

INTEGRATED PROCESS TO TRANSPORT HEAVY CRUDE OILS AS AN O/W EMULSION : RECENT ADVANCES

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Abstract: The long distance transport of emulsified heavy crude oils has been shown to be a feasible alternative in the 1980's with the orimulsion project in western Venezuela, and may be an alternative in cold climate as in the peruvian Andes mountain range or in Canada plains. Most studies have been focussing on the O/W emulsion transport stage, though the overall process involves three stages, i.e. the emulsification, the O/W emulsion flow through a pipeline and the demulsification, which cannot be considered as independent issues. An integrated approach may be designed by fine-tuning formulation changes that provide property adjustments in each stage and allow to optimize the process as a whole.

Keywords: heavy oil, O/W emulsion, transport, emulsification, breaking

1. INTRODUCTION

The long distance transport of emulsified heavy crude oils has been shown to be feasible in Venezuela when more than 100,000 Bbls/day were transported over 300 km in the orimulsion venture (Salager *et al.* 2001). Similar projects are under study to transport heavy hydrocarbons in cold temperature regions such as in the peruvian Andes or canadian plains. Up to now the studies have been concerning mostly stability and rheology issues dealing with the O/W emulsion pipelining. Nevertheless, the overall process involves three stages, i.e. the emulsification, the emulsion transport through a pipeline and the demulsification, which cannot be considered as independent issues although the involved phenomena are quite different, and sometimes with conflicting requirements.

An integrated approach may be designed by fine-tuning formulation changes that provide property adjustments in each stage and allow to optimize the process as a whole. The specification list compels some choices such as the selection of a temperature sensitive nonionic surfactant, and the rigorous use of temperature as the reversible formulation variable, which controls the changes in emulsion stability and other properties.

The initial O/W emulsification may be attained either directly down hole or at the well head by an inversion process. The transport through a pipeline depends on the selection of the proper water-to-oil ratio, and the drop size distribution shape to provide the adequate rheological conditions. Finally the emulsion breakup process must take into account the eventual occurrence of a double w/O/W emulsion. Consequently, this last stage should be designed to break the main O/W emulsion first and then, as the ultimate step, to fully dehydrate the separated heavy crude oil. Moreover, these final operations must result in a separated water as clean as possible.

The selection of the process steps and the required formulation conditions in each stage are discussed next according to the current know-how.

2. SUM-UP OF CURRENT KNOWHOW

2.1. Generalized formulation

The effects of the many formulation variables on the emulsion properties have been studied in the past decades and a general phenomenology has emerged (Salager 1999, 2000). A generalized formulation variable such as SAD (surfactant affinity difference) or its dimensionless equivalent HLD (hydrophilic-lipophilic deviation) is used (Salager *et al.* 2000). For polyethoxylated nonionic surfactant – alkane – NaCl brine – alcohol simple systems such a generalized expression may be written as :

$$\text{HLD} = \alpha - \text{EON} - k \text{ACN} + b \text{S} + C_T (\text{T} - 25) \quad [1]$$

Where α is a parameter depending on the surfactant lipophilic group, EON the average number of ethylene oxide group per surfactant molecule, ACN the alkane carbon number, a characteristic parameter of the oil phase, S the salinity of the aqueous phase in wt%. NaCl, and T the temperature expressed in °C. k, m and C_T are constants depending on the nature of the system components. More complex (not shown for the sake of simplicity) but formally identical relationships, have been reported for systems containing other surfactants, oil and aqueous phases.

2.2. formulation effect on emulsion properties

The emulsion properties have been related directly to the variation of HLD in the vicinity of HLD = 0 (so-called optimum formulation), whatever the variable actually used to produce the change (Salager *et al.* 1982). The general trends are indicated in Figure 1 scheme. The optimum formulation (HLD = 0) corresponds to a physicochemical situation in which the surfactant affinity for the oil phase exactly equilibrates its affinity for the aqueous phase. At this formulation several concomitant occurrences take place in all systems as discussed elsewhere (Graciaa *et al.* 1982; Salager 2000b): the tension becomes ultralow; the emulsion inverts (it is O/W at HLD < 0 and W/O at HLD > 0) as deduced from the conductivity variation; an extremely low stability minimum (essentially instant coalescence of drops) is exhibited. Because of the different variations of tension and coalescence rate close to HLD = 0, the emulsion drop size (at constant emulsification conditions) exhibits two minima at some formulation distance (typically ± 1 HLD unit) from HLD = 0: one on the O/W side and another on the W/O side.

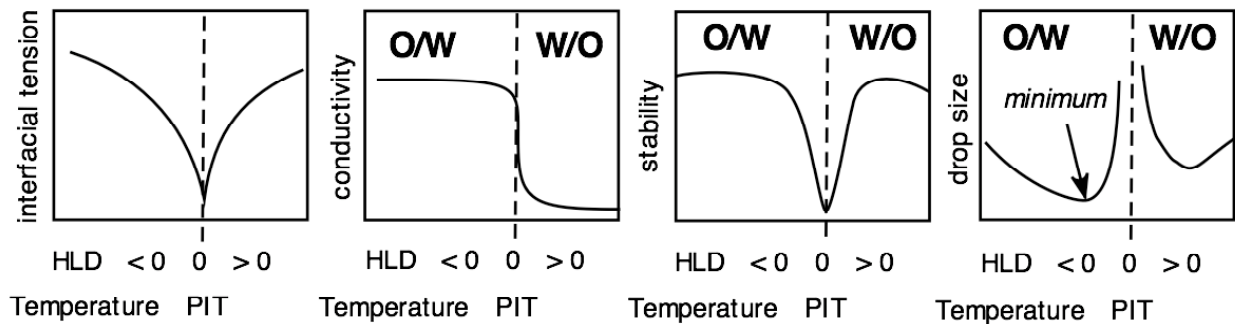


Fig. 1: Interfacial tension at equilibrium and emulsion properties (conductivity and morphology, stability, drop size) versus the generalized formulation in the vicinity of optimum formulation.

This figure indicates that the emulsion properties of interest, such as the stability or drop size, may be adjusted by changing the generalized formulation, e.g., by changing one or more of the formulation variables appearing in HLD expression [1]: surfactant characteristics, oil nature, aqueous phase salinity or temperature.

If the temperature is the scanned variable, its value corresponding to HLD = 0 is the temperature at which the emulsion inverts its morphology, so-called phase inversion temperature (PIT) (Shinoda & Arai 1964).

Equation [1] indicates that the PIT (which is the value of temperature for the system when HLD = 0) depends on the surfactant nature, particularly its EON, as well as the other formulation variables such as the oil nature of the salinity of the aqueous phase. It may be written as:

$$\text{PIT} = 25 + [-\alpha + \text{EON} + k \text{ACN} - b \text{S}] / C_T \quad [2]$$

Typical values of the constants are as follows: $k = 0.15$, $b = 0.1$, $C_T = 0.06-0.10$ (ref) For instance a nonylphenol with EON=15 has a PIT in a system with water and decane of about 120°C, whereas it is 85°C for the EON =10 counterpart. These values have to be measured because they depend on the exact EO distribution of the commercial mixture, and are altered by the surfactant concentration and the water/oil ratio because of the so-called partitioning phenomena of the oligomer mixture (Graciaa *et al.* 1983), with a PIT tendency to increase as the surfactant concentration diminishes and as the water/oil ratio decreases.

2.3. Other effects

Emulsification method. Whatever the stirring device used to produce the emulsion, the adjustment of the formulation at the minimum drop size (figure 1 right plot) reduces the energy cost. Alternatively a so-called HIPR (high internal phase ratio) method of slow stirring of a very concentrated emulsion may be used to cut down the energy cost.

Rheology. The viscosity of a O/W emulsion increases quickly when the internal phase proportion raise beyond 65-70%, and in most case the optimum oil content is rather 50%. However, if a higher oil content is required a larger polydispersity, particularly through a bimodal distribution may be a solution (Ramirez *et al.* 2002). Although the rheology depends on the drop size, it is generally set from stability requirements.

Transport conditions. The transported emulsion should be stable during its transport through the pipeline, but also when it is left motionless in the pipe because of a pumping failure, or stored in a stock tank, at eventually variable temperature conditions. If the emulsion has a high oil content, its resistance to pumping should be also checked, since extreme shear might trigger emulsion inversion. In most cases the stability requirements are met by adjusting the surfactant concentration and the drop size.

Emulsion breaking. The phenomena leading to the emulsion breaking are of great importance because they represent a large part of the cost and worries. To break an emulsion the formulation will have to be adjusted to the situation $HLD = 0$ where the minimum stability is exhibited (Salager 1990). This is a precise setting, which is likely to change with the surfactant EON, the crude oil and the salinity. Accuracy is paramount, since a 5 °C variation may result in an emulsion that takes 10 times longer to coalesce. The transfer of the surfactant to the crude oil is also important to end up with a clean waste water, and this has to do with the formulation and temperature too. Consequently, the adjustment of the temperature is critical and some process flexibility and adaptability is desirable to offset any unforeseen change. Some other effects such as the density difference, use of fiber mats to increase coalescence etc., may be use too to improve the separation rate, but the essential issue is to be exactly at $HLD=0$.

3. STRATEGY TO INTEGRATE THE STAGES

3.1. Compulsory choice

Because of the viscosity of the heavy oil, the emulsification has to be carried out at high temperature so that it is fluid enough to be emulsified. On the other hand, the pipelining is generally carried out at ambient temperature, which may be quite cold in some instances. Finally, the emulsion breaking usually involves a sedimentation process, which requires the external phase to be as fluid as possible. It is then desirable to carry it at high temperature, and it is an essential choice if the external phase is oil. It means that it is practically unavoidable to change the temperature up and down, and up again along the process. In such a case, the formulation changes to adjust the emulsion properties are advantageously induced by changes in temperature.

Ethoxylated nonionic surfactants tends to be less hydrophilic as temperature increases, whereas ionic ones just exhibit the opposite effect. Since O/W emulsion are stable when $HLD < 0$, it means that they are stable below the PIT for nonionic surfactants and above it for ionic ones. Since the emulsion must be made at high temperature so that the oil is less viscous, and then stablized when temperature is lowered, the compulsory choice is a polyethoxylated nonionic surfactant, in practice an ethoxylated alcohol or alkylphenol.

3.2. Overall process optimization

It will be shown next that a proper sequence of temperature changes may satisfy all the process requirements through the phenomenology explicited in figure 1 property changes.

Stage #1: Emulsification (point A in Fig. 2). Emulsification should be carried out at the best formulation, as far as stirring efficiency is concerned, i.e. at the minimum drop size (on the O/W side), which is at about $HLD = -1$. This happens at a temperature slightly (say 15°C) lower than the PIT. Because the oil phase is quite viscous, this temperature should be at least 70-80°C, so that the crude oil is fluid enough and the emulsification does not require too much mechanical energy. Let's assume that an experimental test has indicated that 75°C is a proper

emulsification temperature. Hence, the surfactant EON should be selected so that the PIT is 90°C (90=75+15) by entering the data for the oil and water phases in equation [2].

Stage #2: Transport of a cold stable O/W emulsion (zone B in Fig 2). At 75°C the recently made emulsion is not very secure since it is close to a stability deep fall according to Fig. 2, hence there is a certain probability of coalescence, unless the formulation is displaced to the left, i.e. the temperature is decreased. In practice a 15-20° C drop, which could be easily attained in a simple heat exchanger, insures a shift to a good stability region. The further lowering of the temperature with heat transfer through the pipe wall does tend to make the emulsion even more stable (zone B). The colder temperature transforms the oil drops in oil solid particles, but this does not alter the dispersion stability which is rather insensitive to temperature as indicated in Fig. 2. The only risk to pay attention to is the eventual freezing point of the water, which could be anyway lowered by conventional methods if needed.

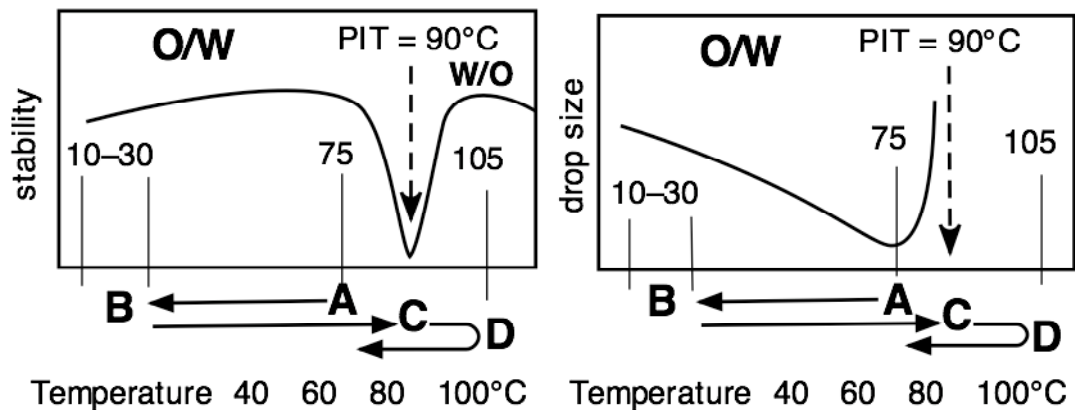


Fig 2. Integrated process with three stages: A Emulsification. B Transport. C/D Emulsion breaking (2 alternatives)

Stage #3: Emulsion breaking and oil/water separation (alternatives C/D in Fig 2). The emulsion breaking process requires the system to reach the low stability narrow range at HLD = 0. This could be attained either by changing the formulation or changing the temperature. Changing the formulation is the typical effect of adding demulsifiers, which in this case will be hydrophobic surfactants, e.g. low EON nonionics, that would combine with the original emulsifier to down shift the average EON, so that HLD = 0 is attained at ambient temperature according to equations [1] or [2]. This is in general costly and not necessarily easy to do since this kind of demulsifier is not water soluble. It is much better to increase the temperature until the PIT, i.e. at 90 °C in this case, and it has to be exactly up to the PIT, since the very low stability occurrence takes place in a very narrow range of temperature. This is represented by point C in Fig 2.

It is however often difficult to reach a very precise temperature in all the emulsion bulk in practice. In most heat exchanger devices, there will be differences in temperature from one point to the other, particularly depending on the vicinity of the hot wall. Consequently, some part of the emulsion could be exposed to a temperature lower than the PIT and others to a higher one. In both cases the stability won't be exactly at its minimum, and a stable W/O emulsion could eventually form in the region with highest temperature (say 100-110°C) if some stirring takes place.

The usual technique to tackle this trouble is to slowly raise the temperature slightly higher than the PIT, and then to come slowly back to a temperature slightly lower than the PIT, with no stirring whatsoever. In such an overshooting and return process (indicated as the D return arrow in Fig. 2) the PIT is reached twice, thus the emulsion undergoes through the very low stability zone (at C) in two occasions. During the period in which the temperature is higher than the PIT, the surfactant tends to migrate into the oil phase, thus disappearing from the water phase. Consequently, at the end the water phase won't contain any surfactant, hence no micelle and no solubilized oil, and accordingly, it is generally very clean and easy to handle as waste water. In this process a typical demulsifier could be added when the temperature is above the PIT, thus helping in crossing back the HLD = 0 condition.

It is worth remarking however that if the attainment of such a high temperature range (90-100°C) is too expensive, the combination of two formulation effects might be the most convenient compromise in some cases, e.g., the addition of some hydrophobic surfactant and a weaker increase in temperature, for instance up to 70°C only.

CONCLUSION

Because of the proper variations of the formulation of the nonionic surfactant system, the proper sequence of temperature changes allows the integration of the three stages of the process, and provides flexibility and adaptability to optimize the whole operation.

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