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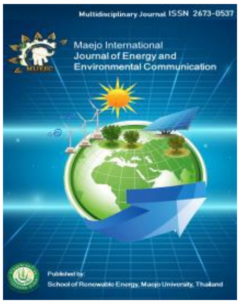

ARTICLE

Paraffin wax deposition and its remediation methods on crude oil pipelines: A systematic review

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ABSTRACT

Due to low-temperature circumstances, precipitation and paraffin wax deposition in manufacturing pipes and transportation tubes from offshore to onshore are significant challenges in the oil and gas sector. It may cause a reduction in output, a shutdown, pipeline blockage, and increased fluid viscosity. The most often used method for resolving this problem is to inject a wax inhibitor into the channel. Most current studies about paraffin wax are disseminated in literary works or exist as tacit knowledge in professional crania. This review research aims to exchange information and fulfil the deficits caused by providing a complete overview of the chemistry of paraffin wax precipitation and accumulation and causes, processes, and detection. It also discusses the overall impacts of paraffin wax deposition, how to deal with it, and several cleaning options. It also includes a conclusion and beneficial tips.

1. Introduction

Currently, every nation on the planet is attempting to get energy. Crude oil is the world's largest energy needs supplier, accounting for 37% of global energy supply when evaluated toward other kinds of energy. Until the end of the twentieth century, the primary commercial source of this energy was hydrocarbon (As' ad et al., 2015; Dewangan and Yadav, 2017; Yang et al., 2013). Crude oils are complex hydrocarbon combinations of polar and non-polar n-alkanes with carbon chain lengths ranging from C_{17} to C_{36}. Crude oil properties vary depending on the substance, such as saturated, aromatic, resins, and asphaltene (Elganidi et al.Elarbe et al.Ridzuan et al., 2021). Aromatic and paraffinic hydrocarbon molecules are found in crude oils, and they include varying quantities of carbon, hydrogen, sulfur, oxygen, nitrogen, and minor amounts of metals, including iron, copper, nickel, and vanadium (Adebiyi, 2020; Akmaz et al., 2011; Chandra et al., 2013; Varjani et al., 2015).

Light crude oil (Brent), medium, heavy, and extra-thick crude oils are classed based on the proportionate amounts of heavy molecular weight components contained in crude oils (Ekaputra et al., 2014; Varjani, 2014). Saturates such as (paraffin/wax), aromatics, resins, and asphaltenes are added to the heavy main components of crude oil (SARA) (Akmaz et al., 2011; Alcazar-

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Vara et al., 2012; Chandra et al., 2013; Speight, 2014; Varjani, 2017). As a result, its intricate nature poses many challenges in manufacture, storage, transportation, and processing. According to the composition of crude oil, which varies with location and age of an oil field, as well as the depth of an oil well, this is the most general approach to identify the chemical components of crude oil (Varjani, 2014; Varjani, 2017), because some fields produce heavy crude oil, which has more complex hydrocarbon compounds and metal concentrations than light crude oils. As a result, in this state of things treating heavy crude oils is far more complicated than treating lighter crude oils (Elarbe et al., Elganidi et al., Ridzuan et al., Abdullah et al., 2021).

API Gravity is the quantitative scale for this rating (American Petroleum Institute). API gravity between 35 and 42 indicates light crude oil from Brent, while API gravity between 22.3 and 32 indicates medium crude oil. Heavy crude oils possess API gravity values of 10 22.3, and extra heavy crude oils have API gravity values of less than 10 (Anisuzzaman et al., 2018; Souas et al., 2020). Lighter crude oils contain low paraffin molecular mass, low asphaltene contents, and viscosity values ranging from 1 cP to less than 100 cP Vladimir et al. (2020) analyzed 22 crude oil samples from various global oil resources, including 9 samples of light crude oil at 25 ºC with a broad range of API gravity values (32.6–42.0◦). The results revealed that samples of light crude oils had low viscosities ranging between 3.1 cP and 58.5 cP (Elarbe et al. Elganidi et al. Ridzuan et al. Abdullah et al., 2021; Volkov et al., 2020).

Crude oil qualities are crucial in production, transportation, refining, and commodity storage. Consequently, it is vital to understand and anticipate the performance of waxy crude oil and its wax to avoid multiple pipeline plugging and clogging concerns. Several industrial observations have shown the frequency of wax generation during the production of crude oil (Atta et al., 2015; El-Dalatony et al., 2019). Table 1 highlights the properties and composition of waxy crude oils from throughout the world, where wax quality, wax content, API gravity, WAT, and pour point was shown to have a significant correlation in most nations.

The temperature at which wax crystal formation begins is referred to as WAT. WAT is also known as cloud point since the formation of wax causes the fluid to become cloudy (Ridzuan et al., 2016a). ASTM D2500, cross-polar microscopy (CPM), light transmission (LT), differential scanning calorimetry (DSC), and viscometry were among the techniques frequently employed in the industry for evaluating WAT in the laboratory. On the other hand, the pour point is the lowest temperature at which oils flow freely under specified test conditions. The ASTM D97 standard test procedure was used to determine it. It was utilized as a standard for comparing the findings of DSC and CPM studies in this study (Coto et al., 2014).

The study of saturates, aromatics, resins, and asphaltenes (SARA) has recently been employed to describe crude oils. On the other hand, the industry has used hydrocarbon group type analysis to split this complicated mixture into individual components. SARA separation is one of the most extensively used group type analyses, and it is often used to classify crude oil into four primary chemical groups based on polarity and solubility differences. Some models have utilized SARA data with other compositional analyses to predict wax phase behavior. In general, crude oil separation may be accomplished by column chromatography, thin-layer chromatography (TLC-FID), and high-pressure liquid chromatography (HPLC) (Rezaee et al., 2020).

a) Saturates (Aliphatic)

Saturates are hydrocarbons that lack double bonds and account for most crude oil ingredients that are non-polar molecules with just a single bond (Varjani, 2017). They are classified into two types based on their chemical structures: alkanes (paraffin) and cycloalkanes. n-Alkanes are classified into four molecular weight groups: (a) gaseous alkanes, (b) lower molecular weight aliphatic hydrocarbons (C_8-C_{16}), (c) medium molecular weight aliphatic hydrocarbons (C_{17}–C_{28}), and (d) high molecular weight aliphatic hydrocarbons ($>C_{28}$) (Abbasian et al., 2015). Saturates can be separated using n-heptane, n-hexane and pentane.

b) Aromatics

Aromatic hydrocarbons are found naturally in crude oil and coal, which are non-polar molecules typically immiscible with water. Aromatic hydrocarbons include one or more aromatic rings that are often replaced with various alkyl groups. They are classified as monocyclic aromatic hydrocarbons (MAHs), which include benzene, toluene, ethylbenzene, and xylenes, and polycyclic aromatic hydrocarbons (PAHs), which have more than one benzene ring and are composed of two or three cyclic rings (Costa et al., 2012; Meckenstock et al., 2016). Toluene is often employed in open column chromatography to elute the aromatic fraction from crude oil (Santos et al., 2020).

c) Resin

Resin and asphaltenes include non-hydrocarbon polar molecules compared to saturated and aromatic fractions. The resin and asphaltene fractions are the most complicated because of the prevalence of heteroatoms such as nitrogen, sulfur, and oxygen (Varjani, 2017). Each component has a distinct chemical behavior that influences biodegradability (Costa et al., 2012). The resin fraction in crude oils contains the most polar chemicals, which may comprise hydrogen-rich and hydrogen-deficient molecules, i.e., saturated and aromatic compounds (Santos et al., 2018). Resins are soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane (Chandra et al., 2013). The resin fraction of crude oil can be eluted from a chromatographic column by dissolution in toluene/methanol or toluene/acetone solutions (Santos et al., 2020).

d) Asphaltenes

Asphaltenes, like resins, are made up of a variety of polar functional chemicals. Nevertheless, they are complicated molecules with a dark brown hue and a considerable size scattered among saturates and aromatics (Chandra et al., 2013). They dissolve in light aromatic hydrocarbons such as benzene and toluene (Parra-Barraza et al., 2003). Asphaltenes are polycyclic chemicals with a high molecular weight. With the increasing carbon number of n-alkane precipitants, the molecular weight, polarity, and aromaticity of precipitated asphaltene typically rise (Chandra et al., 2013; Varjani, 2017).

2. Wax Deposition

The oil and gas sector has a severe operational hurdle in the form of wax deposition. Wax accumulation has been described as an issue that provides many complex issues while being generated, transported, and stored as early as 1928. Wax accumulation problems occur in various locations throughout the petroleum supply chain, including flow lines, surface equipment, topside facilities, and downstream refineries. It may also happen in suitable tubing (Theyab, MA and S Yahya, 2018). The wax deposition was a prevalent hazard during petroleum production on land or onshore supplies in the early to mid-1990s.

It was stated in 1969 that the cost of wax control in domestic US manufacture was $4.5–$5 million per year. Because these resources are readily accessed and controlled, the problem of onshore wax deposition may be addressed with relatively simple techniques such as improving operating parameters (pipeline size, pressure, etc.). Heating the conduit or mechanical removal of the wax layer was also utilized occasionally. The problem of wax deposition became increasingly difficult in the late twentieth century, as petroleum fluids were transported from onshore resources to offshore reservoirs all over the world, including the Gulf of Mexico, the North Slope, the North Sea, North Africa, Northeast Asia, Southern Asia, and South America. Figure 1 depicts a schematic of the late-twentieth-century shift from onshore to offshore petroleum production, such as oil deposits in North America, South America, Asia, Africa, and Europe, to calculate the cost of suitable remediation methods for wax deposition in the subsea pipeline and avoid blockage (Theyab, MA and SY Yahya, 2018). Consequently, wax accumulation has become a global problem for the oil and gas industry. Figure 2 depicts the worldwide distribution of documented wax deposition problems.

Before arriving at onshore processing facilities, offshore crude oil is often carried by long-distance pipelines that reach tens to hundreds of kilometres. The oil typically exits the reservoir at approximately 160°F and is substantially cooled as it goes down the pipelines on the ocean floor, where the surface temperature is about 40°F. The temperature difference (160°F to 40°F) between the oil in the pipeline and the surrounding water on the ocean floor serves as a driving force in cooling the oil in the pipeline. The waxy elements of the oil may precipitate out and form deposits on the pipe wall when the temperature of the oil decreases (Chi et al., 2019).

Once the wax deposition issue has been detected, if it is not addressed, it may lead to a decrease in pipe flow area, an increase in fluid viscosity, and a loss of output due to unmanageable pipe obstruction. The pipeline portion was deposited paraffin, which significantly reduced the effective flow cross-section. The crystallization process occurs when the temperature of the crude oil falls below the Wax Appearance Temperature (WAT) (Alnaimat and Ziauddin, 2020). An example of a pipeline portion impacted by deposited paraffin, as described by (Alnaimat and Ziauddin, 2020), is shown in Figure 3.

Figure 1 A diagram depicting the shift from onshore to offshore petroleum production in the late twentieth century.

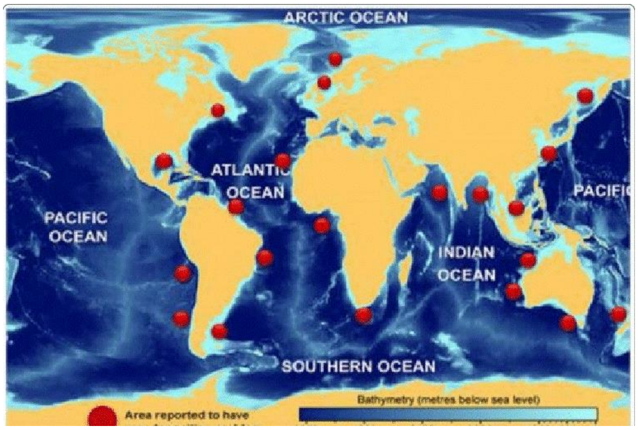

Figure 2 Summary of areas worldwide where wax deposition difficulties have been identified (Theyab, MA and SY Yahya, 2018).

In the worst-case, the deposited wax causes a complete blockage in the pipeline, requiring the renewal of the blocked section of the pipeline. The projected cost of this replacement and downtime is $30,000,000 per incidence. One of the most serious incidents occurred at the Staffa field in the North Sea, UK. The offshore platform was so severely damaged by wax deposition that it was abandoned at the cost of $100,000,000. (Pham et al., 2017). According to studies, solid accumulation in the interior walls of production and transportation pipes and on the equipment surface was the most typical cause of the flow assurance problem (Subramanie et al., 2020).

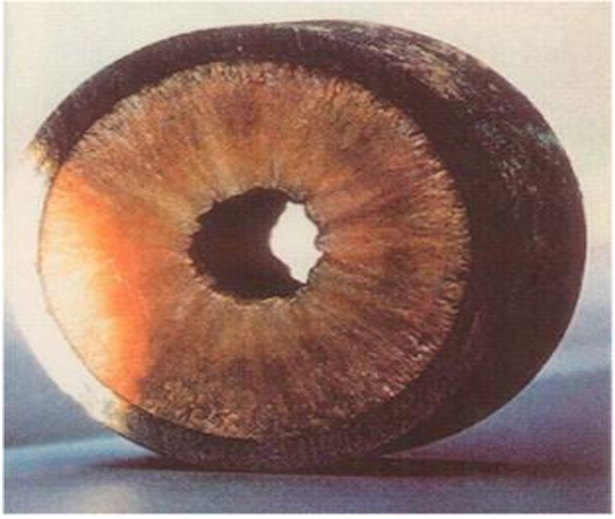

Figure 3 A Section of the pipeline affected by deposited paraffin. Source (Alnaimat and Ziauddin, 2020; Venkatesan et al., 2005).

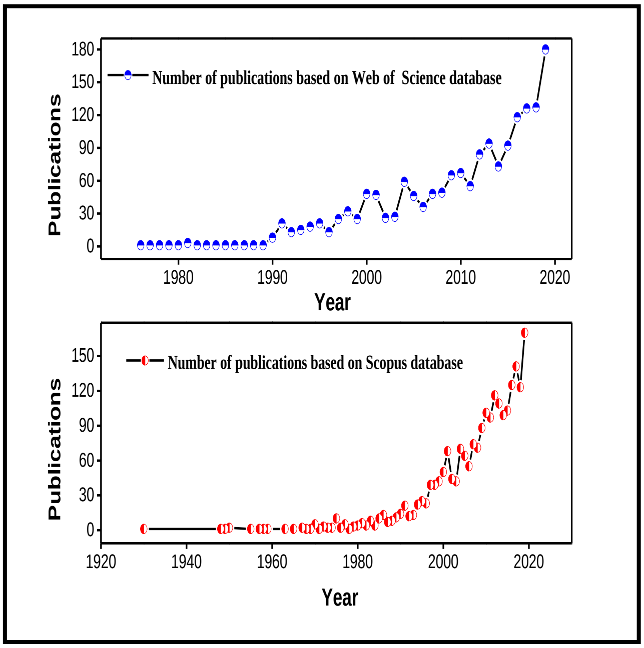

Figure 4 Data from the Scopus and Web of Science databases were used to compile a list of journal articles on "Wax Deposition." (Elganidi et al.Elarbe et al.Ridzuan et al., 2021).

As seen in Figure 4, wax deposition research has garnered a great deal of attention throughout the years. The issue of wax deposition was first mentioned in 1928, and awareness has grown considerably since the 1980s. Consequently, oil firms have spent a large amount of OPEX and CAPEX on mitigation and preventive measures to guarantee crude oil flow (Chi et al., 2019; Elganidi et al.Elarbe et al.Ridzuan et al., 2021).

3. Paraffin Wax

Paraffin wax is a complex mixture of high molecular weight alkanes with straight, branched, and cyclic chains at room temperature (Olajire, 2021). Figure 5 shows the structure of the primary paraffin wax. Paraffin waxes are classified into macrocrystalline waxes and microcrystalline waxes (Adebiyi, 2020; Anisuzzaman et al., 2018). Macro-crystalline waxes are primarily low molecular weight n alkanes (C_{18}-C_{30}), having an evaporation point of 40–60 °C, while paraffin waxes have a straight carbon chain length. Macrocrystalline waxes precipitate to form needle-like or platelet-like crystals at low temperatures. Microcrystalline waxes are made up of iso-alkanes, and cyclo-alkanes with high molecular weight n-alkanes in the C_{30}–C_{60} range and a considerable amount of iso-paraffins and naphthenes and have considerably greater melting point values (above 60–90 °C). Micro-crystalline waxes may mix with far more oil than macro-crystalline waxes. Because of the enormous number of isomer permutations, micro-crystalline waxes precipitate to form tiny crystals and several amorphous particles without a distinct crystallization regime (Li et al., 2018). In general, the molecular weight ranges of paraffinic and microcrystalline waxes are 350–600 and 300–2500, respectively. That percentage of paraffinic to microcrystalline waxes and oils varies depending on where the oils are sourced. However, more significant hydrocarbons with a high molecular weight (microcrystalline type) are often found in minimal amounts or missing in synthesized oils. This is the case because of their poor mobility and limited solubility in crude oil. Consequently, when the temperature and pressure vary, these elements stay in the container rocks or precipitate out in the drilling apparatus. Large molecular weight alkanes were found in high concentrations in solid sediments generated in well apparatus and pipelines (Ganeeva et al., 2016).

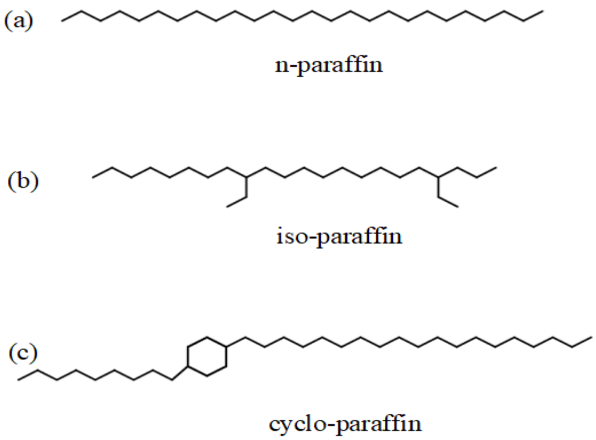

Figure 5 The structure of main paraffin wax: (a) straight, (b) branched, (c) cyclic.

The main cause of paraffin wax precipitation and deposition is its lower solubility due to temperature variations causing changes in the equilibrium state of the solution (Adebiyi, 2020). According to F.M. Adebiyi (Adebiyi, 2020), paraffin wax might precipitate from crude oil when equilibrium circumstances change slightly, resulting in a drop in paraffin wax solubility in crude oil. There have been researchers that have looked into the probable reasons for paraffin wax accumulation. Because all of the heat is released into the environment, the overall temperature falls underneath the melting point, causing the wax to crystallize and settle on the pipeline walls and reservoir (Anisuzzaman et al., 2018).

3.1. Theory of wax deposition

The production of wax crystals is the fundamental cause of crude oil's poor fluidity at low temperatures (Li et al., 2018). Creating a solid ordinate system from a chaotic phase is known as crystallisation. It is most common in thermodynamically unstable situations, the leading force for particle creation. A solute concentration triggers the formation of these wax particles (or, more correctly, its chemical potential) that exceeds its equilibrium or saturation value (Hao et al., 2019). When the temperature drops, the velocity of the molecules in crude oil slows because there is less energy to move about freely. This makes it simpler for the wax molecules to cluster, align, and eventually bind to one other, allowing them to attain a critical and stable size. The cluster of wax molecules is referred to as a nucleus (Anisuzzaman et al., 2018; Thota and Onyeanuna, 2016). The wax production process begins with a precipitate that serves as the nuclei for the crystallization process to commence. The crystallization process is divided into three significant steps: a. nucleation, (b) crystal formation, and (c) aggregation of wax crystal particles (Hao et al., 2019; Ragunathan et al., 2020).

Nucleation is a process that begins in the first step and leads to the production of microscopic solid aggregates. In essence, these atoms in the liquid started to join together and produce a crystal nucleus, and it is these nuclei. They are responsible for the supersaturation of paraffin waxes in the oil phase. Crystal growth is the second procedure. When the initial nucleation stage is complete, and the system temperature is kept low, wax molecules travel from the bulk to the nuclei and begin the wax crystal formation. Most wax crystals feature an orthorhombic lattice with zigzag patterns in each chain. Agglomeration is the third step. As the wax nucleus increases, many wax nuclei consolidate to produce wax crystal particles. The wax crystal particles then combine indefinitely to create a three-dimensional network. In general, wax precipitation may increase crude oil viscosity; however, wax attachment to the pipe wall does not occur (Ragunathan et al., 2020). The waxes crystallize in an interlocking network of thin plates, trapping the leftover oil in cage-like structures and clogging the pipeline. When the environment cools, exceptionally high supersaturation may form primarily at the cooling surfaces, resulting in a large number of tiny crystals. If such crystals are still not found, attracted by system stimulation and turbulent flow, They could remain to each other and a cold surface, resulting in the deposition. When deposition develops on the pipeline's surface, it works as heat retention for the system (Hao et al., 2019).

3.2. Typical problem of wax deposition

Wax accumulation in pipes manufacturing and transportation tubes from offshore to onshore is critical in the oil and gas industry due to low-temperature conditions. The production of wax may be both a downhole and a topside issue, obstructing the flow of hydrocarbon fluids as they cool (Kelland, 2014). The average temperature in the subsea field when transferring crude oil may be as minimal as 5 °C at the bottom. When the crude oil temperature falls below the wax appearance temperature, wax crystallizes and begins to form a 3D network structure (Elganidi et al., 2020; Ridzuan et al. SubramanieUyop, 2020; Yao et al., 2018). The wax's solubility varies with time, and the amount of accumulation rises, resulting in a decrease in the operational flow area or pipeline cross-section area. It might result in a complete pipe blockage, causing supplies to be disrupted (Chala et al., 2014; Junyi and Hasan, 2018).

Specific concerns induced by wax deposition, according to (Adebiyi, 2020; Kelland, 2016), included the following:

a) Reduced pipe internal diameter and final plugging of manufacturing tubing and surface piping
b) Increased crude oil viscosity, resulting in increased pumping pressure.
c) Formation of wax damage near the wellbore.
d) Phase separation causes changes in reservoir fluid composition and rheology as solid wax precipitates.
e) Issues with relatability due to wax gel strength.
f) Reduced operational efficiency and process disruptions due to production interruptions or shutdowns.
g) The significant pressure drops across the pipeline.
h) Removal of accumulated wax is expensive and technically challenging, particularly in deep-water pipes.
i) Deposits interfering with the functioning of valves and instruments pose a safety risk.
j) Problems linked with accumulated wax disposal.

Figure 6 Wax plug in wellbore on platform C in the North Sea (Zhu et al., 2008).

Wax accumulations may clog a pipeline. In the worst-case situation, the output must be suspended to repair the blocked part of the pipeline, as seen in Figure 6.

The dark substance is wax, which has blocked a production line in China. There is no other option except to cut the pipe, which comes at a high cost in terms of lost output, creating a new line linked to the well, and the difficulties associated with resuming production (Handal, 2008).

4. Mechanism of Wax Deposition

The simulation of wax deposition requires an understanding of the mechanisms essential for the transfer of the waxy residue in liquid or solid phases from most of the fluid to the wall of the pipe. Many investigations have been conducted to elucidate the mechanics of wax deposition (El-Dalatony et al., 2019; Leporini et al., 2019; Ragunathan et al., 2020; Theyab, M, 2018). It is critical to better grasp the wax deposition process to manage and control any wax deposition issues that may arise. Several processes, including molecular diffusion, Brownian diffusion, shear dispersion, and gravity settling, have been suggested to explain the production of wax deposits on pipeline walls. However, the processes have not been entirely validated, even though molecular diffusion and stress scattering are assumed to be the primary wax deposition mechanisms (Olajire, 2021).

4.1. Molecular diffusion

Wax transport in pipes is affected by the central temperature and accumulation variations at the laminar sublayer abutting the internal pipe surface. At high-temperature heat flow parameters typically of subsea stream line arrangement, molecular diffusion has been the dominant mechanism. The cooling of a subsea pipeline's pipe wall below WAT generates a temperature variation throughout the laminar sub-layer, and the soluble wax crystallizes and precipitates out from the petroleum. Because wax fluidity declines with temperature, a radial concentration gradient of dissolved wax forms between the bulk solution and the internal pipe surface, with the mass transfer transports soluble wax component from the bulk medium with a higher ratio of wax to the internal pipe surface with a lower concentration of wax (Azevedo and Teixeira, 2003; Olajire, 2021; Theyab. Et al., 2018). As seen in Figure 7, captured oil in the wax layer increases the diffusion of wax molecules into the gel deposit while also promoting counter-diffusion of oil out of the gel layer. A certain proportion of hydrocarbons with carbon values more prominent than a certain threshold (the critical carbon value) precipitate out of the oil as solid crystals, producing a gel with the remaining hydrocarbons retained in the gel network (Theyab and Diaz, 2016). The proportion of molecules with carbon numbers greater than the critical carbon value increases in the gel layer, whereas the ratio of molecules with carbon numbers less than the critical carbon value decreases. The diffusion and counter-diffusion cause the gel layer to hard increase the size of the deposit and the amount of wax in the gel layer; this is known as ageing. It is impossible to overestimate the importance of molecular diffusion in the ageing and hardening of wax gel layers (Theyab, M, 2018).

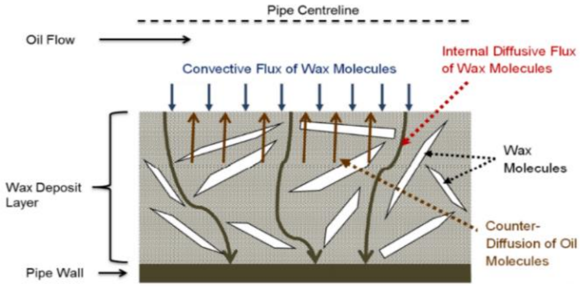

Figure 7 Diagram shows the diffusion of wax molecules to produce the wax deposit surface (Theyab, M, 2018).

As seen in Figure 8, molecular diffusion occurs in four phases. The four steps as disclosed by Huang are as follows: (Huang et al., 2016; Leporini et al., 2019).

- Stage 1: Dissolved wax molecule precipitation.
- Stage 2: The radial concentration gradient of dissolved waxy components is formed.
- Stage 3: Waxy components precipitate on the surface of an existing deposit.
- Stage 4: Internal paraffin molecule diffusion inside the deposited layer.

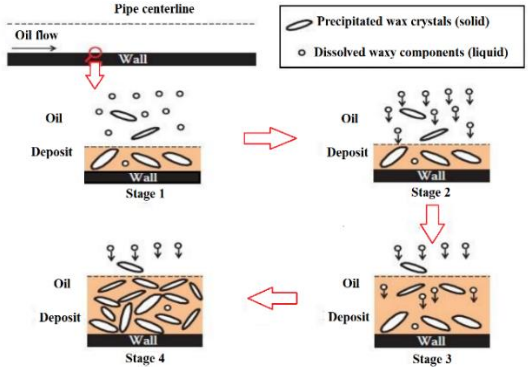

Figure 8 Molecular diffusion as a mechanism for wax deposition is shown in a diagram (Huang et al., 2016).

The first step is the precipitation of solubilized wax molecules, as seen in Figure 8. When the temperature of crude oil falls below WAT, the waxy components precipitate out and form wax crystals. As long as the temperature is under WAT, the waxy component precipitates in the crude oil and the pipeline wall. The wax precipitated in bulk oil flows through the pipeline with the crude oil, but the wax precipitated near pipeline walls creates a layer on the wall. The second stage is caused by the temperature difference between bulk crude oil and pipeline walls. Consequently, the degree of precipitation is often higher near the pipeline surface, resulting in a higher amount of waxy components in bulk oil and a radial concentration gradient. As a result, the waxy components migrate to the wall, as seen in Figure 8. The third stage is the precipitation of waxy components on a wall's layer, which results in the formation of a wax deposit. When a growing deposit layer develops, the oil zone's perimeter becomes the deposit's surface. As seen in Figure 8, the precipitation of the dissolved waxy components on the accumulation layer leads the wax deposit to increase further. Because the waxy crude oil continues to flow along the pipe, the diffusion of dissolved waxy components near the deposit is maintained. As shown in Figure 9, the last phase is the inner diffusion and precipitation of waxy components on the layer (stage 4). When dissolved waxy components do not create a deposited layer on the pipeline wall, internal diffusion occurs, increasing the wax percentage in the deposit. When waxy components precipitate, increasing the solid wax concentration, this process, also known as ageing, happens.

4.2. Shear dispersion

Wax deposition by shear dispersion is a method of moving solid particles in suspension across the stream. The size, relative density, and concentration of solid particles all influence their laminar movement (Azevedo and Teixeira, 2003). The particles prefer to move in the same direction and speed as the surrounding liquid. The particle speed is that of a streamline at its centre, as shown in Figure 9, and the particle spins with an angular velocity half that of the fluid shear rate. The particles' linear and angular velocities decrease as they approach a solid barrier. Because of fluid viscosity, spinning particles create a film of fluid to circulate near the particle. This spinning fluid area tugs on particles nearby. As a result, each particle in a stress field moves through and interacts with particles in slower or faster-moving streamlines. When just two particles are involved, far from a wall and at a deficient Reynolds number, these passing interactions cause massive transient displacements. The particles' routes are designed to bend around one another and return to their original streamline as they pass.

As a consequence, there is no net lateral displacement. However, if the particle concentration is high, there will be many multiparticle interactions. The effect of these multiparticle collisions is net lateral movement and particle dispersion (Theyab, M, 2018).

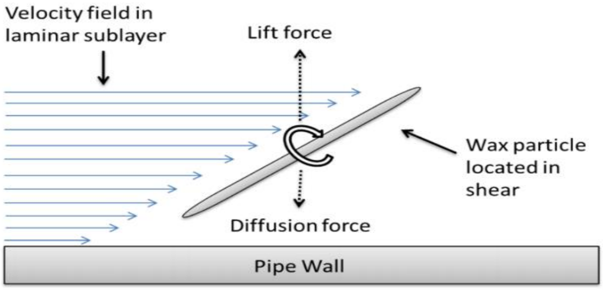

Figure 9 Long wax particle located in shear flow (Theyab, M, 2018).

4.3. Brownian diffusion

Certain parts of the oil flowing across the pipeline are likely colder than the cloud point. In this case, tiny waxy crystals precipitate from the solution and get suspended in the oil. Wax crystals in the oil strike with thermally disturbed oil molecules, causing the crystals to move in an unpredictable wiggling pattern. In the presence of a concentration gradient of solid crystals, there be net transit of waxy crystals towards the region of lower content (Olajire, 2021; Theyab, M, 2018). The Brownian diffusion coefficient of particles (crystals) characterizes this process.

4.3. Gravity settling

Waxy crystals that have precipitated are heavier than the surrounding liquid oil phase. As a result, if particles did not interact, they would settle in a gravitational field and end up at the bottom of pipelines or tanks. There would be a beginning rate of settling followed by a declining deposition rate for an initially homogenous mixture in a vessel, which would asymptotically approach zero at complete settling. As a result, it does not seem to be a viable method for wax deposition. Gravity settling is minor in a typical active system, such as that observed in oil and gas pipelines, since the postulated shear dispersion mechanism, or active fluid forces, promote precipitated wax particle dispersion, hence limiting gravity settling (Azevedo and Teixeira, 2003; Theyab, M, 2018).

According to (Kang et al., 2019a), Brownian diffusion and gravity settling are not included since their effects are minor compared to molecular diffusion, shear dispersion, and shear stripping reduction. Furthermore, the ageing process was not considered since it predominantly influences the hardness and concentration of wax deposits.

5. Factors Contribute to Wax Deposition

The wax deposition process in crude oil pipelines is influenced by thermal gradient, fluid velocity, experimental duration, pressure, and crude oil concentration.

5.1. Temperature differential

Once the temperature of crude oil when the temperature dropped just under the appearance temperature of the wax, wax was deposited on the pipeline wall. The thermal gradient causes an increase in wax among the bulk solution and the cold face of the wall. Consequently, temperature variation is one of the most significant critical variables affecting wax accumulation in crude oil pipelines (Elganidi et al. Elarbe et al. Ridzuan et al., 2021; Theyab, M, 2018). According to Kelechukwu et al. (2010). Wax deposition decreases as the temperature difference between the bulk solution and the pipeline wall increases. This was confirmed by Mahto and Kumar (2013), who discovered that as the temperature difference rose, wax deposition decreased. Furthermore, earlier research has revealed a similar association between the accumulation of wax and the temperature range between the pipeline surface and crude oil (Bott and Gudmundsson, 1977; Wang et al.Huang et al.Wang et al., 2015).

These results, however, contrasted what had previously been reported by those who discovered a rise of precipitated wax as the temperature difference rose (Kelechukwu et al., 2010; Mahto and Kumar, 2013).

This study's results confirmed prior research that looked at the drop in crude oil temperature as wax accumulation occurred, while the crude temperature was higher than the wax appearance temperature. To begin with, the rate of wax deposition on the pipeline wall is relatively high; but after a while, the velocity at which wax is accumulated drops, and the thickness of the wax layer grows. Furthermore, when the chilling rate increases, the wax accumulates in big and small crystals due to the number of crystallization sites. In wax accumulation, the amount and size of crystals created are regarded as significant parameters (Elganidi et al. Elarbe et al. Ridzuan et al., 2021).

5.2. Flow rate

According to earlier research, thirty tap water samples, the velocity of flow in the crude oil pipeline is an additional significant factor influencing wax accumulation (Kang et al., 2014). The bulk of existing research shows that as the flow rate rises, the thickness of the wax deposit decreases. However, this result may mislead field engineers, who believe that increasing the flow rate is always good in terms of wax deposition mitigation. The observed temperature rises as the flow rate increases. In the higher flow rate scenario, the shorter residence time is expected to reduce heat loss (Kang et al., 2019a).

According to experimental and quantitative modelling, research on wax deposition was carried out. It was discovered that increasing the flow rate increases the mass deposited up to a specific flow rate, known as the critical flow rate. A further increase in flow rate produces a drop in deposit mass over this critical point. The interpretation was that the deposition mass in turbulent flow reduces dramatically at high flow rates due to a sloughing action. His investigation discovered a significant Reynolds number of 2,700 (Swivedi et al., 2013).

Jennings and Weispfennig (2005) demonstrated the impact of deformation on wax accumulation was studied, and the findings reveal a reduction in precipitated wax. Cabanillas et al. (2007) revealed that when the fluid velocity in laminar flow increased, the layer of the precipitated wax decreased. Kelechukwu et al. (2010) discovered that raising the flow rate to turbulence reduces the quantity of wax deposited gradually. Swivedi et al. (2013) exposed that raising the shear stress reduces the thickness of the wax accumulation.

Mahto and Kumar (2013) observed a comparable pattern at a constant temperature gradient and time spent in residence. In laminar flow, wax precipitation increases as fluid velocity decrease due to the greater accessibility of the wax particles deposited on the surface. Consequently, the dominant in turbulent flow stages, tension propagation occurs, the precipitated wax diminishes steadily whenever the flow velocity shifts to turbulent flow, as indicated by Theyab, MA (2018). This is explained by viscous dragging, which rises as the liquid's speed increases and serves as a flow velocity limiting factor. The thickness of the wax precipitated layer is lowered due to the tremendous shear stress induced by the viscous drag.

(Jessen and Howell, 1958) discovered that the quantity of accumulation of wax changes concerning flow rate achieving its highest point quickly after converting to turbulent fluid and subsequently diminishes as turbulent flow increases. According to Creek et al. (1999), modern accumulation modelling techniques for turbulent and laminar flow show that the deposition rate reduces rather than increases with increasing flow rate. Nazar et al. (2005) reported that the quantity of accumulated wax rose as the velocity of the stream increased and continued unless the necessary stream velocity was reached. During the flow loop experiment, Panacharoensawad and Sarica (2013) discovered that wax deposition thickness was thicker at a high flow rate than at a low flow rate. However, (Kang et al., 2019b) suggested a rise in wax accumulation produced by a greater flow rate might be due to an excess of wax in the crude oil injected.

Therefore, as result of their cohesive solid qualities, the wax crystals may be concluded to attach to the pipeline wall. However, this generally fractures crystal wax into microscopic pieces, reducing wax deposition and, as a result, diminishing the crystal's adherence to the pipeline surface. On the other hand, wax crystals that attach at a fast flow rate are particularly stiff and closely linked because wax crystals may stick firmly to the pipe wall and are difficult to dislodge. Based on these findings, one might infer that most previous research has shown a decrease in wax density as the stream velocity increases, when laminar flow (Elganidi et al. Elarbe et al. Ridzuan et al., 2021).

5.3. Experimental time

The retention duration of crude oil in pipelines is a key factor determining wax deposition. The wax deposition steadily rises during the two-hour inspection, which might be attributable to the majority in terms of liquid paraffin in the oil accumulated on the pipeline's external face. Regardless of reduced quantity of paraffin in the crude, wax accumulation expands somewhat as the residence duration increases (Hammami and Raines, 1997; Kasumu, 2014). Furthermore, during 4 hours of testing, there was a slight increase in the mass of accumulated wax. Due to the bulk of the crude wax particles have collected on the pipeline surface (Kasumu, 2014). According to Kelechukwu et al. (2010), increasing the residency period increases wax accumulation at a stable level. On the other hand, Wax deposition persists until the amount of accumulated wax diminishes with extending the duration of residence.

Moreover, the more considerable temperature loss resulted as a consequence of the longer retention duration, and it caused the wax should be kept on the pipe surface. Mahto and Kumar (2013) reported that they discovered a similar tendency from their examination at a long retention time. The above results agree based on past research (Bott and Gudmundsson, 1977; Junyi and Hasan, 2018; Mahto and Kumar, 2013; Shahrabadi et al., 2013). With a steady supply of fresh oil, wax accumulation increases in the downstream sector of the petroleum sector. Furthermore, most studies used a closed-loop system because there isn't a constant flow of extra crude oil delivered by pipeline. As a result of the thermal insulation provided by the wax accumulation layers, the wax layers will decrease after a more extended residence period. Previous research found that the combination reached a thermal pseudo-steady state after 30 minutes (Elganidi et al.Elarbe et al.Ridzuan et al., 2021; Theyab, M, 2018).

5.4. Pressure

This is considerable evidence that crude oil is stored in containers and transferred through pipelines under high pressure, with surrounding pressure being critical (Aiyejina et al., 2011; Li et al., 2012). Few research examined the impact of high pressure on the flowability of crude oil due to the limitations of available measuring methodologies (Velusamy et al., 2017; Webb et al., 2014). Pressure lowers throughout crude oil extraction derived from the containers, letting aside light hydrocarbons. Kang et al. (2019a) discovered. It left a wax film on the interior wall of the pipeline, increasing surface harshness, reducing efficient radius, and increasing decrease of suction. The accumulation of wax on the pipeline's inside surface increases surface irregularity, reduces effective diameter, and increases pressure loss.

Furthermore, crude oil is often deposited in reservoirs or transferred under high pressure through pipes. In the case of a large oil leak, the ambient pressure is also more critical (Li et al., 2012; Magda et al., 2013). Due to the limits of current monitoring technologies, only a limited amount of research has been carried out on oil permeability at elevated pressure (Velusamy et al., 2017; Webb et al., 2014). According to previous studies, oils are persistent, and the components rest quickly during crude oil transit under high pressure. Furthermore, it demonstrates that high pressure causes high viscosity of lubricants and non-Newtonian behaviour (Mortazavi-Manesh and Shaw, 2016).

Similarly, the cold quality crude oils and the influence of chemical additions on wax accumulation, especially rheological and wax crystallizing properties, have also been studied thoroughly at atmospheric pressure (Li et al., 2011; Xu et al., 2013). Nonetheless, the influence of polymeric flow enhancers on crude oil flowability has seldom been studied below extreme stress settings. Polymeric components work as a wax adjuster or as a pour point depression (PPD) mix using crystallized wax at room temperature, interrupting the wax accumulation process by avoiding crystallized wax from becoming entangled in big agglomerations.

Most studies, however, assessed pressure as playing a minor influence in wax accumulation, notably for petroleum housed in barrels and expired oil (Lashkarbolooki et al., 2010; Valinejad and Nazar, 2013). On the other hand, the influence of pressure should not be underestimated since it helps to increase the solubility of wax in the oil, resulting in less wax deposition (Theyab, MA, 2018).

5.5. Crude oil structure

The execution Petroleum is a complex blend of homogenous organic components, including asphaltenes, aromatic resins, saturated hydrocarbons, and other hetero-functionalized substances, for example, oxygen, nitrogen, and sulphur (Chen et al., 2018). Furthermore, certain crude oil-derived compounds have been molecularly examined. Aromatic compounds include many weak polar heterogeneous molecules, for example, pentathiophene, dibenzothiophenes, and dibenzofurans. Resin fractions also include porphyrins and carboxylic acids with varying oxygen, nitrogen, and sulphur groups (Chen et al., 2018; Honse et al., 2012). However, several studies have demonstrated that the crude oil composition significantly influences the thickness and pour point lowering wax accumulation and the low-density proportion and paraffin in the petroleum (Valinejad and Nazar, 2013).

Consequently, it has been observed that the presence of water in the crude composition lowers wax deposition (Adeyanju and Oyekunle, 2019); mentioned that the light and heavy molecules may be separated in petroleum. Low-density particles are often involved in producing solid hydrates; meanwhile, big particles like iso-paraffins and linear alkanes undergo phase transitions to form macrocrystalline and microcrystalline solids (Theyab, M, 2018). As a result, the structure and shape of wax crystals are influenced by crude oil content.

Because waxy crude may form waxy crystals, transport crude oil due to a thick crystalline covering. In general, a petroleum sample has more than 5% wax, known as waxy oil, and research shows that 2-4% wax is sufficient to create waxy crystals at lower temperatures than the sample's WAT (Zhang and Liu, 2008). Because of the low temperature, the petroleum content has a wide range of rheological characteristics, including pour point and viscosity. Crystals of wax will form from the temperature falls to a specific level, crude oil threshold. Wax crystals are fused into a three-dimensional network structure, and crude oil elements of fluids are contained, lowering or eliminating crude oil flexibility (Gang et al., 2013). The typical relative molecular weight of the most essential and polar elements in petroleum is hydrogen bonding among molecules of resin and asphaltenes, and it is what leads to the crude's high viscosity making extraction and transportation more difficult (Gang et al., 2013). Asphaltenes are among the polar and heaviest chemicals in crude oil, composed of fused polynuclear flavourings, alkyl chains, and heavy metals such as nickel and vanadium, and have the most outstanding value of aromaticity and polarity.

Furthermore, asphaltenes are available in 3D due to solid intermolecular interactions such as hydrogen bonding (Murgich, 2002). The interplay of petroleum elements is crucial for crude oil transportation and extraction. Consequently, if the connection among petroleum elements has been fully explored, the producer may predict crude oil flow and wax precipitation, preventing poor fluidity issues and taking early preventive actions. Nonetheless, research on the interaction of petroleum components has been restricted, notably the effect of petroleum elements on the crystallization of petroleum waxes (Elganidi et al.Elarbe et al.Ridzuan et al., 2021).

6. Remediation methods of Wax Deposition

The petroleum industry is interested in reducing wax deposition in subsea flowlines because of the significant cost savings that may be gained. The most efficient way to deal with flow assurance difficulties caused by wax deposition is to prevent them from arising first. Thermal, chemical, and mechanical techniques are among the well-established wax mitigation methods employed in the petroleum sector. The wax composition and crude oil types in the reservoir, on the other hand, determine the success rate of any mitigating technique. Consequently, in many cases, a combinatory procedure comprising two or more treatment methods has been used to mitigate wax accumulation (Olajire, 2021) effectively. The following is a summary of several mitigation methods.

6.1. Thermal methods

Because wax deposition is temperature-sensitive, thermal methods may be a very efficient means of avoiding and eliminating wax deposits in the reservoir. The wax will be heated past its cloud point by hot water, oil, or steam flowing through the system to soften and melt the wax layer, enhancing the flexibility of the oil in streamlines. Although, the temperature of the oil should not be too high to avoid petroleum coal burning, which might choke the wellbore. The various thermal methods processes are mentioned in further detail below.

6.1.1. Hot oiling

Hot oiling is a common practice used to dissolve and remove wax in flow lines and downhole, reducing blockage in wellbores and tubing. The process involves heating the oil over the melting point of the wax and then injecting the heated oil down to soften waxes in healthy tubing or fitting that hinder flowability in downhole apparatus (Thota and Onyeanuna, 2016). Meanwhile, one notable disadvantage of the hot oiling method involves the evaporation of the lighter elements., which impacts the oil price value created throughout the dewaxing method. This approach has also been shown to damage permeability if melted wax comes into the structure (Olajire, 2021).

6.1.2. Hot water

Hot oiling has been replaced in a few procedures by steam or hot water to melt the wax, albeit they are seldom because of the possibility of emulsion and corrosion. Water has a greater heat capacity than oil at the same temperature, making it an essential solvent for arriving at the deposition site at a higher temperature while remaining cost-effective. Furthermore, Water does not contain any of the pollutants that oil does. However, water cannot supply the requisite solvency effects in hot oiling, necessitating the application of surfactants to improve wax dispersion into the water phase (Thota and Onyeanuna, 2016). Injection of steam into the distance from the tube and the casing may also be used to remove wax layers. Wax accumulation may be avoided by heating the crude oil with hot vapour at a depth under the lowest point of concentration (Olajire, 2021).

6.1.3. Direct heating

Heating that is applied directly includes moving a substantial amount of electric current flowing along the pipeline surface to produce enough heat to melt the wax (Thota and Onyeanuna, 2016). Because the temperature above the formation zone can be controlled, this approach may effectively solve the flow assurance problem caused by wax precipitation. It is the most appealing and dependable alternative for transportation in deep-water field operations flowlines. Generally, the direct heating approach is intended to maintain the produced fluid temperature over WAT during blackouts. The downsides of using this method are the high cost of heating system maintenance and the lack of an electricity generation source (Olajire, 2021).

6.2. Mechanical methods

Pigging is by far the most often utilized wax reduction method, particularly in offshore subsea systems (Wang et al., Huang et al., Liu et al., 2015; Wei, 2015), in which the wax is retrieved physically by washing the streamline. Pigging must all be prohibited regularly to avoid significant quantities of wax from accumulating. Assume the pressure necessary to force the pig through the pipeline in front of the pigging equipment is inadequate. In such circumstances, the flowline may get clogged, resulting in the closure of production operations (Olajire, 2021). The only option to clear this clog is to send divers down to repair the pipe part clogged by the trapped pig, which will cost several million dollars (Zheng et al., 2013).

A moving piston-driven through a pipe by a pressure difference is a pig. Pigs are meant to push loose fluid into pipelines and remove trash by applying mechanical force to the pipe wall. The pig's tiny bypass holes enable liquid to be 'flushed' due to the pressure drop across the pig, which is an essential characteristic for effective wax pigging. The pig pushes the wax ahead as it enters the pipeline, eliminating the wax coating on the pipe wall. The amount of wax in front of the pig increases in direct proportion to the duration of the pigging. If a more rigorous cleaning technique is necessary, this pig is generally bullet-shaped, with bristles or studs formed into a stiff gel coat. Hard deposits, such as hard wax and scale, need a particularly aggressive tool, which is often a metal-bodied pig outfitted with brushes, ploughs, scrapers, and pin-wheels to enhance efficiency (Thota and Onyeanuna, 2016; Tordal and Statoil, 2006; Wang et al.Huang et al.Liu et al., 2015).

Furthermore, the pigging operation may entail a one to three-day production halt and should only be undertaken when required due to the cost repercussions. Although the pigging process has a low operating cost, the possible economic losses due to a production stop might be enormous (Olajire, 2021; Wei, 2015).

Scrapers and blades are used to remove wax layers from suitable tubing. Pigging is the most often used field operation for removing wax layers from surface pipes (Figure 10). Although these procedures are generally effective, there are a few drawbacks. Removed paraffin deposits, for example, may cause formation damage or hole filling. Moreover, if there is an excessive deposit deposition in front of the pig, the pig may get attached, forcing further expensive treatments or the pipeline's abandonment. (Chi et al., 2019).

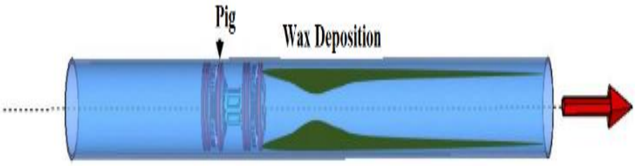

Figure 10 Pigging process for removing the deposit from the pipeline (Shi et al., 2019)

6.3. Chemical Methods

A chemical wax inhibitor may considerably reduce wax deposition rate in specific crude oil production systems, making it economically appealing to enhance output or reduce wax remediation expenses (Jennings and Weispfennig, 2005). Solvents, dispersants/surfactants, and pour point depressants PPDs or wax crystal modifiers are some of the compounds often used to remove wax deposition (Makwashi et al., 2019). Solvents are employed to dissolve paraffin deposits here. Paraffin deposits are broken down into considerably tiny particles using dispersants. Surfactants dissolve paraffin in oil. PPDs inhibit the formation of paraffin crystals by changing their development. PPDs may also influence the rheological qualities of crude oil, such as viscosity and pour point (El-Dalatony et al., 2019). Adding wax inhibitors to crude oil can delay wax deposition build-up, resulting in a lower pigging frequency. Table 2 shows the many types of chemical inhibitors that were employed.

6.3.1. Solvent

Solvents are often employed to cure wax deposition in manufacturing strings, but they may also be utilized to repair formation damage. Depending on the wax molecular weight, temperature, and pressure, the solvent may dissolve a certain amount of paraffinic wax before depleting the solvent power. Depending on the wax's molecular weight, temperature, and pressure, the solvent may dissolve a certain amount of paraffinic wax befordeplete the solvent powered (Olajire, 2021). Solvents are often used in regular batch treatments or continually. The most common solvents utilized in the oilfields are aliphatic and aromatic solvents. Aliphatic solvents are hydrocarbons with straight or ring structures (diesel kerosene is mainly used). On the other hand, aromatic solvents have a carbon ring with dipolar electron double bonds, such as xylene and toluene (Thota and Onyeanuna, 2016).

There are numerous approaches for improving solvent performance: (a) Using xylene or toluene in conjunction with an aliphatic solvent increases wax elimination (Makwashi et al., 2019); (b) The use of a surfactant increases the solvent's ability to distribute the waxes (Sahai et al., 2018); (c) The efficiency of wax removal is improved by heating the xylene and toluene solvents. Regardless of the benefits of the solvent mixture, the typical organic solvent has some restrictions, including a low value for specific gravity that inhibits the solvent from reaching the downhole (to dissolve the deposited paraffin waxes). Because of their low flash point, solvents are difficult to operate and keep in general (Hao et al., 2019).

6.3.2. Wax dispersant

Wax dispersants are a kind of surfactant that adsorbs on pipe side walls and reduces wax adhesion by altering the wettability of the pipe wall or forming a thin layer where wax crystals may easily shear off (Ragunathan et al., 2020). Wax dispersion prevents wax accumulation, reduces oil viscosity, and reduces wax emulsifier ability. Solvents may help to disperse accumulated wax into minute particles that may be carried in the oil flow. Wax accumulation is hampered by the continuing use of wax dispersion or stationary procedures for cleaning (Olajire, 2021). The majority of cost-effective wax dispersants are composed of alkyl sulfonates, alkyl aryl sulfonates, fatty amine ethoxylates, and alkoxylate derivatives (Chi et al., 2019). Wax dispersants experiencing low pour point and are hence appropriate for use in cold temperatures environments where they are used in low quantities. They may also be manufactured including both aqueous and petroleum solutions, making them safe and cost-effective (Thota and Onyeanuna, 2016).

6.3.3. Pour point depressants

Wax inhibitors, known as pour point depressants (PPD), wax crystal modifiers, or flow enhancers, have been employed with unexpected efficacy in profitable wells for many decades (Elarbe et al.Elganidi et al.Abdullah et al., 2021; Manka et al., 1999; Sousa et al., 2019). Most polymeric wax inhibitors and pour point depressants have two fundamental moieties: a polar and a nonpolar moiety. Nonpolar moieties are long alkyl chains that interact with paraffin waxes through nucleation, adsorption, or co-crystallization. Polar moieties such as esters, vinyl acetates, maleic anhydrides, and acrylonitriles may disturb wax crystal growth, modify the shape, and impede large wax crystal formation (Yang et al.Zhao et al., 2015). PPDs are polymeric compounds generated by a hydrocarbon chain interacting with the inhibitor, blocking the formation of wax crystals and decreasing the crude oil's wax deposition, viscosity, pour point, and yield stress. In the presence of water, they perform effectively by wetting paraffin particles, tubing, formation, and flowlines. These formulas dissolve the wax and prevent it from clumping in the reservoir farther downstream.

PPDs lower the pour point of mineral oil by reducing the formation of three-dimensional wax networks, hence enhancing crude oil fluidity. The action of a pour point depressant (PPD) is based on the contact or co-crystallization of its linear, non-polar structure with wax molecules. The polar or otherwise non-wax-like portion, on the other hand, disrupts oil solidification due to wax molecules aggregating into a three-dimensional network. (Olajire, 2021). The behaviour of crude oil has also been investigated in terms of its rheological properties, both with and without the inhibitors acting as pour point depressants (PPD) (Anisuzzaman et al., 2018).

PPDs are WAT-influencing chemicals known as wax inhibitors or wax crystal modifiers. PPDs, or flow improvers, are compounds that change pour points. Chemical inhibitors often function by modifying crystal development and structure, which may drastically alter crystal form and surface features rather than influencing the quantity of wax that comes out of a solution (Elarbe et al. Elganidi et al. Ridzuan et al. Abdullah et al., 2021; Elarbe et al., 2019).

Table 1 The characterization and composition of waxy crude oils from different regions of the world

Region	Wax Content (wt, %)	API Gravity	WAT (°C)	Pour Point (°C)	Asphaltene Content (wt %)	References
Shengli (china)	18.2	24.2	N/A	43	2.6	(Fang, Zhang, Ma, & Zhang, 2012)
Dulang, Malaysia	3	12.6	33.7	31	N/A	(Ekaputra et al., 2014)
Angsi, Malaysia	2	42.6	33.3	28	N/A	(Ekaputra et al., 2014)
Penara, Malaysia	18	22.8	55.7	36	N/A	(Kelechukwu, 2011)
South America	N/A	27	36.4	9	N/A	(Coto et al., 2014)
Egyptian	11.9	31.6	N/A	27	0.728	(Al-Sabagh, El-Hamouly, Khidr, El-Ghazawy, & Higazy, 2013)
South East Asia	18-38	25-40	26-68	15-60	NA	(Chala et al., 2018)
Mexico (PC)	11.26	36	26.9	-30	2.3	(Alcazar-Vara et al., 2012)
Mexico (IRI)	10.9	28.4	38.8	-26	1.5	(Alcazar-Vara et al., 2012)
Iran	5.2-13.1	25.1-34.9	N/A	8-26	0.3-7.8	(Taraneh, Rahmatollah, Hassan, & Alireza, 2008)
India	22.4	44.2	N/A	22	0.18	(Patel et al., 2017)
China (Changqing)	20.7	34	N/A	-30	0.13	(Y. Wu, Ni, Yang, Li, & Dong, 2012)
Qarun (Egypt)	12.3	40.87	N/A	27	2.56	(Al-Sabagh, Betiha, Osman, & Mahmoud, 2019)
PETRONAS, Malaysia	9.2	42.4	28	11	0.65	(S. VijayaKumar, J. Zakaria, & N. Ridzuan, 2021)

Wax inhibitors with wax crystal modifier properties are chemical substances having the same chemical structure as crude oil wax. Polymeric compounds made of hydrocarbon chain molecules similar to wax but with a polar component are typical modifier chemicals. This kind of substance will agglomerate with the wax by attaching the hydrocarbon chains of the wax molecules to the crystal lattices. Furthermore, the inhibitor will impede the formation of wax crystals, lowering the cloud point of the crude oil (Anisuzzaman et al., 2018; Machado et al., 2001). Hoffmann and Amundsen (2013) discovered that depending on the concentrations, the thickness of the wax might be reduced by 60% to 90%. Furthermore, their efficiency varies with molecular weight, which influences agglomeration.

Shorter or lower molecular weight polymers, for example, may cause less disruption to wax crystal agglomeration and development, while longer or higher molecular weight polymers may interact more with wax crystal structures. The contact has a significant influence on the rate of wax production, resulting in the formation of softer wax that flows easily alongside the bulk fluid (Adeyanju and Oyekunle, 2014). Diaz and Theyab (2016) Polymers classified as pour point depressants were used to dissolve the wax crystals in the pipeline.

Table 2 Types of chemical inhibitors used in the previous studies

Type of inhibitor	**Applications**	**References**
Toluene	Solvent	(Ridzuan et al., 2016a)
Acetone	Solvent	(Ridzuan et al., 2016a)
Cyclohexane	Solvent	(Ridzuan et al., 2016a)

Xylenes	Solvent	(Li et al., 2020)
Gasoline	Solvent	(Sousa et al., 2019)
Methyl Ethyl Ketone (MEK)	Solvent	(As'Ad et al., 2015)
Polyester amine surfactants	Wax Dispersant	(Al‑Sabagh et al., 2007)
Polyalkylated phenols	Wax Dispersant	(Sun et al., 2019)
Phthalic anhydride−polyethylene glycol ester (PAP)	Wax Dispersant	(Zheng et al., 2014)
Poly methylsilsesquioxane (PMSQ)	Wax Dispersant	(Yang et al., 2017)
Poly (methacrylate-co-maleic anhydride)	Wax Dispersant	(Xu et al., 2018)
Silane-based surfactant/SiO_2	Wax crystal modifier	(Lim et al., 2019)
b-cyclodextrin	Wax crystal modifier	(Wei et al., 2016)
Nanocomposite of attapulgite/EVA	Wax crystal modifier	(Tu et al., 2018)
Poly (ethylene-co-vinyl acetate)	Wax crystal modifier	(D'Avila et al., 2020)
Methacrylate-co-acrylamide copolymers and ethylene-co-vinyl acetate copolymers	PPD	(Lin et al., 2021)
Poly (fatty esters-co-succinic anhydride)	PPD	(Deka et al., 2020)
Benzyl methacrylate-co-methacrylate copolymer	PPD	(Zhang, F. et al., 2020)
Poly (octadecyl acrylate-co-styrene)	PPD	(Fu et al., 2020)
PMMA/modified graphene oxide nanocomposite	PPD	(Sharma et al., 2019)
Poly (octadecylacrylates derivatives)/montmorillonite	PPD	(Al‑Sabagh et al., 2019)
Poly (tetradecyl methyl-acrylate)-graphene oxide	PPD	(Zhao et al., 2018)
Maleic anhydride copolymers with alkyl linoleate or tetra-esters	PPD	(Soliman et al., 2018)
Poly methyl Methacrylate-Graphene Oxide	PPD	(Al-Sabagh, A. et al., 2016)

7. Interaction Mechanisms of Pour Point Depressants with Wax Crystals

Crude oil's wax molecules retain a constant thermal motion, and the wax molecules' surrounding atoms spin around the C-C single bond. PPD reduces the motion order of wax molecules and the force of contact between wax molecules. The exact mechanism of interaction between wax molecules and inhibitors such as polymeric pour point depressants is being researched. Nonetheless, research by Chi et al. (2016), Yang et al. (2015), and Li et al. (2018) have shown some of the processes, such as nucleation, adsorption, co-crystallization, and solubilization interactions, that effectively control the shape of wax crystals. Table 3 displays the many types of PPDs and their procedures.

7.1. Nucleation

The formation of critical-size paraffin crystals (nuclei) that are stable in hydrocarbon fluid and stimulate crystal growth is known as nucleation. Certain PPDs act as nucleation promoters, lowering wax particle size and avoiding agglomeration (Sivakumar et al., 2018). At temperatures above WAT, PPDs self-assemble into micelle-like aggregates with a crystalline structure. The growth of a single gigantic wax crystal is slowed by producing a large number of sub-critical size wax nuclei (Li et al., 2018; Yang et al.Zhao et al., 2015). Wax crystal size reduction shrinks wax particles, enabling them to remain stable in the oil phase mobility. Inhibitors are preferentially adsorbed on the surface of wax nuclei, according to Duffy and Rodger (2002), resulting in a poor wax surface that weakens interaction with surrounding crystals. According to Duffy and Rodger (2002), Inhibitors are preferentially adsorbed on the surface of wax nuclei, resulting in a poor wax surface that weakens interaction with surrounding crystals (Figure 11).

7.2. Co-crystallization

Wax inhibitors are either co-crystallized with wax molecules or adsorb on the growing surfaces of precipitated wax crystals when the temperature is near or below the WAT. PPD affects the wax crystal structure and aggregation state by interfering with the crystallization process (Li et al., 2018; Sivakumar et al., 2018). In some aspects, the polymer inhibitor structure is similar to wax molecules. Because of their similarity, the molecules may interact with wax crystals during crystal formation. The peculiar structure of the wax crystal is responsible for preventing and interfering with crystal formation. This allows the flow (drag) forces to slough off the weaker wax coatings. They may also impede the proper incorporation of wax crystals into the deposit and weaken it.

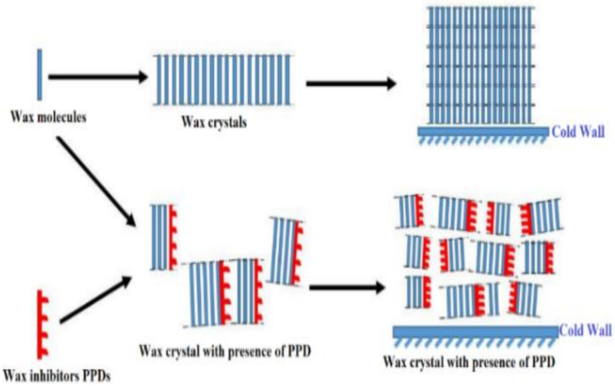

Figure 11 Schematic representation of nucleation mechanism.

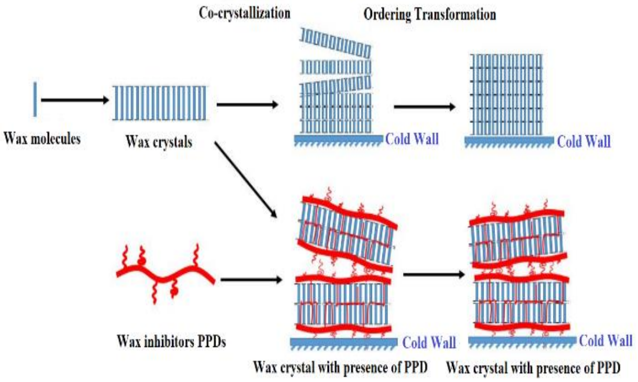

Figure 12 Schematic representation of a co-crystallization mechanism.

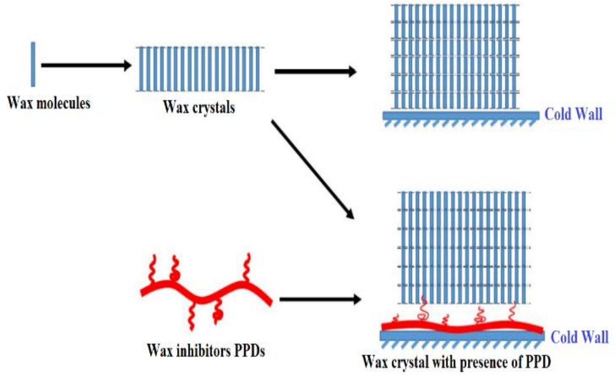

Figure 13 Schematic representation of adsorption mechanism.

The flow (drag) forces might then slough off the weaker wax deposits (Chi et al., 2019). According to Jang et al. (2007), the inclusion of an inhibitor reduces the cohesive energy density (driving force for ordering change) three times when compared to the pure system. As a result, the inhibitor considerably slows the development and agglomeration of wax crystals (Chi et al., 2019). This mechanism is shown in Figure 12.

7.3. Adsorption

In this approach, inhibitors with a high affinity for the pipe wall generate oleophobic surfaces, preventing paraffin molecules from sticking to it. This may lead to producing a weak deposit layer that is sloughed off by the flow (Chi et al., 2019). PPD molecules adsorb into the wax crystals and redirect their growth, resulting in smaller, more isotropic crystals that obstruct oil flow less (Sivakumar et al., 2018). This process is shown schematically in Figure 13.

7.4. Solubilization

As PPD in crude oil grows, small, spherulitic-like crystals replace crystals with long-stick-like or plate-like characteristics (Cao et al., 2013). The solid particles in the crude oil system with precipitated wax crystals behave as a dispersion phase, while the liquid operates as a continuous phase. Furthermore, van der Waals interactions between wax crystals and the PPD's long alkyl chain improve wax solubility in crude oil (Yang et al.Zhao et al., 2015). There is a massive solid-liquid interface between the wax crystal and the liquid phase in the absence of polymeric PPDs, and the energy of the system is extraordinarily high, resulting in system instability. To minimize the system's energy, the solid-liquid contact must be lowered; nevertheless, this will result in the coalescence of wax crystals. Consequently, wax crystals have a proclivity for forming large solid crystals and then forming a three-dimensional network structure. Polymeric PPDs ensure that little wax crystals are broadly disseminated (Li et al., 2018).

8. Types of Pour Point Depressants

8.1. Crystalline-amorphous polymers

Crystalline-amorphous chemical inhibitors and pour point depressants are often composed of polyethylene (PE) groups as crystalline groups and amorphous moieties such as polybutene (PB) and polyethylene-propylene (PEP). PEB and polyethylene-polyethylene-propylene (PE-PEP) have been used successfully in diesel and crude oils as wax deposition inhibitors and rheological modifiers (Radulescu et al., 2007; Tinsley et al., 2007). PEB and PEPEP form micelle-like structures with a crystalline core surrounded by amorphous brushes. The generated micelles may interact with waxes through the nucleation effect and co-crystallization, resulting in more numerous but smaller wax crystals (Yang et al.Zhao et al., 2015).

Table 3 Summary of pour point depressants and their mechanism.

Crude oil	PPD	PPD Mechanism	References
Albacor, Brazil	Poly (ethylene-co -vinyl acetate)	Co-crystallization	(Machado et al., 2001)
Umbaraka	Hexa-triethanolamine	Co-crystallization	(Hafiz and Khidr, 2007)
Karama	Poly (cinamoyloxy ethyl methacrylate-co-octadecyl acrylate)	Co-crystallization Nucleation Adsorption	(Farag, 2008)
Qarun, Egypt	Oleic Acid-Maleic Anhydride Copolymer	Co-crystallization	(Al-Sabagh et al., 2013)
Norpetco, Egypt	Poly (octadecyl maleate-co-Vinyl Acetate)	Co-crystallization	(Atta et al., 2015)
Changqing, China	Poly octadecyl acrylate /clay nanocomposites	Nucleation and growth	(Yao et al.Li et al.Yang et al.Zhang et al., 2016)

Shanghai, China	poly (methacrylate-co-maleic anhydride)	Co-crystallization	(Xu et al., 2018)
Songjiang, China	Benzyl methacrylate-methacrylate copolymers	Co-crystallization Absorption	(Xie et al., 2019)
Shanghai, China	Benzyl methacrylate methacrylate copolymers / Nanosilica	Co-crystallization	(Zhang, F. et al., 2020)
Petronas, Malaysia	Terpolymer of (BA-co-SMA-co-MA)	Co-crystallization	(Elganidi et al.Elarbe et al.Abdullah et al., 2021)

8.2. Comb polymers

In general, comb-type copolymers are becoming more common, and their influence on lowering the pour point and viscosity of crude oil has been steadily acknowledged. Nonpolar elements such as long-chain alkyl groups are often found in comb polymers, as are polar chemicals such as aromatic bases, amine groups, ester groups, maleic anhydride groups, and vinyl acetate (VA) groups, which may interfere with the production of wax crystals (Yao et al., 2018). Incorporating nonpolar groups and paraffin waxes into PPD molecules by nucleation or co-crystallization may increase the interactions between PPD molecules and paraffin waxes. Incorporating nonpolar groups and paraffin waxes through nucleation or co-crystallization may increase the interactions between PPD molecules and paraffin waxes. On the one hand, the polar group may reach the core of asphaltene and partly decrease the bond between asphaltene molecules, so boosting crude oil fluidity (Li et al., 2018).

Despite this limitation, research has shown that the higher the grafting ratio of particular comb polymers, the better the crude oil flow performance improvement. This is because the length of the side chain has a significant impact on the flocculation effectiveness of the comb polymer, and the closer the carbon number of the side link is to the average carbon number of the wax components in the crude oil, the greater the effect on pour point drop.Four comb-like copolymers derived from styrene-co-maleic anhydride copolymer esters were examined as waxy crude oil flow improvers (Al-Sabagh et al., 2009). The sample with the longest branch chain achieved the greatest depression of pour point from 27 °C to 3 °C, the Bingham yield value ($\tau\beta$) declined from 6.0 Pa s to 0.5 Pa s, and the dynamic viscosity also decreased from 110 m Pa s to 24 m Pa s for the same sample. (Xu et al., 2013) studied comb-type poly (maleic alkylamide-co-a-octadecene) copolymers (MACs) with various ratios of polar/nonpolar group (r) were synthesized by the amidation of poly (maleic anhydride-co-aoctadecene). The findings reveal that these copolymers significantly lower the pour point and yield stress of model oil and the size of paraffin crystals and the production of crystal platelets. MACs also lower the temperature and enthalpies of paraffin crystallization, hinder the development of paraffin layer structure, and accelerate the growth of monoclinic paraffin crystals.

8.3. Ethylene vinyl acetate (EVA) copolymers

Ethylene-vinyl acetate (EVA) copolymers were among the earliest and most widely utilized polymeric PPDs. Figure 3 depicts the molecular structure of EVA. The crystalline phase is made up of polyethylene sections of varying lengths on the left, while the non-crystalline phase is made up of a copolymerized vinyl acetate (VA) comonomer with a polar group on the right. Polyethylene chains of variable lengths and VA comonomers of varied content make form EVA copolymers. Furthermore, the molecular weight and dispersion state in the solution of EVA copolymers significantly influence their effect and mode of action. The EVA copolymers act as either nucleating agents or crystal inhibitors by modifying the size and structure of the wax crystals. The addition of vinyl acetate chains increases crude oil flowability while limiting wax crystal formation (Li et al., 2018; Yao et al., 2018).

Norida (2016) evaluated the influence of inhibitor selection on wax deposition in crude oil from Malaysia. In comparison to other inhibitors, EVA generated the least amount of wax deposit while having the highest PIE by 36.6% (Ridzuan et al., 2016a).

Based on paraffin inhibitor efficiency value, cloud point, and pour point of 28.42 percent at 10 °C and 5 °C, respectively, EVA-co-DEA inhibitor has demonstrated to be the best inhibitor to decrease wax production. However, the crude oil's viscosity did not decrease substantially (Anisuzzaman et al., 2017).

8.4. Nano-hybrid pour point depressants (NHPPD)

Nano-hybrid materials have emerged as a new field of study for improving crude oil's rheological qualities. They are made up of polymer matrices on the surfaces of inorganic nano-particles created by organic alteration of nano-clay materials and coated with polymeric PPDs such poly-methyl acrylate, ethylene vinyl acetate copolymer, poly-olefin, and so on (Sivakumar et al., 2018).

Nanoparticles have the potential to be used in polymer modification because of their unusual size, huge surface area, and quantum tunnelling effects. As a result, scientists are studying how to make polymeric nanocomposites by dispersing nanoparticles into the polymer phase. The use of scattered nanoparticles improves nanocomposite qualities such as mechanical and thermal stability, abrasion resistance, and tenacity compared to pure polymers (Li et al., 2018; Yang et al.Zhao et al., 2015).

Nanohybrid pour point depressants, which combine ordinary polymeric pour point depressants with nanoparticles, have recently been developed. Nano-hybrid pours point depressants outperform standard EVA in viscosity/pour point decrease, shear resistance, and crude flowability. Furthermore, a prior study found that silica nanoparticles coated with PPDs could be made and that these modified silica nanoparticles had a more considerable influence on model waxy oil than either silica or PPD alone. The exact mechanics of these nanoparticles are being investigated, specifically the coating of fresh PPD on silica and how this covering affects the nanoparticle's potential to generate wax crystallisation. In addition, research is needed to better understand the mechanism of nano-hybrid pour point depressants and develop new nano-hybrid pour point depressants with the maximum efficiency (Li et al., 2018; Yang et al.Zhao et al., 2015).

8.5. Alkyl acrylate copolymer

A solid form of the polymer acrylate polymer has also been used as a pour point depressant (Admiral et al., 2016). They observed that adding acrylate polymer to the pipeline could enhance the flow of crude oil. Alkyl acrylate, which comprises numerous sets of alkyl groups with carbon values ranging from C14 to C26, is one of the most widely investigated families of paraffin depressants. According to previous studies, combining alkyl acrylate with other co-monomers can lower the pour point of crude oils significantly more than using alone alkyl acrylate polymer (Kazantsev et al., 2016). The alkyl chain's length and the polymer's polarity are thought to influence the efficiency (Kuzmi et al., 2008). Traditional acrylate polymers have a lower viscosity in solid form than in emulsified form. Emulsified PPD of acrylate polymer (brand name: PD90) can be used to make PPD droplets, which are more effective than solvent-based depressants at lowering PPD (Trade name: PD90). The molecules of wax travel freely around the molecules of crude oil in emulsified PD90 because it has a more considerable kinetic energy than pure PD90, avoiding wax crystallisation (Admiral et al., 2016). Four methods were used to explore the alkyl chain lengths of n-alkyl acrylate-vinyl acetate-maleic anhydride terpolymers. The data show that the alkyl chain length of the terpolymer has a strong relationship with the content of the corresponding n-alkane in diesel fuel. The effects of terpolymers on the solidifying point SP and viscosity are constant. The terpolymer, which helps reduce SP, also helps to reduce the viscosity (Feng et al., 2014).

PPDs are very efficient interracial polymers that change crystal structure and intercrystalline interactions. Polymeric wax inhibitors come in various forms and are used as PPDs in the oil and gas industry to ensure crude oil flowability (Yang et al.Paso et al., 2015). Ethylene-vinyl acetate copolymer (EVA) (Machado et al., 2001; Tu et al., 2017), octadecyl acrylate polymer (POA) (Handayani et al., 2019; Yang et al., 2018; Yang et al.Paso et al., 2015; Zhu et al., 2004), alkyl (Xu et al., 2018). According to this study, the chemical structure of PPD performance is important in enhancing crude oil flowability at low temperatures, especially when the polar and nonpolar groups are balanced effectively. According to the data, all PPDs had a beneficial influence on crude oil viscosity and flowability.

One of the long-chain alkyl groups is stearyl acrylate (SA). It's an acrylic monomer with a high affinity for non-polar solvents commonly used in the production of PPDs. Stearyl acrylate, on the other hand, has a crystalline structure. Long alkyl side chains may harden despite an amorphous backbone that reduces oil absorption (Farag, 2008). Since they are the most prevalent multilateral type used to produce acrylate polymers and are generated by acrylic-based acid-structure polymers incorporating carboxylic acid and vinyl groups, several studies on acrylic monomers have been conducted in recent years (Ballard and Asua, 2018; Zhao et al., 2015). Furthermore, acrylic and methacrylic ester groups are commonly used because of their high capacity to prevent wax deposition and act as flow modifiers (Zhao et al., 2015). Sjöblom et al. (2016) discovered that the length of the monomer's alkyl chain has a substantial impact on the performance of PPDs.

The long chain of behenyl acrylate was generated by mixing behenyl alcohol and acrylic acid. Behenyl acrylate (BA) is a chemical additive that improves the efficiency of other chemicals. Because of the long hydrocarbon chains with polar ends of BA molecules, copolymeric additives have better PPD performance. Copolymers of behenyl acrylate (BA) and dodecyl methacrylate (DDMA) showed the best viscosity improvement and pour point depressant performance as lubricating oil additions (Upadhyay et al., 2018). At a molar ratio of (1:1:1), a novel terpolymer (maleic anhydride-co-stearyl methacrylate-co-benhely acrylate) was effectively synthesised and described, yielding the maximum yield (87%) of terpolymer (Elganidi et al., 2019). Many researchers (Darvishi et al., 2013; Ghosh et al., 2017; Goswami et al., 2019; Yang et al., 2018; Yang et al.Paso et al., 2015; Zhu et al., 2004) have extremely reactive vinyl connections. PPD chemical inhibitors, for example, may aid in improving crude oil flowability and reducing wax deposition in the crude oil pipeline.

Some scientists have looked into the effects of employing nanoparticles, polymers, or surfactants to prevent wax from forming. For example, Subramanie et al. (2019) investigated the effect of EVA and MA as wax inhibitors on Malaysian crude oil viscosity at different temperatures and shear stress with and without the inclusion of Sodium cloisite Na+ nanoparticles. According to the findings, although EVA and MA reduced viscosity by 88 percent and 86.4 percent, respectively, adding nanoparticle to EVA and MA reduced viscosity by roughly 94 percent and 89.2 percent (Subramanie et al., 2019). Toyin et al. (2019) looked at the effects of aluminium oxide (Al2O3) nanoparticles and a poly (ethylene-butene) (PEB) blend on crude wax deposition in the Niger delta. Before being introduced to a crude oil sample at various temperatures, a 100-ppm aluminium oxide nanoparticle was combined with varied amounts of PEB.

The results revealed that combining 2000 ppm PEB copolymer with 100 ppm Al2O3 nanoparticle produced the best results for offshore applications, reducing viscosity by 77.9% at 10 °C and 73.7 percent at 10 °C and 15 °C, respectively (Odutola and Idemili, 2020). Yang et al. (2015) examined the rheology of Malaysian crude oil using a poly octadecyl acrylate (POA) blend with nano-silica nanoparticle (SiO2). With increasing POA concentrations, the gelation point has been seen to drop. However, it was revealed that a small dose of poly octadecyl acrylate mixed with (SiO2) nanoparticles had a more significant impact on crude oil rheology than using polymers as a pour point depressant and that the best result was achieved at 100 ppm (Paso et al., 2015). Bo Yao et al. (2016) modified a poly octadecyl acrylate (POA) mix with a nano-clay nanoparticle. They discovered that adding POA/clay nanoparticle PPD resulted in a more compact crystal shape, preventing the formation of a network structure and that further addition could improve the rheological properties of waxy crude oil (Yao et al., Li et al., Yang et al., Sjöblom et al., 2016). Table 4 shows the chemical inhibitors and empirical evidence findings.

9. Factors Affecting on the Performance of Pour Point Depressants

9.1. Pendant alkyl chains

The length of the alkyl side chain influences the polymer's adsorption on the wax, much as the molecular weight of paraffin governs its solubility in oil. Longer alkyl polymers efficiently lower the pour point of high pour oils, while shorter alkyl polymers work in low pour oils. If the alkyl chains are too short, they are adsorbed on the wax below the oil's pour point and are ineffectual at decreasing the pour point. If it is too lengthy, the polymer from the oil solution will crystallize at temperatures over its pour point. The interaction between additives and crude oil is critical; additives operate best when their pendant alkyl chains match the paraffin in crude oil extremely well (Ashmawy et al., 2021).

9.2. Polymer backbone

The polymer backbone is not thought to substantially affect pour point depression. In most situations, the backbone just serves as a framework from which the crucial pendant chains are strung (Manka and Ziegler, 2001).

9.3. The molecular weight of the polymer

Polymer volume in an oil solution increases as the molecular weight of the polymer increases. The viscosity of a high molecular weight polymer is greater than that of a low molecular weight polymer of the same chemical type.

The large percentage of chemical inhibitors are polymers with a framework and a hydrocarbon dangling chain that engages with the wax molecule in crude oil and prevents the production of large wax crystals. This is in addition to the polymer backbone, lengths of the hydrocarbon pendant chain, and molecular weight, which all impact chemical inhibitor activity. Despite previous discoveries that the polymer backbone component had no effect on pour point reduction, the polymer backbone of an ethylene vinyl acetate co-polymer was discovered to affect the polymer's inhibitory action.

The length of the hydrocarbon pendant chain must match the lengths of the wax molecules in the crude oil to have the best inhibitor activity. A short, low molecular polymer will not have enough molecular volume to disrupt wax crystal co-crystallization, whereas a long, high molecular weight polymer may be intractable or interact with the wax molecule in crude oil rather than the wax molecule. Furthermore, the polymer's solubility in crude oil may be limited, leading to wax crystallisation and a rise in the crude oil's pour point (Elganidi et al.Elarbe et al.Abdullah et al., 2021; Ragunathan et al., 2020).

10. Rheological Behavior of Crude oil

The flow characteristics are highly influenced by the applied shear rate during cooling (shear history effect), implying that shear history significantly impacts the viscosity and rheological behaviour of waxy oils. This results in a definite minimum operating value beyond which flow in a waxy oil pipeline would halt. The rheological behaviour of untreated and treated waxy crude oil is determined using viscometrical shear stress-shear rate measurements at temperatures above and below the WAT (Al-Sabagh et al., 2013; Elarbe et al.Elganidi et al.Ridzuan et al.Yusoh et al.AbdullahVijayakumar, 2021). Crude oil has Newtonian properties above WAT and non-Newtonian shear thinning behavior when the temperature drops below WAT. The apparent viscosity changes inversely with temperature, which means that when the temperature drops, the viscosity rises due to the crystallization of wax molecules.

As a result, the fluid exhibits complicated flow behavior with non-Newtonian properties. Shear stress rises dramatically with increasing shear rate in untreated crude oil, resulting in a cold flow pattern with non-Newtonian yield rheological behavior. When the shear rate is increased, the gel wax structure in the crude oil matrix partially collapses, resulting in a large increase in shear stress (Deka et al., 2018). The polymer modifies the wax crystal structure as a result of the interaction between the polymeric flow improver and the wax, and the crystal aggregates formation is easily destroyed when the oil is subjected to shear, resulting in particles of varying sizes and shapes that are conducive to different rheological behavior (Al-Sabagh et al., 2013).

Table 4 List of chemical inhibitors and methods used from empirical evidences.

Type of Inhibitor	Finding	References
Poly (hexyl oleate-co-hexadecyl maleimide-co-n-alkyl oleate)	The point of pour of langhnaj crude oil decreased from 22 to 16 °C at 1000 ppm. while small dosage of PPD was more efficient for reduce the viscosity from 148.5 to 20 cPs at 100 ppm. The flow improvers that have been prepared Pour point depressants and viscosity index improvers are both effective with FIs.	(Patel et al., 2017)
Poly methyl methacrylate-graphene oxide (PMMA-GO) nano-hybrids	When PMMA-GO nano-hybrid was added to waxy crude oil, the pour point and perceived viscosity of the oil were dramatically lowered. PMMA-GO lowered the pour point of crude oil from 27 to 6 degrees	(Al-Sabagh et al., 2016)

	Celsius. The viscosity of the PMMA-1 percent GO was reduced by 82.2 percent (from 56.79 cp vs 10.11 cp).	
EVA	The result found that EVA attained the least quantity of wax deposit and demonstrated the highest PIE by 36.6% compared to other inhibitors. While the viscosity decreased gradually from 43.20 to 11.10 mPa.s, as EVA concentration increased from 500 to 5000 ppm.	(Ridzuan et al., 2016a)
Poly (octadecyl acrylate) /nanosilica hybrid particles	According to the findings, the nanoparticles changed the size and form of the wax crystals and lowered the oil's gel point. At 100 times the concentration of POA, the gelation point drops from 24.7 to 22.6 °C, and the WAT drops from 25.6 to 23.6 °C. The gelation point dropped to 18.7 °C and the WAT rose to 24.0 °C when 100 ppm of hybrid particles were added to the solution. At a dose rate of 100 ppm, the hybrid particle system achieves optimal PPD performance.	(Paso et al., 2015)
Nano-hybrid pour point depressant (NPPD)	The results revealed that NPPD outperformed the typical polymer PPD (N6) in terms of viscosity, yield stress, and pour point decrease for crude oil. The pour point of waxy crude oil was reduced from 30 °C to 21 °C when doped with 100 ppm of NPPD; NPPD had a viscosity reduction of 82.1 percent, while N6 had a viscosity reduction of 75.7 percent. The NPPD reduced yield stress by 99.3 percent but only 78.8% of N6 was lowered.	(He et al., 2016)
POA/clay nanocomposite PPD	When POA/clay nanocomposite PPD is added, the crystal shape becomes larger and more compact, limiting the formation of a network structure and increasing the rheological characteristics of waxy crude oil.	(Yao et al.Li et al.Yang et al.Sjöblom et al., 2016)
Poly (Octadecyl Acrylate-Vinyl Acetate)	The PPD-3 has the best performance in lowering the crude oil's WAT, pour point, and viscosity, with the WAT dropping from 34 to 31 °C at 400 ppm, the pour point dropping to 13 °C with 200 ppm, and the average viscosity reducing rate of PPD-3 being 51.45 percent at 5 °C.	(Yao et al., 2017)
Comb-like Polyoctadecylacrylate (POA)	The results demonstrated that adding POA to the model waxy oil significantly changes the shape of precipitated wax crystals, resulting in a significant change in the oil's wax deposition behaviour.	(Yang et al., 2018)
Polymethylsilsesquioxane (PMSQ) microspheres	The optimal PMSQ microsphere dosages for the two oil samples are 200 ppm but adding the PMSQ microspheres considerably lowers the gelation point and greatly lowers the oil samples' perceived viscosity at temperatures below WAT, and greatly lowers yield stresses.	(Yang et al., 2017)
Ethylene vinyl acetate co-methyl methacrylate (EVA co-MMA) Ethylene vinyl acetate co-diethanolamine (EVA co-DEA)	Based on paraffin inhibitor efficiency value, cloud point, and pour point of 28.42 percent at 10 °C and 5 °C, respectively, EVA co-DEA inhibitor has been demonstrated to be the best inhibitor that inhibits wax formation. When compared to EVA and EVA co-MMA, it can be stated that EVA co-DEA is a better wax inhibitor.	(Anisuzzaman et al., 2017)
α-octadecene-co-styrene copolymers	Compared to a blank, crude oil treated with the developed copolymers at a dose of 2,000 ppm lowers PPT to 6°C and improves paraffin inhibition (PI) to 80%.	(Elbanna et al., 2017)
The ethylene-vinyl acetate copolymer (EVA) modified by alkali-catalyzed alcoholysis	The results revealed that EVAL outperformed EVA in lowering the pour point and viscosity of crude oil. The EVAL has the potential to alter the wax crystal habit and, as a result, reduce the amount of crude oil wax precipitation.	(Ren et al., 2017)
Alcoholized ethylene–vinyl acetate copolymer (EVAL) modified by grafting n-alkyl acrylates	Grafted n-alkyl acrylates reduced the pour point of crude oil by 11 °C and 14.5 °C, respectively, when alcoholized ethylene–vinyl acetate copolymer (EVAL) was chemically changed by grafting n-alkyl acrylates. The addition of an alkyl side chain to grafted EVAL could boost wax solubility and encourage it to adsorb and crystallise with wax molecules.	(Ren et al., 2018)
Poly Octadecyl Methacrylate and Poly Octadecyl Methacrylate-Co-Methylmethacrylat	Compared to pure base oil, the pour points of most homopolymer and copolymer base oils declined. The pour points of 70 percent octadecyl methacrylate units were reduced by 15°C. As the concentration of additives increases, the efficiency of the Octadecyl methacrylate-co-methylmethacrylate copolymer as viscosity index improvers improves.	(Ahmed et al., 2017)
Modified nano-silica/EVA	Modified nano-silica/EVA had a better effect than pure EVA and nano-silica/EVA; when doped with 500 ppm, the pour point of the model oil containing 20 wt percent wax was decreased from 33°C to 0°C. According to the findings, modified nano/silica/EVA can lower the size of wax crystals and disperse them by heterogeneous nucleation.	(Sun, Z. et al., 2018)

Poly (octadecylacrylates derivatives)/montmorillonite	The polymer as pour point depressants showed a considerable reduction from 27 °C to −3°C. The inclusion of the (ODA/MMT) polymers greatly reduced the apparent viscosity of waxy crude oil, and the synthesised nanohybrid polymers' long-term stability was superior to that of a normal polymer.	(Al-Sabagh et al., 2019)
Surfactants and their blend with silica nanoparticles	The results showed that employing 400 ppm of silane-based surfactant substantially influenced paraffin inhibitory efficiency on wax deposition, reducing wax deposition by 53.9 percent compared to untreated crude oil. The wax inhibition was reduced by up to 81 percent when a 400-ppm silane-based surfactant was blended with a 400-ppm SiO2 nanoparticle dispersion at a load ratio of 3:1.	(Lim et al., 2018)
PMMA/modified graphene oxide nanocomposite	When compared to blank crude oil, crude oil treated with PMMA-Graphene Oxide has a 23 °C lower pour point, 99.8% lower apparent viscosity, and a 24 °C lower gelation point of nanocomposite. The yield stress of the crude oil droplets from 60 Pa to 0.1 Pa for PMMA 1 percent Graphene Oxide allowed to treat crude oil at 1500 ppm.	(Sharma et al., 2019)
benzyl methacrylate-methacrylate copolymers	The best depression on solid point SP and cold filter plugging point (CFPP) was found in diesel treated with 3000 ppm MB-C14MC (1:10), with 26 and 12 °C, respectively. Furthermore, MB-C14MC PPD reduces the viscosity of diesel at low temperatures, improving its cold flow properties.	(Xie et al., 2019)
tri-triethanolamine di oleate esterified by oleic acid	Optimum concentration of PPD B1 was 750 ppm for this crude oil. The initial pour point of the crude oil sample was 37 °C, and the application of the synthesized PPD reduced the pour point by 17 °C, making them flow at lower temperature. WAT value decrease from 53.7 to 51.9 °C and PPD B1 is also able to reduce the viscosity of the crude oil, the effect of synthesized PPD is much better than the commercial flow improver.	(Deka et al., 2018)
Poly Octadecyl acrylate Octadecyl-acrylate-maleic anhydride (POA-MA) Acrylate-maleic anhydride-aniline (POA-MA-AN) Polyoctadecyl-acrylate-maleic anhydride-naphthylamine (POA-MA-NA)	The results showed that the four PPDs could improve the flowability of MO-1 crude oil to some extent, with adding 500 ppm POA exhibiting the best performance: the pour point decreased from 29 °C to 22 °C, and the yield stress at 10 °C decreased from 627.20 Pa to 69.58 Pa, and can delay the precipitation of wax crystals and reduce the WAT; the average viscosity reducing rates of the four comb-like PPDs are 64.4%, 55.3%, 46.4% and 42.8%, respectively. The ability of the comb-like PPDs to improve the flowability of MO-1 is: POA > POA-MA > POA-MA-AN > POA-MA-NA.	(Zhang, X. et al., 2020)
Alkyl methylacrylate-vinyl acetate - methacrylic acid terpolymers	Increase the concentration of these additives from 250 ppm to 2000 ppm and the alkyl chain length of n-alkyl methacrylate from C12 to C22 to improve the efficiency of the created compounds terpolymers on crude oil pour point.	(Khidr, 2019)
Poly (ethylene-co-vinyl acetate) (EVA) Poly (maleic anhydride-alt-1-octadecene) (MA) EVA/ sodium cloisite Na+ MA/ sodium cloisite Na+	The viscosity of crude oil was reduced by 92.5 percent using only sodium cloisite Na+ nanoparticles. EVA and MA were able to reduce viscosity by 88 percent and 86.4 percent, respectively, while EVA and MA blended with Na+ reduced viscosity by 94 percent and 89.2 percent. The combination of wax inhibitor and nanoparticle reduces crude oil viscosity significantly.	(Subramanie et al., 2020)
Comb-like copolymers of poly (n-alkyl linoleate-co-succinic anhydride) and poly (n-alkyl linoleate-co-tetra-esters	The results show that copolymers obviously reduce the pour point and yield stress of model oil, decrease the paraffin crystal size, and suppress crystal platelets' formation. Pour point testing revealed that utilising 3000 ppm poly (alkyl linoleate-co-tetra-esters) resulted in the greatest pour point depression (PP = 18 °C).	(Soliman et al., 2018)
Combined of methacrylate-acrylamide copolymers and ethylene-vinyl acetate copolymers	The strongest inhibitory effect was seen when PPDs (C-5) was coupled with EVA in a 1:2 mass ratio. Diesel treatment with 500 ppm PPDC-5 had the lowest CFPP (25 C) and SP (43 C), and the combined PPDs increased wax crystal solubility and delayed wax crystal precipitation.	(Lin et al., 2021)
poly (fatty esters-co-succinic anhydride)	PPD treated crude oils showed significant reductions in pour point, gelation point, WAT, and viscosity compared to virgin crude oil and improved crude oil restart flowability in the event of pipeline shut down. According to a cold finger test, adding PPDs to the flow via tubing of pipelines reduced wax deposition significantly.	(Deka et al., 2020)

Benzyl methacrylate-methacrylate copolymers with nano-silica. MB-C14MC/ SiO2	Results show that nano-SiO2/PPD exhibited better depressive effects in diesel than that of PPD at the exact dosages. At 0.3 weight percent, the cold filter plug position and solid point were lowered by 16°C and 32°C, respectively, using nano-SiO2 /PPD in 1: 6 mass ratios.	(Zhang, F. et al., 2020)
PETRONAS PPD blend with Sodium cloisite Na+	The viscosity of crude oil treated with PPD and PPD/Nanoparticle blend was reduced by 4 percent and 8 percent, respectively, when treated with PPD and PPD/Nanoparticle blend. Using a PPD/Nanoparticle combination, the maximum PIE of 88.27 percent was achieved at a temperature of 15 °C. As a result, the PPD/Nanoparticle combination reduces viscosity effectively and has a higher PIE than PPD. The inhibitor performance as follows, PPD/Nanoparticle > PPD	(Ridzuan et al.SubramanieUyop, 2020)
Poly (ethylene-butene) and nano-aluminium oxide blend	The results showed that a mixture of 2000 ppm PEB copolymer and 100 ppm Al2O3 nanoparticle gave the highest performance for offshore applications, reducing viscosity by 77.9% at 10 °C and 73.7 percent at 15 °C.	(Odutola and Idemili, 2020)
Benhely acrylate-co-stearyl methacrylate-co-maleic anhydride (BA-co-SMA-co-MA) Terpolymer.	The most important and influential viscosity decline of the synthesised terpolymer PPD was observed at a concentration of 1500 ppm, which demonstrated the superior results in terms of the degree of viscosity reduction from 87 percent at 5 C to 47 percent at 35 C, where crude oil viscosity reduced from 70 mPa.s of the blank crude oil to about 9.2 mPa.s after being treated with terpolymer PPD.	(Elganidi et al.Elarbe et al.Abdullah et al., 2021)

Understanding crude oil's rheological behaviour is required for flow modelling analysis and investigating crude oil's complicated behaviour. It's also essential to understand the link between shear rate and shear stress. To design flow parameters that assure crude oil transit via pipelines, it is necessary to understand the influence of various variables on rheological behaviour (Elarbe et al.Elganidi et al.Ridzuan et al.Yusoh et al.AbdullahVijayakumar, 2021). For example, the pressure drop across a channel is often directly associated with the fluid's viscosity. Several rheological investigations have been conducted to establish this crude oil's flow activity despite various experimental models for fluid flow via pipelines. However, none of them can forecast their behaviour with certainty (Kumar et al., 2018). Crude oil viscosity is a rheological parameter that influences crude oil qualities, particularly during cold flow. As a result, two things influence viscosity: temperature and shear rate. Several research studies have looked at the past's viscosity measurement, as seen in Table 5. Newtonian and non-Newtonian fluids have very distinct rheological properties. In the case of a Newtonian fluid, the viscosity is independent of the shear rate. Whereas the viscosity of a non-Newtonian fluid does rely on the shear rate, the viscosity is sometimes a complex function of the shear rate (Zhou et al., 2010). Above WAT, practically all crude oil may be considered as a Newtonian fluid, implying that the oil viscosity is a constant value independent of shear rate. Its value varies with temperature (Wei et al., 2016).

11. Cold Finger Analysis

Various testing devices, such as cold fingers and flow loops, have been used to study the wax deposition behaviour throughout the previous few decades (Yang et al., 2018). The cold finger device is the most often used experimental setup for studying wax deposition rate (Chi et al., 2017; Ridzuan et al.Subramanie et al. Elarbe et al., 2020). The cold finger experiment is suitable for studying paraffin deposition and comprehending the correlation between bulk crude oil's high temperature and the wall temperature exposed to lower WAT temperatures. The critical component influencing wax deposition is cold finger temperature (Huang et al., 2011). More hard, crude oil is produced when the difference in temperature (T) between the bulk of the fluid sample and the surface of the cold finger is more significant. Furthermore, higher T values enhance the rate of wax accumulation.

Table 5 Factors studied in the viscosity measurement.

Crude oil	Factors			References
	Temperature, °C	Shear rate, S^{-1}	Concentrations of PPD, ppm	
Qarun, Egyptian	15-39	0-40	1000-5000	(Al-Sabagh et al., 2013)
Indian	20-40	0-100	250-1000	(Deka et al., 2018)
Alamin, Egyptian	15-30	0-250	1000-5000	(Soliman et al., 2018)
Bituminous	20-60	10-100	100-600	(Sahai et al., 2018)
Malaysia	10-50	35-135	200-1000	(Lim et al., 2019)
Malaysia	5-35	20-61.2	500-5000	(Subramanie et al., 2020)
Qarun, Egyptian	25-45	72.6-150.5	500-1500	(Al-Sabagh, A. et al., 2016)
South China	10-80	1-100	1000	(Sun, H. et al., 2018)

Amera, Iraq	25-35	0-42		
Malaysia	10-40		500-5000	(Ridzuan et al., 2016a)
Malaysia	10-30	34-68	200-600	(VijayaKumar et al., 2021)
China	60-10	0-200	500	(Zhang, X. et al., 2020)
Malaysia	5-40	34	1000-5000	(Elarbe et al.Elganidi et al.Ridzuan et al.Abdullah et al., 2021)
Malaysia	5-40	61.2	1000-3000	(Elganidi et al.Elarbe et al.Abdullah et al., 2021)

The cold finger temperature was set below the WAT amount to assess the effect of temperature on the rate of wax accumulation. As a result, the wax molecules readily cling to one another at low temperatures and precipitate on cold finger surfaces. Additionally, because of the extended residence time, temperature loss is higher. It adds to a drop in oil temperature, causing the wax to form on the pipeline wall. Because the experiment was conducted in a cold finger device, there was no continuous stream of the fluid sample, resulting in less wax precipitation over a prolonged period. It was discovered that the layers of hastened wax offer heat insulation at the most significant degree of residence time. Rotation speed is also essential in minimizing wax deposits since it negatively affects the number of wax deposits. This is proportionate to most of the data in the narrative, indicating that wax deposits may be minimized as rotational speed increases (Salam et al., 2014). This data could be accounted for by viscous drag, which increases as fluid velocity increases. According to fluid dynamics, viscose drag is a resistance force to fluid flow that increases with speed. If the shear stress of the generated wax is exceeded, the force tends to dissolve the wax deposit layer or even disintegrate the deposited wax entirely. The shear-thickening behaviour of the fluid because of a very viscous liquid, the disparity in the shear's untreated wax deposit, the volume of liquid in the wax layer, and the impact of viscosity on the cold finger that surrounds it all contributed to this phenomenon. At lower shear forces, the capacity of wax to deposit from fluid and form waxes through crystallization is reduced (Subramanie et al., 2020).

Table 6 Parameters affecting the wax deposition.

Crude oil	Parameters				References
	Apparatus	**Cold finger temperature (°C)**	**Impeller speed (rpm)**	**Duration time (h)**	
Azerbaijan	Cold finger Flow loop	35-25	750	2-24	(Chi et al., 2017)
Alfa Aesar		5-30	100	0-2	(Mahir et al., 2018)
Venezuela		10-30	200	1-24	(Li et al., 2020)
Malaysian	Cold finger	7-18	200-600	2-15	(Lim et al., 2018)
Malaysian		28-55	100-500	3-15	(Salam et al., 2014)
China		50-35	0-2000	3-48	(Wang et al., 2013)
Malaysian	Cold finger	5-15	0-600	2-24	(Ridzuan et al., 2016b)
Malaysian	Cold finger	5-20	100-600	2-6	(Ridzuan et al.Subramanie et al.Elarbe et al., 2020)
Indian	Flow loop	17-32	300-500	1-5	(Mahto and Kumar, 2013)
Malaysian	Flow loop	13-28	100-500	3-18	(Kelechukwu et al., 2010)
China	Cold finger	10-30	1000	1-9	(Wang et al., 2020)
Iranian	Flow loop	40-50	700-1300	1-5	(Valinejad and Nazar, 2013)

Previous research performed a literature study on the effects of the temperature difference between the pipeline wall and the fluid inside, flow rate, and residence time on wax deposition (Elarbe et al. Elganidi et al. Ridzuan et al. Yusoh et al. Abdullah Vijaya Kumar, 2021). It is found that the temperature difference between the pipeline wall and the fluid inside is critical for wax deposition. Due to conflicting findings provided by different investigations, it is still unclear if a significant temperature differential leads to less wax deposition. The quantity of deposited wax, on the other hand, decreases with higher flow. Furthermore, the deposited wax rises with residence time but reverses when a particular maximum duration value is reached (Junyi and Hasan, 2018). Table 6 shows the range of each component influencing wax deposition utilizing cold finger and flow loop equipment.

12. Conclusion

Paraffin wax deposition is one of the most prevalent causes of oil transportation pipeline and pump blockages and/or damage, resulting in production losses. Paraffin wax deposition is a global issue in the oil and gas sector. Paraffin waxes in suitable fluids precipitate and deposit into solid form at lower temperatures depending on their composition. A long cooling time and a high solvent ratio increase the amount of wax that forms; wax formation affects crude oil properties, including pouring point and viscosity, which alters fluid flow conditions and leads to the production of gel fluid. This results in significant problems such as flow string obstruction, hydrocarbon loss, and increased production costs.

Declaration of competing interest

The corresponding author declares that none of the writers has a conflict of interest.

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