Determination of Paraffin and Asphaltene Precipitation Conditions: A Study of Flow Assurance for Heavy Oil Production

Lim Zhen Hao, Elhassan Mostafa Abdallah Mohammed

Abstract: Raw petroleum is a perplexing blend of hydrocarbons which comprises of aromatics, paraffin, naphthenic, saps and asphaltenes. At the point when the temperature of raw petroleum is decreased, the overwhelming parts, similar to paraffin, will accelerate and store on the pipe inner divider as a wax-oil gel. The gel store comprises of wax gems that trap some measure of oil. As the temperature gets cooler, more wax will precipitate and the thickness of the wax gel will increase, causing gradual solidification of the crude and eventually the oil stop moving inside the offshore pipeline. The presence of paraffin wax in heavy crude oil has caused variety of problems and fouling in wellbore, production tubing and refineries. It has change the flow behaviour of the heavy crude oil.In this study, nature of heavy components in heavy crude oil will be studied to understand well about the paraffin wax precipitation and depositional. Two type of heavy crude oil samples were used in this study and determination of Wax Appearance Temperature (WAT) by using three different method i.e. ASTM Standard Visual Method, Say-bolt Viscometer Methods and Differential Scanning Calorimeter. Comparison will be made among these three methods to test the experiment accuracy and its WAT sensitivity. Next, wax inhibitor i.e. Toluene and Cyclohexane will be added to the heavy crude oil specimen to test the possibility in WAT reduction. An overall understanding on the nature of paraffin wax, wax depositional mechanism and remediation techniques will be achieved.

Keywords: Wax Appearance Temperature (WAT), crude oil, ASTM Standard Visual Method, Say-bolt Viscometer Methods.

I. INTRODUCTION

Most raw petroleum contains waxes which can hasten amid cooling and cause surely understood issues, for example, statement in pipelines, fouling in refineries and generation gear [1]. The stop obstruction properties of rough oils are characterized by the accompanying parameters, the wax appearance temperature (WAT): the temperature at which unmistakable wax crystallization happens [2]. It relies upon the focus and atomic load of the waxes and the substance idea of the non-waxy piece of the raw petroleum [3]. Next, the wax precipitation temperature/pour point (WPT/PP): as the temperature falls, precious stone development proceeds and all the while the measure of accelerated waxes increments [4].

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A cross section is acquired prompting the cementing of the overwhelming raw petroleum at the pour point. WAT is generally decided utilizing the ASTM D2500 technique but then there is no explicit standard methodology for WAT. Past research [5] has considered on the wax precipitation from North Sea unrefined oils by utilizing distinctive test procedures such as cross polarization microscopy, differential scanning calorimeter (DSC) and viscometer. However, cross polarization microscopy will be replaced to ASTM D2500 method. Therefore, in this work, it was decided to undertake a comparative study on wax determination by these few methods.

II. MECHANISM

Paraffin encourage as wax stores in rough oils because of the drop in the temperature of the framework or vanishing of unpredictable light segments C5 [6]. Wax precipitation happens amid the procedure of division of strong stage from fluid stage, the isolated a strong stage showed up as precious stones while wax testimony happens amid the development and development of a layer of accelerated strong on a surface in contact with the unrefined petroleum. Next, wax precipitation process is predominantly controlled by factors, for example, weight, raw petroleum arrangement, temperature, surface-strong cooperations and stream hydrodynamics [7]. Ordinary paraffin are will in general hasten promptly in the vast majority of the raw petroleum. The procedure of crystallization begins with the development of a core, which is the littlest stable molecule of wax gem conceivable under the framework conditions. As the dissolvability furthest reaches of raw petroleum has achieved, the active vitality of paraffin atoms is diminished because of the decrease of temperature [8]. Atoms inspire tangled proceed to join and separate from these arranged locales until the point when the groups become bigger in size and wind up stable after achieving a specific basic size. This procedure of connecting and disconnecting of atoms is called nucleation and the steady groups shaped are the cores. Typically in profound water locales, the temperature is kept at or underneath the WAT (or the point of solidification), following the arrangement of the cores, more particles will connect themselves progressively to the nucleation destinations as an overarching conditions stays ideal conditions to wax precious stone development. Wax affidavit is the development of a layer of the isolated strong

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stage and the possible development of this layer, on a surface in contact with the raw petroleum [9]. Wax affidavit can be framed through system, for example, atomic dissemination, shear scattering, Brownian dispersion, gravity settling and warmth exchange [10]. Wax precipitation/crystallization occurred because of the adjustment in balance states of unrefined when wax particles contained in the raw petroleum has achieved their solvency level, losing paraffin dissolvability [11]. The solvency is the capacity of weight, temperature and raw petroleum arrangement. Other contributing elements are pipe surface unpleasantness, stream rate and gas-oil proportion. Be that as it may, the pivotal factor which is the temperature, it is specifically relative to the solvency of wax in the raw petroleum which will be further talk about later on.

III. EXPERIMENTAL METHODOLOGY

The WAT of a "waxy" unrefined petroleum test is the most elevated temperature that wax solids, darkness or precious stones can be identified when the example is cooled. Different gear and techniques have been produced to decide the WAT of rough oils since the start of oil and gas industry. The deliberate temperature relies upon the oil arrangement, the estimation method, warm history, the living arrangement time of estimation, and the liquid properties identifying with precious stone nucleation and development. Various tests were performed in the oil research facility at University College Sedaya worldwide amid February of 2017 to decide the WAT and WPT of two sort of substantial raw petroleum test. Goals were to test the WAT tentatively on both example; gather An and B tests and to decide a reasonable wax inhibitor for the example and break down the progressions in WAT.

ASTM Standard Visual Method D2500

The ASTM strategies for assurance of the beginning temperature of wax crystallization (D2500 and D3117) depend upon the visual assessment of a 30 mm thick example to recognize precious stone arrangement [1]. This strategy displays various shortcomings in what concerns the cooling rates, temperature estimations and the emotional decisions of the administrator on the cloud point. Notwithstanding when a programmed optical gadget replaces the administrator, expanding the reproducibility of the estimations, the measure of solids required for an adjustment in appearance of the oil to occur or for a recognizable flag to be delivered may at present be very critical. This strategy utilizes visual system to distinguish the darkness of unrefined petroleum test in test tube when the temperature is diminished. Straightforward dimension for test is required to be around 30-40mm, anyway this technique will in any case be considered as one of the test strategies. Examination were kept running for both example by following ASTM Standard Manual strategy.

Say-Bolt Viscometer Method

Mechanism of viscosity bath is that viscosity bath has the operating temperature range of ambient temperature to 120 °C and a proportional temperature control at temperature of 40 °C and 100 °C. Cooling curve temperature range started from 70°C until 40°C to find its first trial WAT, then second trials were performed to close up the temperature gap to obtain the most accurate results. Next, viscometer has a designated column to hold the specimen. Precipitation of wax from "waxy" blends changes the stream conduct of the blend bit by bit from Newtonian to non-Newtonian relies upon temperature setting. At temperatures over the WAT, the example is Newtonian and its consistency is a component of temperature as it were. At the point when the temperature falls beneath the WAT, precipitation of wax gems influences the rheological properties of the example to wind up progressively reliant on the shear rate also. In this manner, by utilizing a rheometer to quantify the consistency of the example as it is cooled, the temperature at which the thickness temperature relationship abruptly begins to change can be recorded as the WAT.

Differential Scanning Calorimeter Method

DSC procedure is broadly used to explore wax hardening and its collaboration among inhibitors and waxes. This method has the advantages of its straightforwardness and quick reaction. It gauges the warmth discharges from the unrefined petroleum test amid the crystallization. Alongside cross polarization microscopy technique, just a little amount of test is required for this strategy. The warmth discharged or ingested and the variable explicit warms displayed by the segregated example as amid cooling or warming is resolved as the temperature changes. Since crystallization will discharge warm, on the DSC bend it will appear as on 'exothermic top' amid cooling. For DSC, it is distinctive with the ASTM Standard Visual Method which it permits dark oil test to be utilized and without administrator's communication.

Selection of Wax Inhibitors by ASTM Standard Visual Method

Two type of solvent were being used in this experiment with different ratio to test its best performance on WAT reduction. Before proceeding to ASTM Standard Visual Method, specimen were diluted with solvents with a designed ratio.

IV. RESULT AND DISCUSSION

WAT from ASTM Standard Visual Method

The WAT & WPT (Pour Point) of crude oil A is very high compared to the results from different literature reviews in this case study. The WAT is at 40°C and the WPT is at 35.5°C, usually the range between WAT & WPT is about 3-4 °C. Based on the findings, it is imperative to say that the crude oil has a very high tendency towards forming wax crystals especially in onshore pipeline facilities as far as the minimum low temperature is kept above the cloud point ≈ 20°C or higher. However, the WAT of 40°C is higher than most of the crudes, in the other hand meaning extreme wax deposition management and remediation have to be done if wanted to avoid severe deposition on pipelines. There are some recommendations when performing ASTM D2500 method i.e. when lifting test jar up for cloud inspection,

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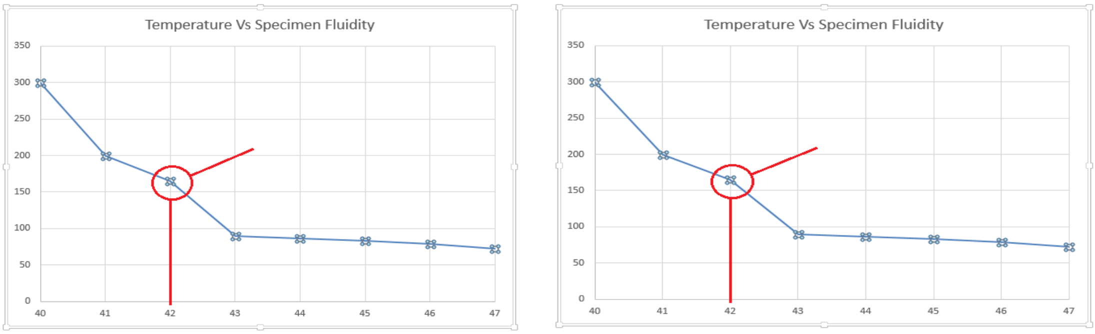
ensure it will not affect the sample condition and each inspection for cloud should not be more than 3 seconds. Specimen B were obtained by blending Specimen A with light crude oil with the ratio of 3:1 since the Specimen A is extremely heavy crude oil. Results were expected that the WAT of the Specimen B to be lower than the initial results. ASTM D2500 & D97 were conducted on the Specimen B and WAT found is at 38°C while the WPT is at 34.5°C. Both are lower than the Specimen A, which has WAT at 40°C and WPT at 35.5°C. It is outstanding that light closures of raw petroleum i.e. C5 go about as solvents in decreasing WAT because of its capacity to hold waxes in the unrefined petroleum. This is a direct result of their solvency in oil which prompts wax disintegration and anticipate long hydrocarbon segments to encourage at low temperatures. Blending of the light and heavy oils is happening more and more at refineries. The main advantage of blending oils is to upgrade its comprehensive value, as the total blended volume value is higher than the heavy and light crude oils alone. Furthermore, heavy crude oil that is blended with light crudes can reduce its' viscosity or resistance to flow. High viscosity crude commonly causes heavy oil to transport inefficiently, especially through pipelines [2]. Next, author will test both specimen WAT again by using viscometer bath.

WAT from Say-bolt Viscometer Method

First trials was carried out to determine the range of both WAT and WPT. Based on the time taken for liquefied specimen to flow out, author able to determine its WAT due to the fact that certain amount of waxy crude were stuck in the viscometer column and for semi-solid specimen at low temperature to flow out will definitely take a much longer time than usual. Second trials was conducted to close up the temperature gap to maximize its accuracy, according to first trials results table, the turning point of time taken was at 45 °C and gelation happened at 40°C which could be assumed as its WPT. During the second trials, at 44°C, time taken for liquefied specimen to flow out was 86 seconds which was much higher than results in first trials, however justification could be obtained from the total volume collected at 44°C which was 30 ml (100% collection). This has denied that WAT fall at 44, experiment was continued until sharp change in time found. At 42°C, time taken has increased drastically and total volume collected were 27ml. Hence, author could conclude that WAT determined by viscometer bath is 42°C. For specimen B, first sharp changes was observed at temperature 38°C - 39°C which was the WAT of specimen B, however to be specifically, at 39°C, total volume of liquefied specimen collected was 30ml, while at 38°C is 27ml, the lost volume were the semi-solidified wax precipitation that stuck in the viscometer column. WAT of specimen B by using viscometer bath was 38°C. Next, after performing two different viscometer bath experiment, author found out that the time taken for viscometer bath column temperature to decrease were too time consuming. There were uncertainties and variation between sample temperature and column temperature, hence it will affect the results significantly. Figure 1 shows temperature vs. specimen fluidity graph for both specimens.



(a) (b)

Fig. 1Temperature vs. Specimen Fluidity Graph (a) specimen A; (b) specimen B

WAT from Differential scanning calorimeter

From DSC results in Figure 2 and Table 1, it measured the energy absorbed and released by a sample when specimen was heated or cooled, especially on the heat flow at a given temperature, it may provide a lot of information author need, with current specimen B, since it was heavy crude oil, it was best to measure the crystallization in the temperature range of 80°C to -20°C at a cooling rate of 10K/min, it will produce an exothermic peak as above to show the temperature of peak crystallization. For the evaluation of DSC curve, the turbidity point which was known as WAT corresponded to the temperature at which the crystallization began (ASTM D2500). At the cooling curve, the onset temperature was 43.2°C and the peak of exothermic reaction was at 37.27°C. During exothermic reaction, at 37.27, was which the peak of heat released from the specimen B = -0.680568 Wg^-1, meaning to say when heat started to release from specimen, it was undergoing crystallization process. As from the Figure 3 , the effect of temperature was increasingly huge for rough oils with higher WAT as they had higher hydrocarbon chains.

The outcomes were very steady with the WAT of the raw petroleum tests, as the measure of the wax precipitation strong is higher at temperatures lower than WAT. The decrease in temperature backed off the sub-atomic movement of the particles in the raw petroleum and causes not to move uninhibitedly in light of less vitality.

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This can bring the wax atoms closer and caused to adjust together lastly prompted hold fast together to a basic and stable size. The development procedure and the bunch of wax particles are called cores and nucleation separately. The security of the cores relies upon the temperature which ought to be lower than the softening purpose of the wax. Be that as it may, raising the temperature expanded the warm movement and caused disturbance in the cores structure. After arrangement of the cores and keeping in mind that the temperature stays low, more wax particles accelerate and keep on following together on the nucleation site. This alluded to as the development procedure [4]. Along these lines, as a vital factor, it is basic to have a learning of the WAT of rough oils so as to guarantee a protected hindrance of wax precipitation and affidavit for stream confirmation [3].

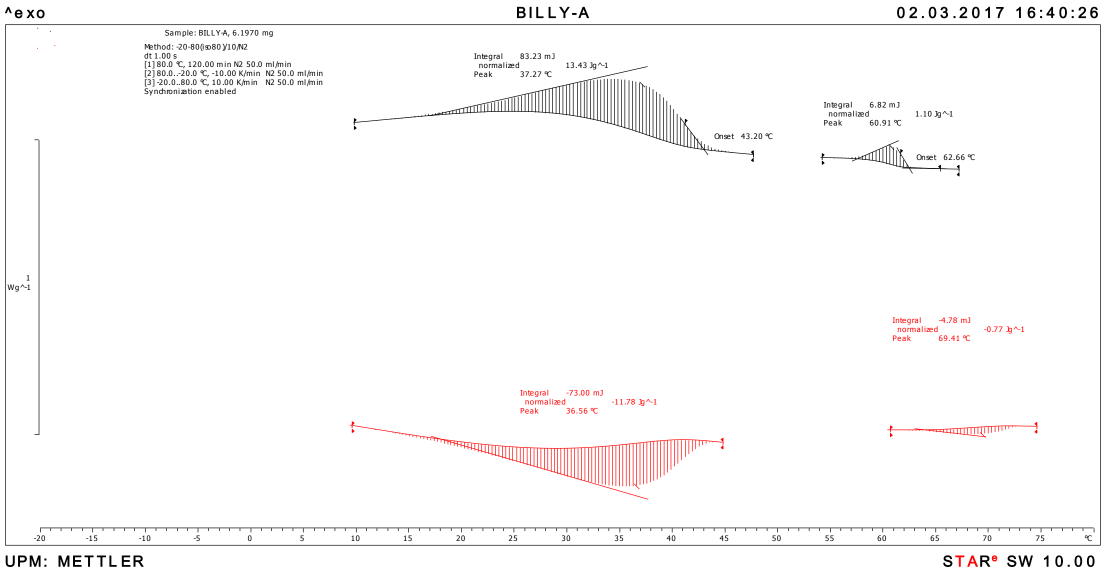

Fig. 2 Dsc Thermogram

Table. 1 Dsc Results

Index	Time (s)	Ts	Tr	Value (Wg^-1)
1	1	-19.9801	-20	0.198693
70	70	-8.37679	-8.33333	-0.395071
144	144	3.94535	4	-0.453761
209	209	14.7663	14.8333	-0.517023
251	251	21.7557	21.8333	-0.572984
304	304	30.5723	30.6667	-0.660114
346	346	37.5653	37.6667	-0.680568
347	347	37.7322	37.8333	-0.678795
373	373	42.0802	42.1667	-0.566364

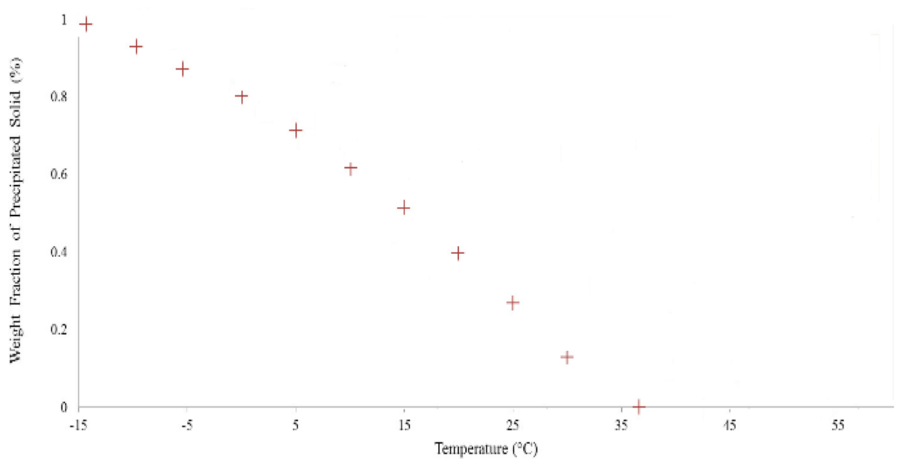

Fig. 3 Precipitated Solid (%) vs. Temperature Graph

Overall Comparison of Measured Results

The main technique utilized, ASTM strategies depended on visual perception of the wax gems; they required the fluids to be straightforward in layers around 30 mm in thickness and, thus, regularly can't be utilized to test dull rough oils (e.g. dark oils). Be that as it may, because of the instrument restriction in college, understudy has picked ASTM as first strategy to test its WAT and WPT run as a benchmark. For Specimen A, the distinction among ASTM and Viscosity technique were 2°C which was inside the adequate range. Normal of WAT was 41°C. For viscometer, consistency for most unadulterated fluids and numerous suspensions at given temperature and weight is an all around characterized property that is free of shear pressure and speed inclination gave the stream is laminar (Newtonian conduct). Fig.3 has demonstrated the plot of example smoothness versus temperature for two of the unrefined petroleum tests previously mentioned. Consistency has an exponential reliance on temperature. [5]. In this examination, one of the disservices was the viscometer that utilizing were not ready to give the consistency incentive to us as a kind of perspective. For Specimen B, understudy has performed 3 most regular kind of WAT estimation procedure which gave a normal of 37.75°C as WAT. Table 4 has appeared between WAT from consistency estimations, DSC estimations, and the ASTM strategy. The WAT from consistency estimations and ASTM strategy were similar estimations with the exception of DSC. In view of the past writing survey and diaries, DSC has perceived as one the most exact WAT estimation system. In addition, ASTM technique and viscometer shower that performed in this examination had a great deal of vulnerabilities i.e. example utilized for analysis was unreasonably dim for ASTM to have an exact perception and viscometer shower utilized has a variety in temperature between the structured section and example temperature. In spite of the way that DSC has given the most precise WAT to example correlation of WAT from thickness estimations and DSC demonstrates that the previous is constantly higher. In this way, it was increasingly fitting to utilize WAT from consistency estimations for planning of pipe lines and creation hardware. As appeared Table 2, all the unrefined oils having WAT values higher than 25 °C. Contingent upon the profundity of these fields and their geological area, the normal seabed temperature in Malaysia is around 22 °C at a profundity of 75m and the surface temperature of 34 °C which are very underneath or nearly equivalent to the WAT of the Malaysian raw petroleum tests [6]. The outcomes recommended that these rough oils were probably going to create wax in transportation pipelines, particularly those with higher WATs. In this manner, it was fundamental to utilize a wax inhibitor to counteract pipeline stopping [4] and chipped away at the Malaysian waxy raw petroleum has demonstrated that utilizing wax inhibitors and single-pipe protection covering were inescapable in light of their high WAT and normal seabed temperature (22 °C).

Table. 2 Overall Results Comparison Table

Sample Name	ASTM D2500	Viscometer Bath	Differential Scanning Calorimeter	Average WAT
Specimen A	40°C	42°C	-	41°C
Specimen B	38°C	38°C	37.27°C	37.75°C

Selection of Wax Inhibitors by ASTM Standard Visual Method

Table 3 and Table 4 have shown that two type of chemical inhibitors were added to both specimens and tested its reduction in WAT and WPT. Highlighted column indicated the optimum results obtained by the ratio and type of chemical inhibitors. The correlation between WAT and WPT reduction can be more easily interpreted from table. Overall, the data has shown that for a reduction in WAT of minimum ~ 6 °C, as well as WPT. For specimen B, it has shown a great reduction in its WAT which was about minimum of 9.75°C and a maximum of 19.75°C. It also indicated that it was difficult to predict an additive's effectiveness at reducing wax crystallization from WAT results determined by the ASTM D2500 method. However, in term of selection the most suitable wax inhibitors as per the study objective, Toluene was the best in this case with at least 75% of ratio if mix with the other chemicals. The decrease of WAT of the waxy unrefined petroleum was up to a 19.75 ºC which is around 49.67% with the nearness of toluene. This one of a kind mix of the inhibitory properties and huge decrease in WPT temperatures, wax appearance temperatures and unrefined petroleum consistency is giving a forward advance in wax relief innovation to be contemplated.

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Table. 3 WAT with Wax Inhibitor Results Table A

Specimen A in ml	Solvent Type	Ratio	Results at room temperature 28°C	Results at 8°C	Initial WAT	WAT (1st)	WPT (1st)	WAT (2st)	WPT (2st)
10ml	Toluene	-	Gelled	GC	41	35	31	30	25
10ml	Toluene & Cyclohexane	3:1	Gelled	GC	41	34	30	31	27.5
10ml	Toluene & Cyclohexane	2:2	Low fluidity	GC	41	35	28	36	32
10ml	Toluene & Cyclohexane	1:3	Gelled	GC	41	35	19	32	28
10ml	Cyclohexane	-	Gelled	GC	41	33	29	31	27

Table. 4 WAT with Wax Inhibitor Results Table B

Specimen B in ml	Solvent Type	Ratio	Results at room temperature 28C	Results at 8°C	Initial WAT	WAT (1st)	WPT (1st)	WAT (2st)	WPT (2st)
10ml	Toluene	-	Cloudy appearance formed	GC	37.75	25	23	20	18
10ml	Toluene & Cyclohexane	3:1	High liquidity	GC	37.75	24	21	19	16
10ml	Toluene & Cyclohexane	2:2	Partial wax precipitation at bottom part	GC	37.75	28	17	28	23
10ml	Toluene & Cyclohexane	1:3	Partial wax precipitation at bottom part	GC	37.75	28	17	20	17
10ml	Cyclohexane	-	High liquidity	GC	37.75	28	14	28	14

V. CONCLUSION

This paper shows a comprehensive review on the use of WAT system and WAT idea. The immense number of accessible references demonstrates that the change stage comprise of 3 primary stages; wax precipitation, wax testimony and wax gelation. It offers ascend to an assortment of issues to the oil business, for example, increment of siphoning power necessity, increment in weight misfortune and stream confinements. Subsequently a few relief systems should be intended to limit the issues identified with wax. The moderation ventures to be attempted requires the information on the property of the waxy unrefined petroleum, for example, the WAT, which is identified with the wax precipitation process. This diary can give a short understanding on the general idea of WAT in substantial unrefined petroleum and its test philosophy and results.

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