

THE FORMATION OF PARAFFIN WAX CRYSTAL IN FLOW

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Abstract

The flow of crude oil from oil reservoir to the surface is controlled by the pressure difference between the subsurface pressure and wellhead pressure the platform. The pressure drop is also required to pump the crude oil from the platform to the inland processing plant. A significant amount of heavy paraffin components may solidify to form needle-like crystals as the flow temperature reaches the temperature of supercritical fluid. The drop of temperature is due to heat losses to the surrounding and low initial operation temperature. The crystallization temperature is measured via the Differential Scanning Calorimeter. The Scanning Calorimetry method provides the initial indication of phases transition at simulated heat loss at isobaric condition. The result was correlated to flow properties such as the pour point and fluid rheology.

1. Introduction

Crude oils are very complex chemical systems. The fluid contains from hundreds to thousands of individual components in the range of simple low molecular weight n-alkanes to high molecular weight waxes and asphaltenes. Paraffin wax is commonly known as wax crystal formed from the cooled crude oil. Asphaltene is made-up of heavy hydrocarbon components that deposited in production tubing due to the effect of pressure. Due to the content of these high molecular weight substances, crude oils are somewhat colloidal in nature. Reservoir crude oils are very close to the thermodynamic equilibrium, but during production, changes of pressure and temperature cause a disturbance of the equilibrium and phases separation may result.¹ The formation of asphaltene will not be discussed in this paper.

Crude oil is an example of supersaturated solution because the concentration of dissolved solute is higher than that of a saturated solution. In crude oil system, light hydrocarbon components such as methane and ethane act as solvents to the supersaturated solution and the saturation depends on the temperature. Crude oils often being processed or transported at conditions where fluid temperature may decrease due to greater heat loss to the surrounding. When the crude oil is cooled, a transition from none equilibrium to the equilibrium is accompanied by crystallization. The conditions under which supersaturated

crude oils are formed and the properties of the crude oils govern, will affect the nature of crystallization or waxing.

This paper discusses an experimental technique to determine the crystallization of paraffin wax under simulated operating conditions. The data is used as input to control and predict the deposition of paraffin wax while oil is flowing through the conduit or pipe.

2. Paraffin Wax Classification

Two types of waxes are commonly encountered in crude oils, i.e., macrocrystalline waxes composed of mainly straight-chain paraffins (n-alkanes) with varying chain length (about C_{20} to C_{50}) and microcrystalline or amorphous waxes also containing a high proportion of isoparaffins and naphthenes (cyclic alkanes) with somewhat higher carbon numbers (C_{30} to C_{60}).² These waxes have different properties regarding crystal growth and morphology. Crystallization of wax (high molecular weight) which basically is a result of decreased carrying capacity of the fluid solvent (low molecular weight)³, commences when the temperature is below the cloud point. The crystals formed may develop an interlocking 3D structure that can effectively entrap the solvating oil; this will lead to higher viscosity and ultimately gelling and congealing.

3. Experimental Section

3.1 Method

The study of wax formation was made based upon the method IP 389/90⁴ known as differential scanning calorimetry. This method covers the determination of temperature at which waxy solids form when distillate fuels are cooled. The method is rapid, convenience, precise and needs only a very small portion of sample (about 10-14 mg). The procedures of sample preparation and temperature programming were modified to meet the pipeline environment. Slow cooling rates were used ranging from 0.5 to 2°C/min which was equivalent to the seabed cooling rate. The technique recorded the energy necessary to establish zero temperature difference between oil sample and a reference material as the two specimens were subjected to identical temperature regimes in an environment cooled at a controlled rate.

3.2 Apparatus

All analyses were performed via the Metler-Toledo System thermal analyzer including the Differential Scanning Calorimeter (DSC), a microprocessor controller, an interface and a STAR data station running under UNIX operating system. In order to extend the analyses beyond the melting temperature of crude oil, a liquid nitrogen cooling system was constructed and connected to the DSC. In order to avoid the condensation of moisture during cooling of oil sample, a plexiglas cover was installed at the top of the sample holder and constantly purged with dry nitrogen.

3.3 Sample Preparation and Analysis

Oil samples to be analyzed were heated to 60°C in closed containers and shaken thoroughly to ensure complete dissolution of any precipitation solids. They were then left to cool to an ambient temperature and shaken again to homogeneity before samples were taken out and

transferred to tared sample capsules and weighed. Aluminium 15 μ l capsules consisting of a pan and lid were used for both samples and reference (blank). The pan was filled with crude oil sample range between 10 to 12 μ l and then sealed with lid by using pressed machine. A small hole was made on blank reference capsule on the lid to avoid expansion of air in the capsule. Both capsules (sample and reference) then transferred to the DSC sample holder for analysis.

All samples were analyzed using both cooling and heating temperature program. Under cooling conditions the DSC was ramped to 60°C and remained about 10 minutes to eliminate any thermal history of the sample. The sample was cooled at controlled rate to -10°C. All samples were analyzed at least five times to improve precision.

4. Results and Discussion

Two Terengganu and three Sabah crude oils of varying composition and paraffinicity, have been analyzed by the DSC. The samples were Penara and Larut from Terengganu and Tembungo, Erb West and North Sabah Trunkline from Sabah. The results of the DSC analyses in the temperature range of +60°C to -10°C are shown in Figure 1 to Figure 5 by representative thermograms for all 5 oils. Figure 6 shows an enlarged set of typical thermograms illustrating the most important features common to all oils, exothermal peaks, the processing baseline and the onset temperature. The observed exothermal peaks are associated with the thermal transitions (liquid-solid) of macrocrystalline wax consisting of mainly n-paraffins. Samples were taken from live crude and all samples were categorized as waxy oils.

The onset temperature which was determined by the intersection of the inflection line of the peak front with the processing baseline is called wax appearance temperature (WAT). At this temperature the thermal transition from liquid to solid phase had occurred and the first paraffin crystals appeared upon cooling of an oil as an effect of the decreased solvating capacity of the oil matrix. The WATs were determined manually because automatic peak detection gave unreliable results for irregular leading edges i.e Penara and Larut oil samples. The results of WAT, degree of crystallinity and the change of heat capacity (latent heat) are listed in Table 1. It is observed that WATs increase with increasing wax content, in particular with increasing n-paraffin content.

Generally it is also found that oil with higher WAT exhibits higher ASTM pour point. Pour point is a measure of fluid ability to flow at low temperature. High pour point oils cause greater flow pressure drop and therefore adequate initial pressure must be obtained to generate flow. The correlation between ASTM pour point and measured WAT by the DSC is shown in Figure 7. The data was obtained from the study using Penara and Larut oil samples. WAT is directly proportional to the ASTM pour point and may be used as a first signal to indicate the increase of pressure drop.

5. Wax Crystal in Flow

Wax crystals mainly consist of paraffinic constituents and are usually formed when the flow temperature drops below the WAT. Generally values of WAT determined in the laboratory are higher than those detected in the flowing fluid. The effect of shear force, turbulence and small proportion of wetting phase that present in the flow decrease the actual

WAT of oil. Shear force and turbulence control the radial temperature distribution and the exposure time of fluid while passing through at any point in flow. Shear force associates with laminar flow regime allow longer exposure time for fluid in cooler area. Heat loss will be higher in laminar regime as compared to the turbulence flow regime. However turbulence effect expedite the precipitation of wax crystal if the mechanism of precipitation present in the flow.

The presence of wax crystal in flow alters the rheological properties of fluid flow condition. This is due to the change of fluid content and the fluid behaviour which is shifted from Newtonian to the Non Newtonian characteristics. The situation was observed when conducting the rheological study of North Sabah Trunkline crude oil. The result is shown in Figure 8 based upon the Power Law Equation. As the flow temperature decreased below the WAT, oil characteristic deviated from the straightline Newtonian to Non Newtonian. The fluid required additional shear stress to initiate flow by extrapolating to zero shear rate. This shear stress is sometimes called gel strength used to estimate restart and shutdown pumping pressure.

6. Conclusion

The characterization of wax formation from a series of Malaysian crude oils had been achieved via the DSC by measuring the wax appearance temperature, wax transition enthalphy and exothermal peak. The wax onset temperature increases with the wax content in oils. The precision of measurement however depends on the number of experiment and samples preparation which were not explained in details. The study of ASTM pour point showed a good correlation with measured WATs but only performed for two crude oil samples. The formation of wax crystal affects the rheological properties of oil and causes additional pressure drop to the flow system.

References

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3. Burger, E.D., Perkins, T.K., Striegler, J.H.: "Studies of Wax Deposition in The Trans Alaska Pipeline," Jour. of Petrol. Techn., June (1981) 1075-1086.
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TABLE 1 : Crude oils thermal properties from Calorimetry analysis and ASTM pour point measurement.

Crude samples	Wax Content %	WAT °C	Crystallinity %	Enthalphy J/g	Pour Point °C
Larut	20	36	79	47.6	32
Penara	25	47	85	86.3	43
North Sabah Trunkline	18	23	75	14.7	21
Erb West	12	19	33	15.6	18
Tembungo	12	18	39	10.2	17

Figure 6 : A typical thermogram curve

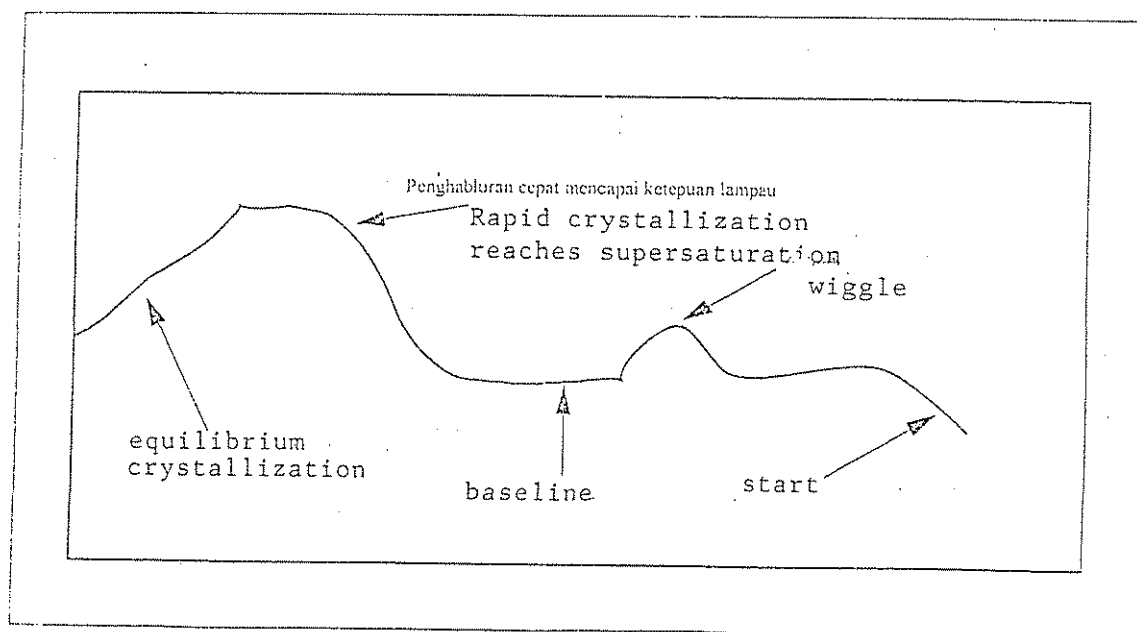


Figure 1 : DSC curve for Larut.

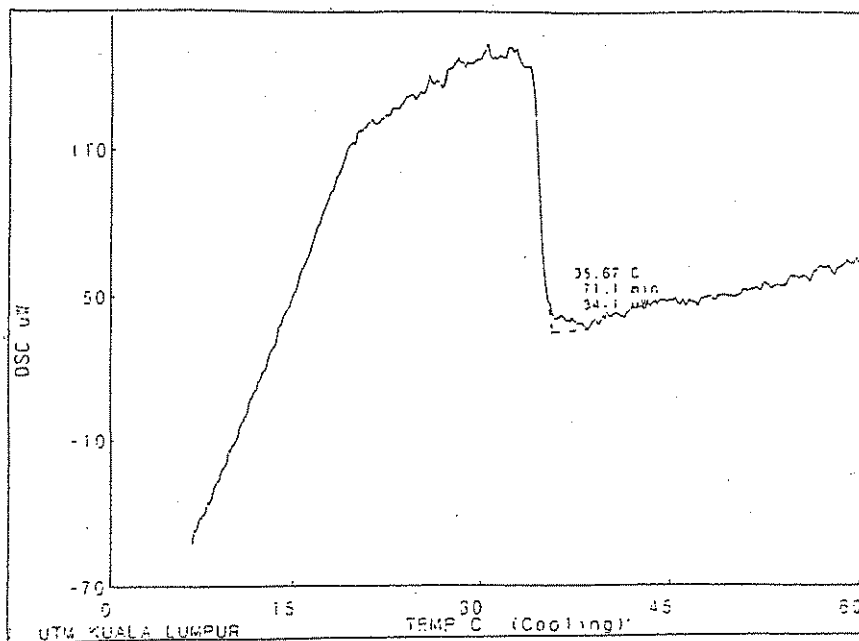


Figure 2 : DSC curve for Penara

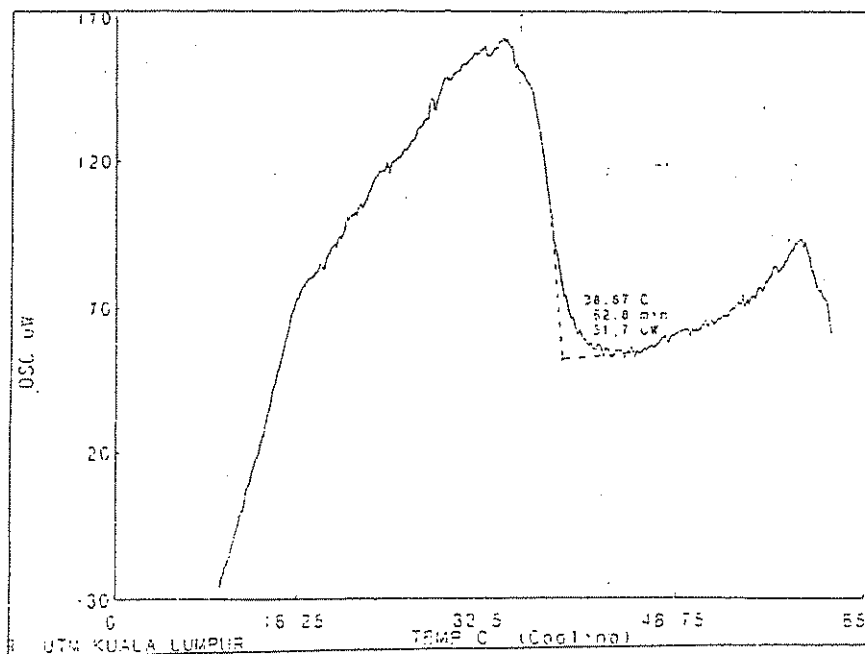


Figure 3 : DSC curve for North Sabah Trunkline

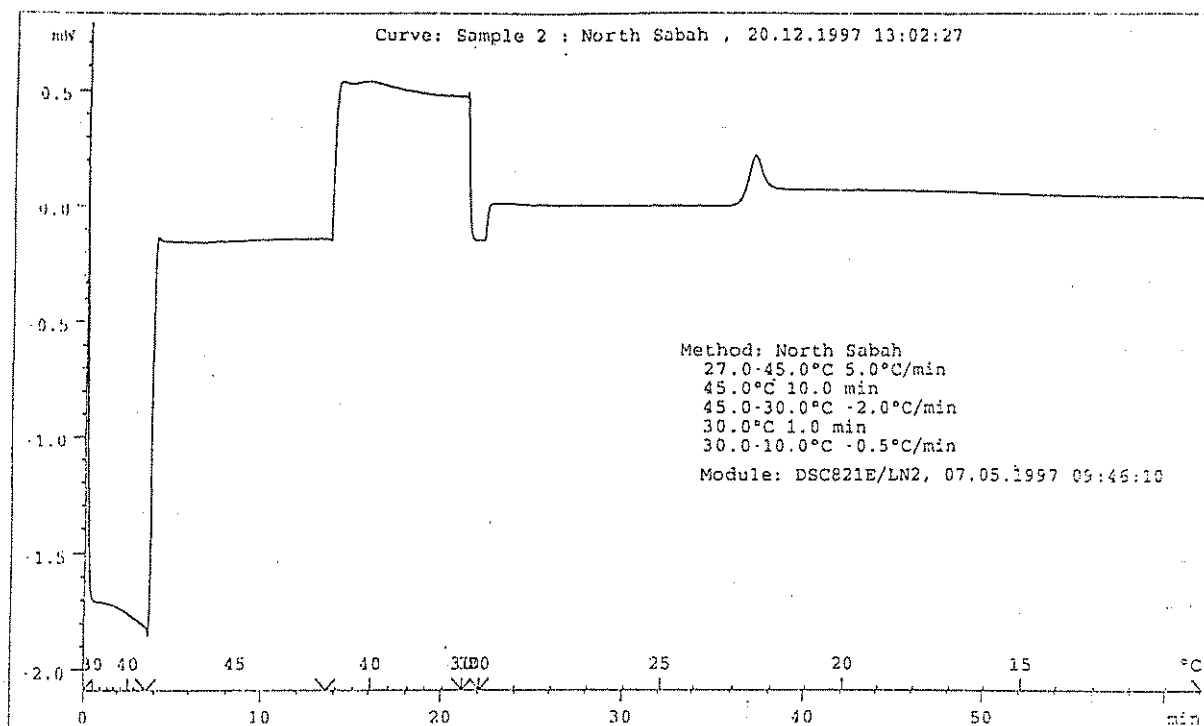


Figure 4 : DSC curve for Erb West

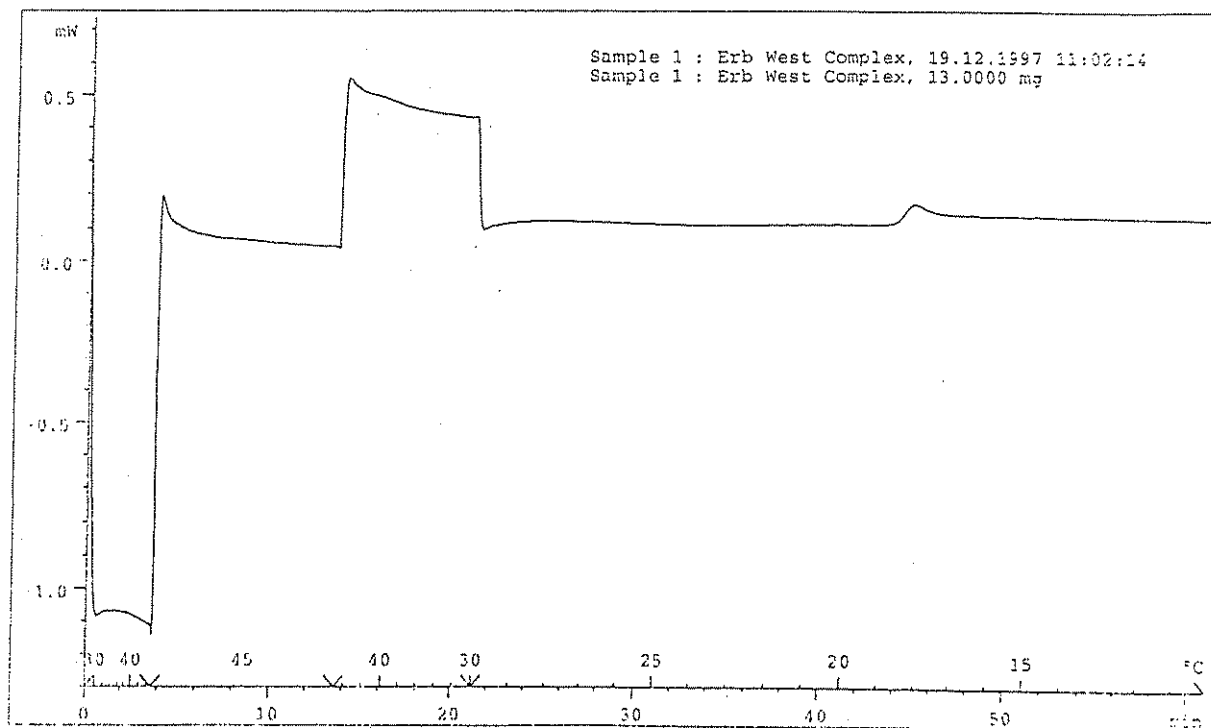


Figure 5 : DSC curve for Tembungo

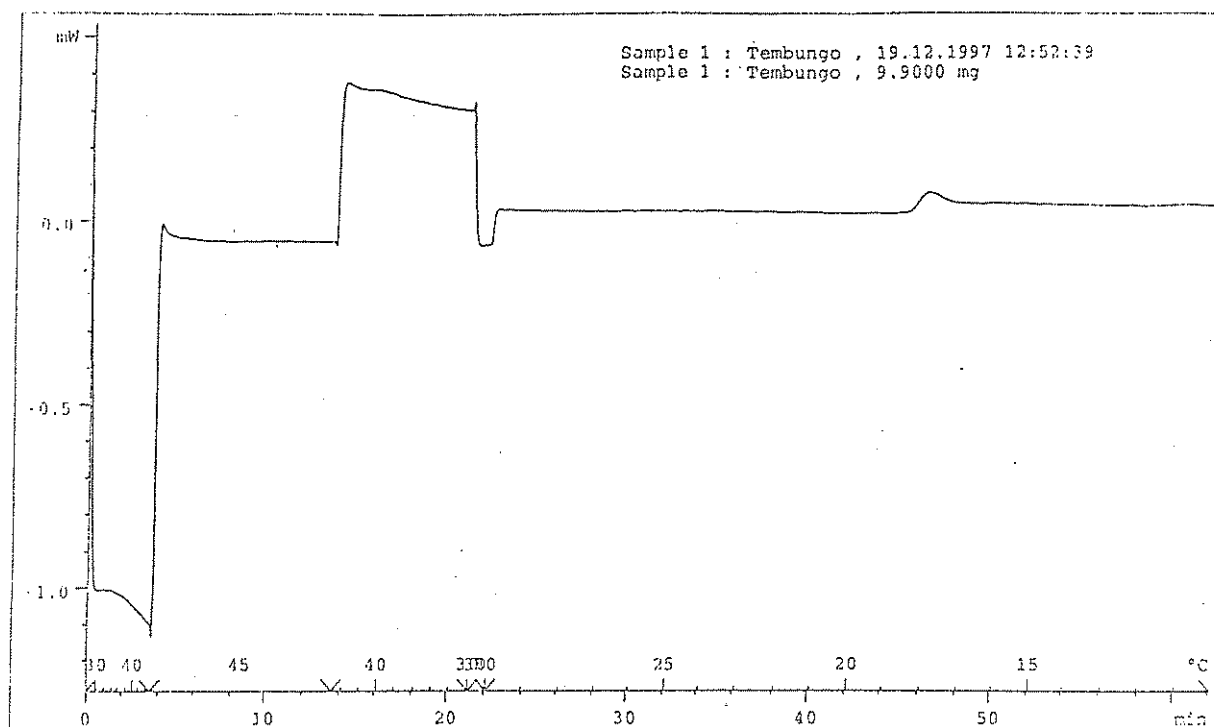
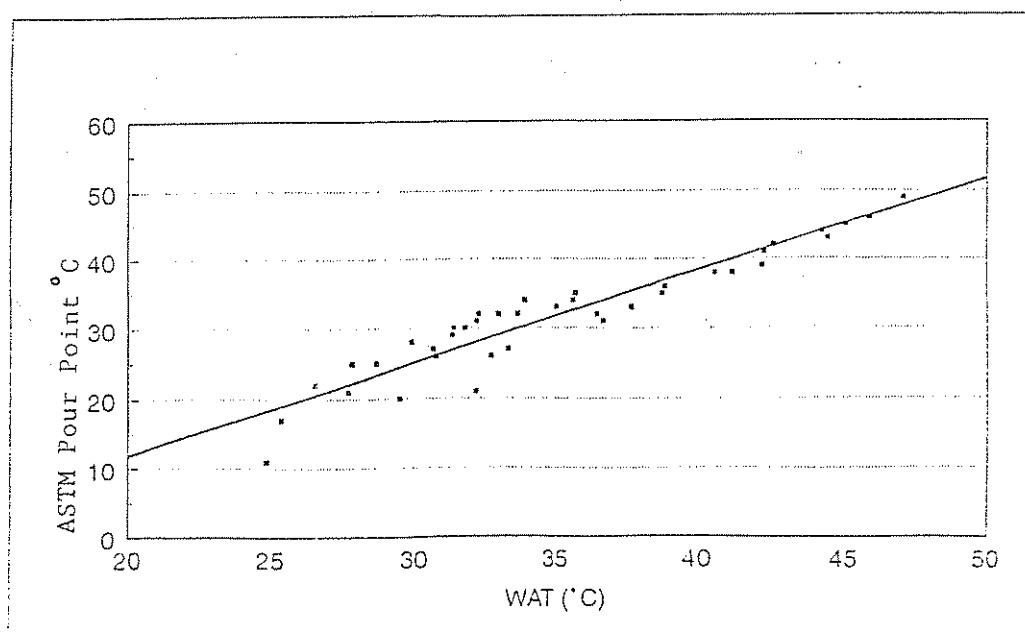


Figure 7 : WAT - PP correlation



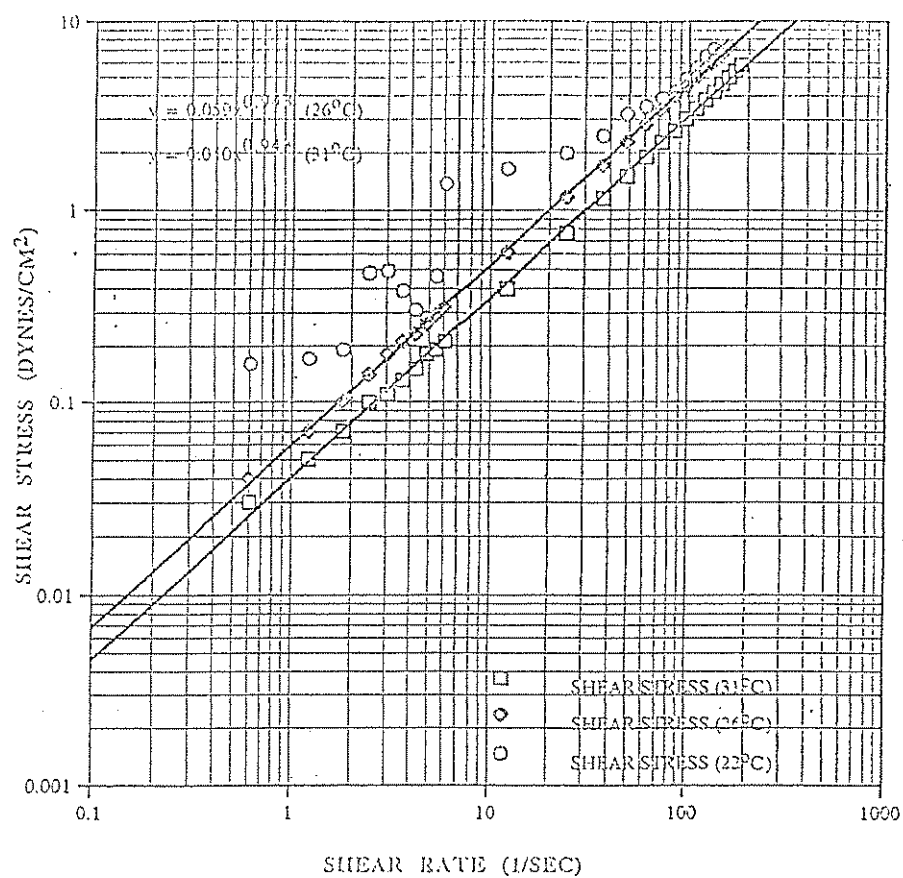


Figure 8a : Shear stress versus shear rate for North Sabah trunkline based on The Power Law equation

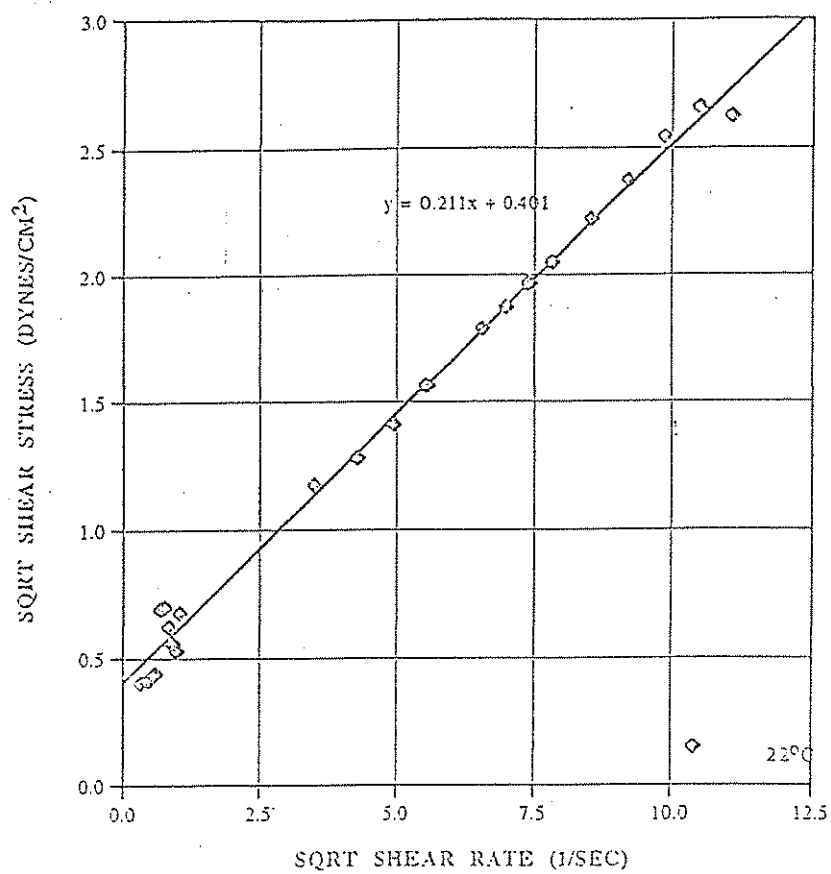


Figure 8b : Shear stress versus shear rate for North Sabah Trunkline based on The standard Casson equation