of waxy crude oil, but there are certain restrictions that these WIs or PPDs cannot satisfy—certain WIs or PPDs exhibit limited depressive effect, particularly for crude oil with high wax content (Yang et al., 2015). With the recent progress in nanotechnology, there have been new developments such as the polymer/inorganic nano-composites or nano-hybrids for the industrial applications. The nanoparticles exhibit potential in modifying the polymers due to their unique size, high surface adsorption effect, and quantum size effect.

Various studies have successfully demonstrated the efficiency of nano-hybrid PPDs with the organic modification of nanomaterials by polymeric PPDs (such as polyoctadecyl acrylate, EVA copolymers, and methacrylate) (Wang et al., 2011; Yang et al., 2015; Norrman et al., 2016; Song et al., 2016; Sun et al., 2018).

Wang et al. (2011) and Song et al. (2016) modified the polymeric PPDs to enhance their performance (such as introducing the nanomaterials into the polymeric PPDs), which reaffirmed the capability of nanoparticles in altering the morphology of crystals (into spherical shape) to reduce the WAT, gelation temperature, and rheological behavior. In addition, Wang et al. (2011) recommended several possible mechanisms that may account for the enhanced performance—the changes in nucleation (the nanoparticles serve as dispersed nucleation sites), co-crystallization (the incorporation of nanoparticles into the wax crystals hinders their growth), or the adsorption of nanoparticles on the surface of wax crystals (which modulates or hinders the growth of wax crystals). Moreover, Yang et al. (2017) and Sun et al. (2018) demonstrated that the nano-hybrid PPDs did exhibit superior pour point depression than the EVA copolymers alone. In the presence of nanoparticles, the crystallized waxes were found smaller and more dispersed. Furthermore, the nanoparticles that were coated with PPDs performed more efficiently than the neat PPDs. Apart from the commonly known copolymers, the magnetic surfactant-coated nanoparticles were reportedly suspended in the carrier fluid to assist the dispersion of wax in the production tubing (Haindade et al., 2012). Table 3 summarizes the difference in pour point reduction between the pure EVA copolymers and the nano-hybrid PPDs.

Table 3
Difference in the pour point reduction between the pure ethylene vinyl acetate copolymers and nano-hybrid pour point depressants

Sample	PP (°C)
Native crude oil	30.5
EVA treated crude oil	23.0
Nano-hybrid EVA treated crude oil	16.5

Source: Wang et al., 2011

Organic Solvent

The dilution method is one of the oldest, effective methods to reduce the viscosity of oils, which improves the mobility of oils through the pipelines (Gateau et al., 2004). The classical (light ends) diluents include gas condensates, naphtha, and kerosene (Bassane et al., 2016). In the case of heavy crude oils, the organic solvents have been widely used as PPDs over the past decades prior to the emerging of polymeric WIs (Hart, 2014; Santos et al., 2018). Light ends and organic solvents are two main groups of solvent used on the

oilfields. The addition of light ends and organic solvents downhole and to the flow lines effectively remove the deposition of these waxes, which ease the transportation of crude oils to the surface. Other effective organic solvents with proven success include benzene, chlorinated hydrocarbons, and carbon disulphide, but these solvents are not environmentally friendly and pose higher risk (Woo et al., 1984).

There are several methods that enhance the performance of solvents: (1) the mixture of xylene or toluene and aliphatic solvent increases the removal of waxes (Norland, 2012); (2) the incorporation of surfactant enhances the performance of the solvent in dispersing the waxes (Sahai et al., 2018); (3) heating up the xylene and toluene solvent increases the removal efficiency of waxes (Straub et al., 1989). Despite the advantages offered by the solvent combination, the conventional organic solvent has certain limitations, such as low specific gravity, which disallows the solvent to reach downhole (to dissolve the deposited paraffin waxes). The low flash point of these solvents generally presents handling and storage problems too.

Meanwhile, Bello et al. (2005) claimed that the ability of binary PPD system of trichloroethylene and xylene to significantly depress the PP and the deposition of waxes. However, this method may not be economically feasible due to the need to utilize high dosage of chemicals. Accordingly, Santos et al. (2018) significantly reduced the PP on the heavy crude oil with high asphaltene content using gas condensates and turpentine. Moreover, the heavy crude oil was found flowing even at -36°C, which is desirable for the flow assurance in the deepwater region.

The applications of both light ends and organic solvents for heavy crude oils have revealed rather promising outcomes. Considering the cost estimation, the light ends are favored over the polymeric WIs and PPDs because they can be retrieved during the distillation of crude oils. However, the method of using organic solvents is only recommended if there are inexpensive light ends and solvents with substantial amount in the oil field.

Gemini Surfactant

Gemini surfactant (GS) is considered as the novel surfactant for wax inhibition. The surfactant can reduce the growth of wax crystals in diesel oils, but its capabilities in waxy crude oils and heavy crude oils are only recently explored (Maithufi et al., 2010; Ahmed et al., 2017; Sahai et al., 2018). GS contains more than one ionic or polar hydrophilic heads and hydrophobic hydrocarbon tails, which are chemically bonded by a spacer. With that, GS is able to perform more efficiently than the other conventional surfactants. Its enhanced surface properties (to decrease the surface tension) and lower critical micelle concentration (CMC) have gained growing interest among academicians and industrial practitioners (Kamal, 2016).

Accordingly, Ahmed et al. (2017) posited that the length of alkyl chain played a crucial factor in affecting the depression of PP. In particular, the relationships of the surface properties, especially the interfacial tension (IFT) of the GS, the side chain length, and their efficiency in the depression of PP, were evaluated. Under similar conditions, the depression of PP seemed to correlate with the value of CMC, free energy of micellization, and energy adsorption. The negative value for the energy adsorption, which denotes maximum adsorption of surfactant molecules on the surface of growing wax crystals, impedes the formation of an interlocking network of waxes in the crude oils. Similar to the polymeric WIs, the longer the gemini long-chain esters, the higher the reduction of PP and surface tension, which reaffirmed the theoretical similarity in the inhibition mechanisms of surfactants and copolymers based on the chain length. Surfactant with the longest chain ester (C_{18}) in the study adsorbed to the wax crystals and subsequently altered their morphology. Thus, tiny isotropic crystals were formed through the co-crystallization process, which subsequently improved the flowability.

Meanwhile, Sahai et al. (2018) found that the combination of GS and toluene did significantly reduce the viscosity of bituminous crude. Maithufi et al. (2010) also demonstrated that the polymeric WIs improved the performance of GS with the inhibition of wax crystallization in diesel oils. In fact, these experiments on diesel oils addressed the flowability issue of diesel in the car engine, which is particularly beneficial for those in cold countries. More specifically, the flowability is attainable through the interaction of the wax crystals with the self-assembled structures (or micelles), which leads to the growth of one-dimensional aggregates by preventing the growth of the adsorbed or co-crystallized wax crystals (Maithufi et al., 2010). If the micelles are unable to interact with the wax crystals, they are likely to agglomerate without hindrance; thus, resulting to flowability issue with the sedimentation in the storage tank or pipelines.

Conventional Surfactant

The conventional surfactant is also known as the wax dispersant, which typically includes alkyl sulfonates and fatty amine ethoxylates (Kelland, 2014). Accordingly, with the presence of water, these dispersants either function as the deposition inhibitor of waxes or the growth inhibitor of wax crystals, which water-wet and disperse these wax particles to a certain size that is small enough to be carried in the oil stream; thus, preventing these wax particles from uniting and depositing in the production lines (Figure 5) (Al-Yaari, 2011). The wax dispersant was found to successfully prevent the deposition of waxes in the New Mexico field, while other applications involving WIs and PPDs, such as EVA, were found unsuccessful (McClaflin & Whitfill, 1984). Basically, the adsorption of wax dispersant molecules to the growing wax crystals impedes the agglomeration of wax crystals. The wettability of the surface of the pipe wall is enhanced, which establishes

unfavorable circumstance for the wax crystals to deposit or adhere to (Kelland, 2014; Zhang et al., 2014; Lim et al., 2018). Apart from that, the wax dispersant prevents the deposition of wax crystals with the formation of oil-water emulsion. The deposited wax in the presence of emulsion was found softer with lower average molecular weight, compared to the untreated deposited wax. Meanwhile, the polymeric WIs were found to produce harder deposited wax with higher average molecular weight, compared to the untreated deposited wax (Kelland, 2014).

Ridzuan et al. (2016) explored diethanolamine (DEA) (water-soluble wax dispersant) as well as other wax deposition inhibitors, which revealed the ineffectiveness of a single application of DEA. Marie et al. (2004) demonstrated high efficiency of wax dispersants coupled with EVA, compared to the single application of EVA or wax dispersant. The polymeric WIs aggregate and improve the flowability of crude oils whereas the wax dispersants reduce the size of wax crystals and improve the stability of the suspended wax crystals in the bulk fluid. The EVA alone was found to reduce the size of wax crystals to 20 μm with the deposition of harder wax, but with the addition of wax dispersant, the size of wax crystals was reduced to 5 μm (El-Gamal et al., 1998). Thus, different wax dispersants are often mixed with the polymeric WIs for enhanced performance. The wax dispersants, on its own, may experience limited success in the field (Kelland, 2014).
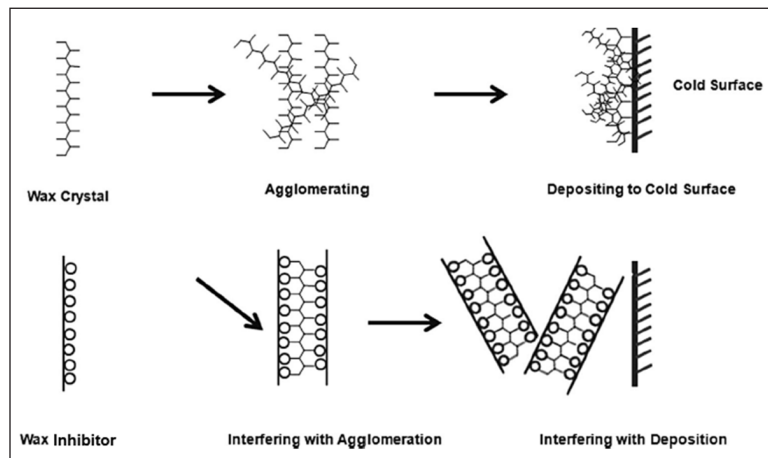

Figure 5. Schematic presentation of the influence of wax inhibitor on the wax deposition (*Source*: Al-Yaari, 2011) Copyright 2011 by the Society of Petroleum Engineers. Reprinted with permission.

Non-ionic Surfactant

New non-ionic surfactants are recently synthesized and considered as PPDs (Khidr et al., 2015a; 2015b). These surfactants appear in the form of viscous sticky liquid, which possesses extra surface-active properties and acts as a stronger emulsifier. Besides that,

they do not ionize in the aqueous solution due to the presence of hydrophilic groups, such as alcohol, phenol, ether, and ester. When these surfactants are in the water of higher temperature, they reveal the following characteristics: (1) they become less soluble, (2) they produce significantly lesser foam, and (3) they are environmentally friendly in removing oily and natural dirt, compared to those of anionic surfactants. The non-ionic surfactants function well in the reservoir temperature and are deemed effective in brines. Additionally, they form less viscous emulsions, which are easier to break in the refinery (Kelland, 2014). Considering all these characteristics, the non-ionic surfactants are highly considered.

Prior studies (Khidr & Mahmoud, 2007; Khidr et al., 2015b) explored several non-ionic ethoxylated surfactants, which revealed similar mechanism between surfactants and polymeric WIs of altering the morphology of wax crystals through co-crystallization that impedes the formation of tri-dimensional structure of wax. The addition of non-ionic surfactants assists in transporting the viscous crude oil in oil and water mixture of low viscosity, which is relatively stable oil in water (O/W) emulsion (Ahmed et al., 1999). Khidr et al. (2015b) selected the non-ionic ethoxylated surfactants with different chain lengths instead, which demonstrated that the increase of alkyl chain length (C_{16}) compared to C_{14} exhibited the most improved interaction between the surfactant and the paraffin fuel oil. Thus, Khidr et al. (2015b) postulated that the occurrence of co-crystallization between the surfactant and the paraffin modifies these crystals. Furthermore, the adsorption of the tested non-ionic surfactants with the increasing hydrophobic chain length (from C_{14} to C_{16}) demonstrated improved effectiveness, which is in line with the literature on GS (Ahmed et al., 2017).

Natural Surfactant

The bio-based surfactants and natural surfactants are also widely studied as PPDs in the petroleum flow assurance chemistry (Okoliegbe & Agarry, 2012). In comparison to the classical surfactants, the natural surfactants possess the following strengths: (1) lower toxicity; (2) biodegradable; (3) wide structural variety; (4) synthesized from inexpensive renewable materials; (5) stable in wide range of pH (Oguntimein et al., 1993). Kumar et al. (2017) discovered that *Sapindus mukorossi*, as a natural surfactant, significantly reduced the viscosity by 80% when it was used as PPD on the heavy crude oil. Furthermore, another type of bio-surfactant, which is generated from *Halomonas xianhensis* bacteria, was found to reduce the PP up to 24°C (El-Sheshtawy & Khidr, 2016). Besides that, the bio-based drag-reducing surfactant also successfully depressed the viscosity up to 70% (Wang et al., 2016).

In other recent studies, the synthesis of polyamine amide from canola oil, as PPD, was found useful for the depression of PP in crude oil. Specifically, the PP was reduced to 10°C with the concentration of only 0.05–0.10% (Chen et al., 2016). Meanwhile, Akinyemi et

al. (2016) explored the application of vegetable oils, such as jatropha, rubber, and castor, on the flowability of waxy crude oil, which revealed the capability of these vegetable oils to depress the PP and the viscosity of waxy crude oil appreciably within the dosage of 0.1–0.3 vol%.

In general, the surfactant can be an excellent flow improver in the crude oil due to the promising flowability improvement. The wax inhibition can be achieved by either water-wetting the surface of production facilities (which reduces the tendency of wax particles to adhere) or adding the surfactant in the crude oil (which reduces the entanglements of long-chain hydrocarbons and eventually forms a thin film over the wax particles); thus, preventing them from agglomerating to larger wax crystals (Kumar et al., 2017).

In addition, the increase in the concentration of surfactant was found to significantly reduce the IFT of crude oil (Ahn et al., 2005). The presence of surfactant in the waxy crude oil enables the formation of stable O/W micro-emulsion, which decreases the IFT and modifies these wax crystals into a needle-like structure. The pumping ability of waxy crude oil was reportedly enhanced with the formation of O/W emulsion and appreciable PP reduction (Kumar & Mahto, 2016).

CHALLENGES OF USING WAX INHIBITORS AND POUR POINT DEPRESSANTS

The applications of WIs and PPDs in waxy crude oils have received growing interest especially in those countries that encounter issues pertaining to the production of waxy oils, such as China, India, and Egypt. Table 2 summarizes the applications of WIs and PPDs for crude oils in these countries. The WIs and PPDs ultimately serve to improve the flowability by reducing the tendency of wax formation. In fact, the applications of WIs have significantly improved the economy with the flow assurance process in waxy oil fields by optimizing the performance of WIs. Nonetheless, these methods have certain economic and technical drawbacks. Even the oldest and the most preferred flow improving technique (light ends dilution) over the past few decades also has limitations despite facilitating the downstream operations (such as dehydration and desalting). Typically, these drawbacks can be observed in the case of high volume of light ends for dilution in order to attain optimum viscosity.

Most WIs and PPDs contain a non-polar moiety and a polar moiety. The non-polar moiety is also known as the long alkyl chain, which co-crystallizes with the alkane chain in paraffin wax, while the polar moiety takes charge of altering the morphology of these wax crystals. Based on the literature, higher number of carbon chain length and molecular weight of polymeric WIs are usually preferred to effectively inhibit the formation of wax

crystals due to the nature of high carbon number of alkane chain in crude oils. These advantages in wax inhibition turn into drawbacks in the downstream refinery as high molecular weight and thermos stability of WIs and PPDs, such as EVA polymers and comb-type polymers, experience difficulty to decompose in the refinery process (Gu et al., 2018). Thus, it is necessary to utilize lighter and smaller molecular compounds that exhibit similar performance to these polymeric WIs. Expectedly, inexpensive and environmental friendly WIs are preferred, which explains the recommendation of applying the bio-surfactants that are synthesized from plants. After all, these bio-surfactants are non-toxic in nature; have lower cost of extraction; are able to recover in the refining process.

Apart from the drawbacks of polymeric WIs in nature, the selection of suitable WIs for different oil fields is complex due to certain factors, such as the properties of inhibitors, the temperature and location of field, the original properties of crude oil, environmental concerns, economic feasibility, and the accuracy of lab findings. These factors govern the selection of a suitable PPD, which is strictly based on a case-by-case basis. In addition, the mechanisms of wax inhibition remain controversial due to the significant uncertainties involved in the interactions between the PPDs and these crude oils.

PARAMETERS GOVERNING THE SELECTION OF WAX INHIBITORS AND POUR POINT DEPRESSANTS

The design and the selection of suitable WI for specific crude oil are imperative to ensure long-term flow assurance. Fundamentally, heavy crude oils or waxy crude oils are complex in nature with wide range of hydrocarbons. Among these components, there are high molecular components that are primarily responsible for the poor fluidity in the production pipelines, such as saturates, asphaltenes, resins, aromatics, and paraffin waxes (de Souza Mendes & Thompson, 2012). The composition of hydrocarbons is the primary factor that governs the WAT and the PP of crude oils, subjected to the location of the oil field (El-Ghazawy et al., 2014; Ganeeva et al., 2016). Table 4 summarizes the composition of hydrocarbons of different oils. Additionally, not all WIs are suitable for all crude oils; thus, these characterizations are expected to assist researchers and industrial practitioners to grasp the nature of these crude oils and assure higher accuracy in the selection of suitable WI. Prior to the selection of WI, it is necessary to analyze the carbon length and the molecular weight of both long-chain saturated paraffin and selected WIs, considering that most polymeric WIs emphasize on their compatibility with these paraffin chain.

Table 4
Properties of different crude oils and their wax inhibitors

Crude oil	PP (°C)	Wax (wt %)	Asphaltene (wt %)	WI/PPD	References
Indian	42	11	6.50	Non-ionic Phenyl-Polyethylene Glycol surfactant	Kumar & Mahto (2016)
Malaysian	3	20	12.2	Ethylene Vinyl Acetate copolymers	Ridzuan et al. (2015)
Russian	21	19	1.28	Alkyl Acrylates-dodecylammonium Acrylate-dodecylammonium Sulfate	Litvinets et al. (2016)
Nigerian	27	35	N/A	Ethylene Vinyl Acetate copolymers	Oyekunle et al. (2017)
China	19	16	1.00	Polyoctadecyl Acrylate nanocomposites	Yao et al. (2016)
Egyptian	24	12	1.32	Polyalkyl Linoleate–co–succinic Anhydride	Soliman et al. (2018)
Egyptian	24	12	2.56	Styrene Maleic Anhydride copolymers-Aniline-Triethanolamine with Oleic acid blend	Al-Sabagh et al. (2017)
Egyptian	27	8	N/A	Modified Maleic anhydride-co-octadecane copolymers	El-Ghazawy et al. (2014)
Iranian	8	5	7.80	Ethylene Vinyl Acetate copolymers	Taraneh et al. (2008)

Note: *N/A denotes not available.

CONCLUSION

It is imperative to grasp how WIs and PPDs, even in small dosage, serve as an effective preventive measure in the transportation pipelines, considering the critical flow assurance problems that are caused by the paraffin waxes. This paper provides an overview on the major mechanisms of these WIs and PPDs in delaying the formation of wax crystals as well as their recent applications. The mechanisms of these WIs are largely similar, which are governed by various factors, such as the composition of crude oil, the structure of WIs, the length of alkyl side chains, the average molecular weight, and the carbon number of alkane chain in the crude oil. The parameters heavily depend on one another to achieve optimum co-crystallization and surface adsorption for these wax crystals. In this regard, the most

common mechanism is the co-crystallization, which highly emphasizes on the compatibility of the length of alkyl side chain to increase the interaction and solubility of WI in the structure of paraffin wax. Despite the documented effectiveness of these polymeric WIs across different oilfields at the global scale, these polymeric WIs have several significant limitations, such as their high molecular weight (that impedes the decomposition in the refinery), the deposition of harder wax in the production pipelines, and the uneconomical cost of polymeric WIs. Meanwhile, it is imperative to critically explore the selectivity of these polymers WIs that is highly dependent on the nature of crude oil. Considering that, it is recommended to seek for cleaner and universal inhibitor for waxy crude oils with small molecules. Additionally, the use of surfactants should be critically explored in the laboratory research or field application settings. These surfactants possess similar co-crystallization ability and the emulsifying ability with the presence of water to form O/W emulsion, which ease the pigging operation. Besides that, their wax dispersion ability places these surfactants as a desirable WI compared to the conventional polymeric WI. Most importantly, certain non-toxic bio-surfactants have lower cost of extraction with the ability to recover in the refining process, which leads to a greener and more economical flow assurance industry. Apart from that, it is recommended for future research to further assess the development of surfactant-polymer hybrid despite the proven results of enhanced performance in prior studies. Moreover, the surfactant nano-hybrids were found to be inadequately explored, which should be comprehensively addressed in the future research, as well.

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