

Article

The Use of Biobased Surfactant Obtained by Enzymatic Syntheses for Wax Deposition Inhibition and Drag Reduction in Crude Oil Pipelines

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Abstract: Crude oil plays an important role in providing the energy supply of the world, and pipelines have long been recognized as the safest and most efficient means of transporting oil and its products. However, the transportation process also faces the challenges of asphaltene-paraffin structural interactions, pipeline pressure losses and energy consumption. In order to determine the role of drag-reducing surfactant additives in the transportation of crude oils, experiments of wax deposition inhibition and drag reduction of different oil in pipelines with a biobased surfactant obtained by enzymatic syntheses were carried out. The results indicated that heavy oil transportation in the pipeline is remarkably enhanced by creating stable oil-in-water (O/W) emulsion with the surfactant additive. The wax appearance temperature (WAT) and pour point were modified, and the formation of a space-filling network of interlocking wax crystals was prevented at low temperature by adding a small concentration of the surfactant additive. A maximum viscosity reduction of 70% and a drag reduction of 40% for light crude oil flows in pipelines were obtained with the surfactant additive at a concentration of 100 mg/L. Furthermore, a successful field application of the drag-reducing surfactant in a light crude oil pipeline in Daqing Oilfield was demonstrated. Hence, the use of biobased surfactant obtained by enzymatic syntheses in oil transportation is a potential method to address the current challenges, which could result in a significant energy savings and a considerable reduction of the operating cost.

Keywords: enzyme catalysis; biobased surfactant; drag reduction; wax precipitation; oil-pipe; Daqing oilfield

1. Introduction

Petroleum as an energy source plays an indispensable role in our transportation fuels, though the issue of the environment continues to be a concern. The world demand for crude oil has increased from 6.0×10^7 barrels (bbls) per day to 8.4×10^7 barrels per day in the last 20 years [1]. It is well known that pipelines as a mean of transporting crude oil from the producing field to the treatment station or the refinery are the least expensive, the most effective and environmentally convenient and have been widely used in the gathering process at the oilfield and for downstream fuel supply [2,3]. The pressure drop loss in the pipeline must be lowered to decrease the pump power to push the oil economically for a long distance [4].

It is usually challenging for a pipeline to transport heavy crude oil because of its high viscosity and density. A significant pressure loss along the pipeline is experienced due to the low flowability of

the heavy crude oil, causing it to be cost and energy intensive (*i.e.*, higher pump power) to transport via pipelines [5,6]. Additionally, blockage is caused by asphaltene deposition at the pipe walls, which reduces the accessible cross-sectional area for oil flow, which will induce a rise in the pressure drop and a reduction in the flow rate [7]. According to statistics, 95% of the heavy crude oil produced in Canada and Venezuela is transported with pipelines [8]. A promising pipeline technique to address the challenges is the transport of viscous crudes as concentrated oil-in-water (O/W) emulsions. The use of suitable surfactants and water to create a stable O/W emulsion with heavy oil to enhance pipeline transportation capacity has been a topic of several investigations, and the technology has been demonstrated in Indonesia in 1963, as well as in a 20 km-long, 0.203 m-diameter pipeline in California [9,10]. The technology can be very effective in the transportation of crude oil with viscosity higher than 1000 mPa·s, especially in cold regions. However, the key factors associated with this technology of transporting heavy crude oil are the selection of the surfactants and cost management.

As one of the low-temperature resistance properties of crude oil, the wax appearance temperature (WAT) can be defined as the temperature at which visible crystallization occurs. When the temperature falls below the WAT, the n-paraffin waxes in crude oil tend to separate from the oil, and the species generally crystallize to form interlocking network structures as temperature decreases, thereby entrapping the remaining liquid fuel in the structures. Wax build-up that occurs in conventional middle and light crude oils is also a complicated and very costly problem for the petroleum industry [11–13]. Wax deposition within pipelines at and below the WAT can result in gelling that restricts flow by causing obvious non-Newtonian behaviour and increasing apparent viscosity when the temperature of a waxy crude oil reaches its pour point. The deposition of a layer of paraffin molecules that can grow over time is promoted when the temperature at the pipeline wall falls below the WAT, causing high frictional pressure losses and constricted flow, as well as increasing the pressure needed to maintain the flow. However, using several pumps in the line is not affordable due to the high energy consumption and possibly exceeding the maximum allowable operating pressure. For crude oil pipelines in cold environments, in particular, the issue of wax build-up has become increasingly significant. Prevention and remediation of paraffin wax deposition costs the oil industry billions of dollars worldwide. Besides the internal coating of pipelines with plastics and heat insulation of pipelines to inhibit the deposition by keeping pipeline temperatures as high as possible, investigations have shown that one of the best alternatives is actually to use different classes of chemical inhibitors [14]. Different mechanisms were reported to prevent gelling or wax deposition in pipelines using chemical inhibitors, and some additives are called drag-reducing agents (DRAs) [15]. They can reduce the pour point or WAT or can modify the wax crystals, so as to prevent their aggregation and deposition. Pour point depressants (PPDs) or flow improvers are applied to affect the pour point, while wax crystal modifiers or wax inhibitors are usually used to modify the WAT [16]. Practically, the reduction of friction can be realized by adding a small concentration of such additives without changing the pipeline conditions. In 1979, the first commercial use of DRAs was in the 1.2 m-diameter Trans Alaskan Pipeline where a 50% drag reduction was achieved [17]. Since then, DRAs have been applied in installations of many petroleum product pipelines, such as the Oseberg Field in the North Sea. However, they are all polymer DRAs in the applications mentioned above. According to industrial statistics, compared to the effectiveness of DRAs in several engineering systems, such as oil production and transportation pipelines, district heating and cooling in 1980, effectiveness was increased 14 times by the year 1994 [18]. The efficacy of different chemicals for wax deposition inhibition and drag reduction in crude oil pipelines has been studied by many researchers, and the limitations of the commercially available chemicals were noted [19–21]. Bello *et al.* studied the efficacy of inhibiting gelation on Nigerian crude oils and demonstrated that the use of a trichloroethylene-xylene (TEX) binary system as an additive was actually more effective and feasible than that of commercial chemicals [22]. In other words, it should be noted that there is a strong relationship between a specific DRA's effectiveness and the crude oil composition, and a case-by-case consideration is necessary for selecting chemicals for use in the field.

The main categories of DRAs include polymers, fibres and surfactants. As mentioned before, these DRAs can play key roles in emulsifying, solubilizing, reducing the WAT or pour point, modifying the wax crystals by contributing to the prevention of agglomeration and deposition or suppressing the formation and growth of turbulent eddies through the absorption of the energy released from the breakdown of the lamellar layer during oil transportation. Furthermore, DRAs reduce friction loss within the turbulent fluid core during transportation, causing high flow rates at a constant pumping pressure [23]. Generally, the surfactants can promote the formation of a stable O/W emulsion, which is beneficial to pipeline transportation, and they can adsorb onto pipe surfaces and decrease the adhesion of waxes to the surfaces, as well, possibly by changing the wettability of the pipe surface, or by creating an environment in which wax crystals are easily sheared off, or by adsorbing onto the wax crystals and preventing their sticking. As previously reported [24], cationic surfactants can form rodlike micelles in aqueous solutions, which align in the direction of the flow and build the so-called shear-induced state under a certain shear stress, causing a damping of radial turbulence components and subsequent reduction in pressure loss. Typical, low-cost surfactants include alkyl aryl sulfonates, alkyl sulfonates, fatty amine ethoxylates and other alkoxyated products, but the efficacy of these surfactants is limited without blending with polymeric DRAs.

The manufacture of surfactants has become increasingly dependent on petroleum. Recently, concerns about the long-term economic and ecological sustainability of fossil fuels have caused renewed attention to biobased feedstocks [25]. A product that is secreted by the metabolism of microorganisms, with amphiphilic molecules and high surface activity, is a biobased surfactant. Compared to classical surfactants, they have some advantages, including low toxicity, biodegradability, a wide variety of structures, synthesis from inexpensive renewable materials and stability in a wide range of pH [26]. Surfactants are traditionally manufactured with chemical processes that cost large quantities of energy, including high acidity and alkalinity and temperatures that exceed 100 °C, and organic solvents may be essential. Bioprocessing methods, as examples of “green manufacturing” are receiving interest, which stems from replacing chemical processes with those that use enzymes [27]. More than 1500 different enzymes have been identified till now, and many have been isolated in pure form [28]. According to the type of reaction involved, enzymes were categorized into six main classes and a number of subclasses by biochemists. Although they are not yet cost competitive with chemical synthetic processes, enzyme-catalysed syntheses as green manufacturing methods possess many intriguing advantages during the preparation of biobased surfactants, including economical processing conditions and the reduction of by-products, which can harm the environment or the users. It has been shown that a biobased surfactant synthesized by the enzyme-catalysed method can enhance oil recovery by interfacial activity and reverse wetting of reservoir rocks [29]. The viability of this method will be improved by further development of more stable and active biocatalysts and new technology in the bioprocessing field [30].

This work involved the use of a biobased surfactant obtained by enzymatic syntheses for wax deposition inhibition and drag reduction in crude oil pipelines. By screening an immobilized lipase as the catalyst and optimizing its reaction conditions, a biobased surfactant was prepared with the method of enzymatic syntheses. The experiments were designed to study the formation of O/W emulsions and the modification of wax crystals of heavy oil and light oil in the Daqing Oilfield (China) using the biobased surfactant. The reduction level of viscosity, WAT and pour point of the crudes were determined, and the agglomeration structure of wax crystals during the temperature drop process was characterized. Then, the drag reduction efficacy of the biobased surfactant in single-phase flow and multiphase flow were evaluated, and the role of wax deposition inhibition and drag reduction with the surfactant in crude oil pipelines during transportation process was discussed. Furthermore, a practical field application of the drag-reducing surfactant in a 6.3 km-long, 0.219 m-diameter pipeline in Daqing Oilfield was presented.

2. Results and Discussion

2.1. Selection and Reaction Conditions Optimization of Catalysts during the Drag-Reducing Surfactant Preparation

Like all catalysts, enzymes accelerate the rates of reactions with no modification because of their participation. Though an immobilized enzyme was fixed in a certain area by appropriate supports, it can retain excellent catalysis properties and can be recovered and reused. Compared to free enzymes, immobilized enzymes can reduce the cost because of their reuse, and the separation process of products could be simplified. Furthermore, the robust reaction can also be realized. Therefore, a commercial immobilized lipase of Chirazyme L-2 was selected as the catalyst during the synthesis of the drag-reducing surfactant.

As shown in Figure 1, the catalyst is most active in the range of 60–80 °C. Meanwhile, we found that the optimal component mole ratio of fatty acid and glycerol is 1:1, that the reasonable proportion of catalyst is 0.5% and that the appropriate reaction time is 30 h at 70 °C. As for water content in the system, catalyst should be activated and the conformation kept flexible by a small quantity of water. However, water generated with the formation of ester bonds and the accumulation of the water will reach the equilibrium of reaction ahead of time, which will reduce the yield. Therefore, a small amount of special fillers and additives as the reaction medium was added during the synthesis process. The water generated during esterification was removed by azeotropic distillation and was regenerated by membrane vapour permeation. A potential biobased surfactant that could be applied to drag-reducing was prepared, and the highest yield (91%) of biobased surfactant was obtained under these optimized conditions.

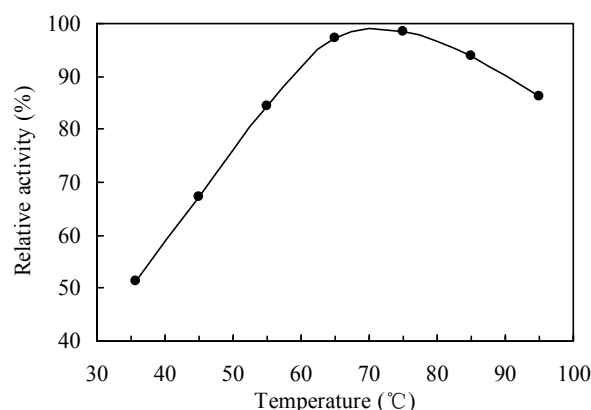


Figure 1. The relative activity of immobilized lipase as a function of temperature.

2.2. Enzymatic Process in the Drag-Reducing Surfactant Preparation

As shown in Figure 2, there are three units of reaction, recovery and purification in the enzymatic process. The reaction unit is a special stirred-tank reactor, and its core component is the membrane. The choice of the membrane material is critical for the success of such a reactor. By comparing and screening of the membrane in selectivity and permeability, PERVAP®2201, a commercial flat polymeric membrane, was employed in the reactor for the enzymatic process. The reaction temperature of the stirred-tank reactor was maintained by a controlled temperature bath, and the realization of stirring was operated by a magnetic stirring system. The substrate and the catalyst at a certain component ratio as mentioned above were added successively to the reactor before running the enzymatic process. The recovery unit is mainly used to recycle the special fillers and additives, which promote the formation of an azeotrope. The core component is a permeate device equipped with a high-efficiency separation membrane, then the special fillers and additives can be recycled and reused with the removal of water. This provides constant removal of the water generated in the reaction and drives the

equilibrium towards esterification. The purification unit is a product collector with the function of stirring, temperature control, flotation and filtration. After the reaction, the immobilized lipase can be effectively separated from the reaction medium with the aid of flotation under a low temperature, and the products can be collected by cooling and filtration. Thus, a high-yield enzymatic process was established.

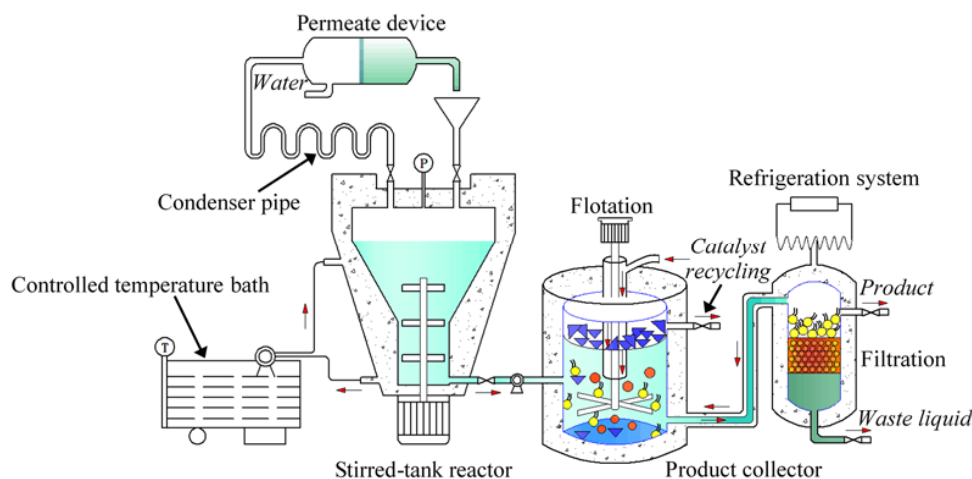


Figure 2. Schematic illustration of the enzymatic process.

2.3. Availability of the Drag-Reducing Surfactant for Heavy Crude Emulsification

The formation of O/W emulsion has been an alternative technique of improving the flowability of heavy crude oil in pipelines. The properties of this adsorbed layer of conventional surfactant stabilizes the oil-water surface and controls the behaviour of the emulsions [31]. The monolayer of the biobased surfactant obtained by enzymatic syntheses sits at the oil-water interface and prevents phase separation into the oil phase and water phase during transportation. As illustrated in Figure 3, the monolayer takes up the interfaces of the O/W emulsion, promoting the formation of coarse dispersed droplets. The polar region is in contact with the water, and the non-polar tail is in contact with the oil.

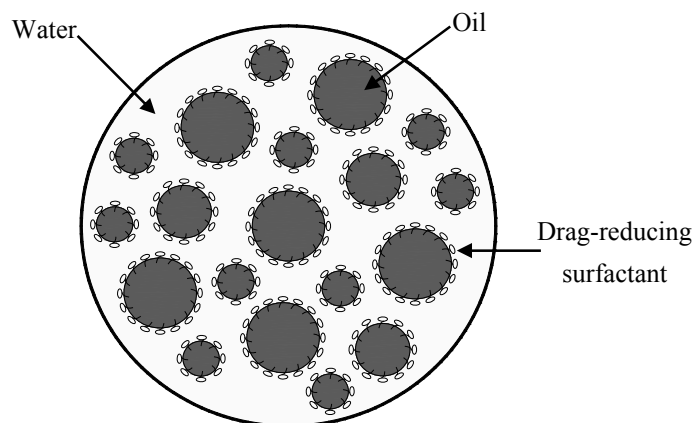


Figure 3. Schematic of the drag-reducing surfactant for heavy crude emulsification.

Emulsions of heavy crude with a volumetric water content of 75% were prepared using a high-pressure homogenizer, as shown in Figure 4. The oil becomes dispersed in the water phase in the form of droplets after the emulsions are created. Just like the explanation for monolayer arrangement, the size of emulsified oil droplets became greater after using the drag-reducing surfactant (Figure 4b). The re-agglomeration of oil droplets was damped; the friction of the flow in the pipeline was reduced;

and a water film was formed on the pipeline walls due to the wettability of the surfactant, which further contributed to the decrease of the frictional pressure losses of the flow. This is in agreement with the flow pattern changes in transportation via pipelines, as seen in Figure 5. The core-annular flow regime emerged in the pipe when the emulsion was stabilized with the aid of the drag-reducing surfactant. The water phase is at the pipe wall surface and lubricates the heavy oil at the core, and then friction is reduced. The same solubilization phenomenon was exhibited when using 100 mg/L of the contrast additive in experiments. This indicates that a stable O/W emulsion with reduced apparent viscosity is produced with the aid of the drag-reducing surfactant, and the transport of viscous crudes as O/W emulsions is effective and promising. This required three stages of producing, transporting and separating the O/W emulsion to transport heavy crudes using emulsification technology [32].

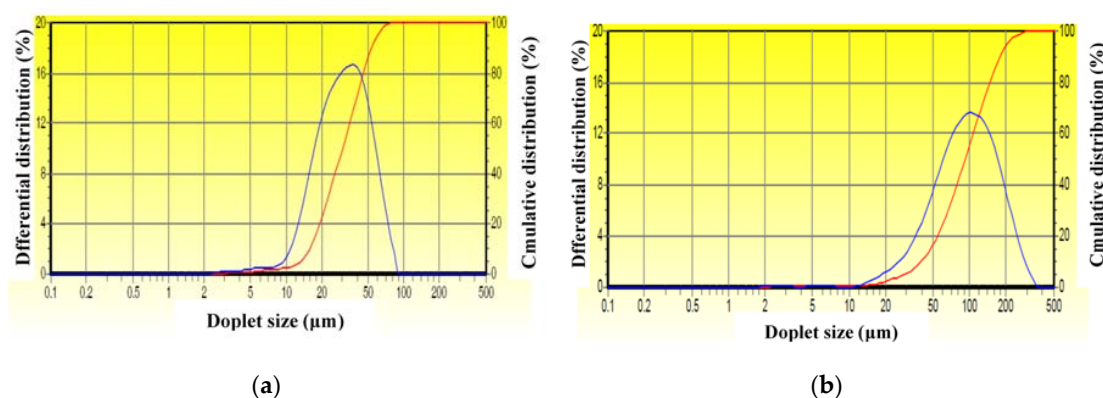


Figure 4. The droplet size distribution of emulsified heavy oil: (a) without using drag-reducing surfactant; (b) using drag-reducing surfactant (100 mg/L).



Figure 5. Flow regime observation of heavy crude emulsions (the flow of emulsions with volumetric water content of 75% was created by 100 mg/L drag-reducing surfactant in a 1.2 m-long, 73 mm-diameter visual glass tube).

2.4. Viscosity and Pour Point Reduction with the Drag-Reducing Surfactant

Thus, the transport of crude oil via pipeline with prior reduction in the viscosity is promising. Heating the pipeline can cause a rapid reduction in viscosity to decrease the resistance of the oil flow, but it can also result in a high energy cost and significant contribution to CO₂ emission [33]. Forming emulsions with surfactant additive and crude oil could also change the fluid viscosity, reduce the pressure drop and friction of the flow and make it easy for the crude oil to flow, as shown in Figure 6. The additive plays the role of viscosity reducer, and the viscosity reduction level is related to temperature, the concentration of drag-reducing surfactant and the base viscosity properties of the crude oils. With the decrease of temperature and the increase of dosage, the viscosity reducing effects of the drag-reducing surfactant reduction were more effective in low viscous oil, and the reproducibility of the experimental data was also confirmed in Figure 6. At primary WAT of different viscous crude

oils, 30% of the viscosity reduction rate could be achieved when drag-reducing surfactant at a 100 mg/L concentration was used, and a maximum viscosity reduction of 70% for low viscous oil was obtained at 25 °C. By contrast, the maximum viscosity reduction rate for different viscous oil is less than 50% when the contrast additive with the same dosage was used in experiments. It can be expected that the biobased surfactant obtained by enzymatic syntheses is effective in decreasing the amount of required energy for pumping by suppressing eddy formation in oil flow, and it might also adsorb and coat the pipe wall to reduce friction effects and increase the percentage of drag reduction (%DR).

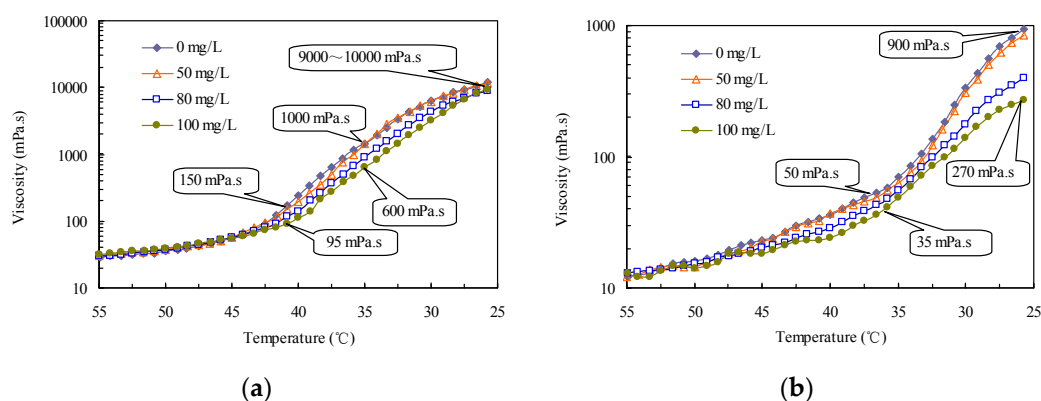


Figure 6. The viscosities of crude oil as a function of temperature before and after the drag-reducing surfactant addition: (a) highly viscous oil; (b) low viscous oil.

Table 1. Pour point of the crudes before and after the drag-reducing surfactant addition.

Crudes	Primary Pour Point (°C)	Adding Additives			Depression Rate of Pour Point (%)	
		Concentration (mg/L)	Pour Point Reduction (°C)		Drag-Reducing Surfactant	Contrast Additive
			Drag-Reducing Surfactant	Contrast Additive		
Highly viscous	30.2	50	28.0	30.0	7.3	0.66
		100	25.5	28.5	15.6	5.63
Low viscous	25.4	50	24.0	25.0	5.5	1.57
		100	22.0	25.0	13.4	1.57

Some researchers have focused on developing correlations between the characteristic temperature and wax deposition in pipelines and considered that the correlations could be used to identify the tendency for different waxy crudes to gel, deposit and harden at particular temperatures [34,35]. From Table 1, we can see that, compared to the contrast additive manufactured with chemical processes, the drag-reducing surfactant can remarkably lower the pour point of crude oils in different degrees, and the additive obtained by enzymatic syntheses could play the role of pour point depressant. There is a noticeable decrease of about 5 °C in pour point with the addition of 100 mg/L of the surfactant, and the depression rate of the pour point in the highly viscous crudes could be achieved as 15.6%. Furthermore, the pour point depression is considerably greater at a higher concentration of the biobased surfactant. The experimental evidence proved that by using the drag-reducing surfactant obtained by enzymatic syntheses, the flowable temperature range of oil was extended, eliminating the formation of a gel throughout the pipeline, including precipitated wax. The drag-reducing surfactant molecules interfere with the wax crystal growth mechanism by preventing the formation of a three-dimensional interlocking network structure, thereby reducing the pour point. Furthermore, the hydrogen bonds between resins and asphaltene were high energy ones among the drag-reducing surfactant, resins and asphaltene, and a solvation layer was formed around the resin and asphaltene molecules. A random close packing (RCP) of heavy constituents in oil was induced where the structure tends to be loose,

disordered and low spatial malleable, getting the depression of the pour point and viscosity, improving the flow characteristics of crude oils.

2.5. Effect of the Drag-Reducing Surfactant on Wax Crystals' Agglomeration Structure

Differential scanning calorimetry (DSC) thermograms for waxy crude oil before and after the drag-reducing surfactant addition were obtained under the same conditions. As shown in Figure 7, there are obvious heat effects associated with this change in the crystallization of waxes. The WAT show detectable decreases, and the peak temperature of wax appearance deviates from the baseline after the drag-reducing surfactant of 100 mg/L was used. This indicates that the surfactant additive is responsible for a delay in wax deposition. This could be attributed to the formation of ester bonds catalysed by lipases, which aid the solubility and change the wax crystals' structure. Thus, it is essential for the depression of the WAT. This is in agreement with the mechanism of ethylene copolymers as wax inhibitors [36]. A reasonable judgement can be obtained that the WAT and wax crystals cannot be modified with the contrast additive, because it cannot lower the pour point of crude oils as presented above

Furthermore, the crystallization of waxes is a kinetic process, the onset of which can be described by the classical Avrami equation [37]:

$$\alpha = 1 - \exp(-\delta_c) \quad (1)$$

where:

$$\delta_c(t) = \ln 2 \left[\int_0^t K(T(s)) ds \right]^n \quad (2)$$

where α is the degree of crystallization; n is the Avrami index which is valued greater than one; K is the rate of crystallization; T is the temperature at a certain moment during the crystallization process; and t is crystal characteristic time.

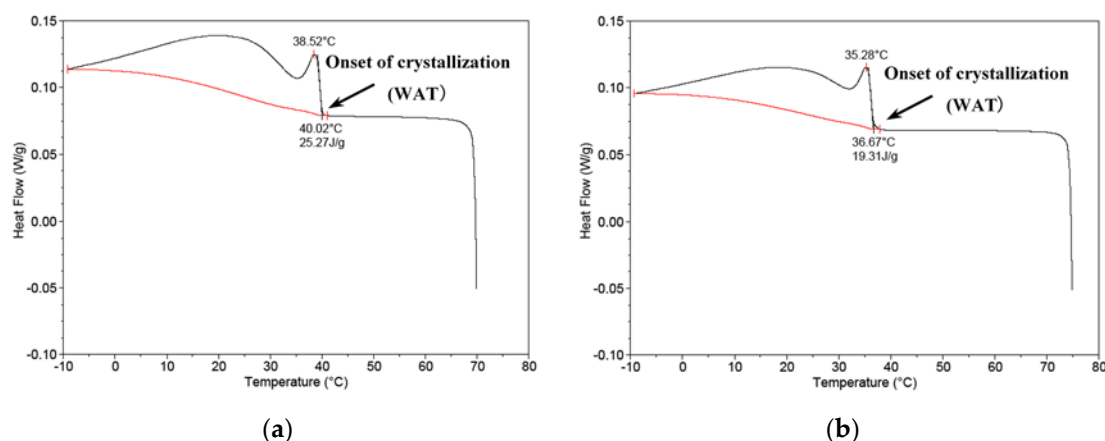


Figure 7. Thermogram for oil before and after the drag-reducing surfactant addition: (a) initial waxy crude oil, (b) adding biobased surfactant of 100 mg/L. WAT, wax appearance temperature.

As differentiated in DSC thermogram measurement, the crystallization characteristic time was extended after the drag-reducing surfactant of 100 mg/L was added under the same cooling rate. However, for a certain composition of waxy crude oil, the final degree of crystallization should be identical in the same temperature range. Then, according to the mentioned dynamic model above, it is evident that the rate of crystallization depends on the additive presence, and the rate reduces when the surfactant additive was used. This reveals that a kinetic effect in the WAT determination cannot be ignored.

The wax crystals with different sizes and shapes can be observed in initial waxy crude oil at 35 °C in Figure 8a. However, the amount of crystals decreased significantly at the same temperature after the drag-reducing surfactant of 50 mg/L was used. This indicates that the appearance of waxes was restrained and the solubility of waxes was enhanced due to the action of the surfactant additive. (Figure 8b). When the concentration of the drag-reducing surfactant reached 100 mg/L, the wax crystals' state could be described as "turbulent agglomeration" during the temperature drop; different sizes of vortices emerged and were interweaving, overlapping and expanding continuously in a certain area, as can be observed (Figure 8c), and the characteristic is still noticeable when the temperature reaches 30 °C (Figure 8d). It can be concluded that polar moieties of the surfactant are inserted into the wax crystal, exist on the surface of wax and reduce the crystal size of the wax, reducing the ability of the wax crystals to agglomerate into a gel network structure. In other words, the biobased surfactant obtained by enzymatic syntheses can lower the pour point and WAT and can modify the wax crystals, which is useful to prevent their agglomeration, growth and deposition in transportation pipelines. This is also in agreement with the significant reduction of crude oil viscosity below the temperature condition at which wax crystals start to form.

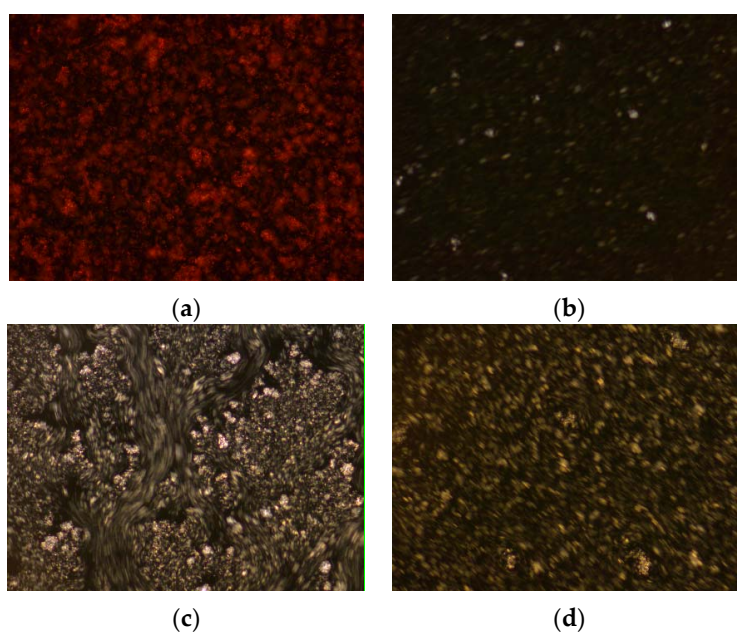


Figure 8. Effect of drag-reducing surfactant addition on the agglomeration structure of wax crystals: (a) initial waxy crude oil at 35 °C; (b) adding biobased surfactant of 50 mg/L at 35 °C; (c) adding biobased surfactant of 100 mg/L at 32 °C; (d) adding biobased surfactant of 100 mg/L at 30 °C.

2.6. Pressure Drop Reduction in Oil Pipelines by the Drag-Reducing Surfactant

Tom's effect, in the classical study carried out by Toms, described the well-known drag reduction effect [38]. This effect is exhibited by adding small amounts of quaternary ammonium salt of cationic surfactants and counter ion sodium salicylate to form rod-shaped micelles or adding straight-chained polymer into the fluid. This is mainly due to the turbulent flow modified by the rod-shaped micelles during fluid transportation in pipelines. In order to investigate the role of surfactant obtained by enzymatic syntheses in drag reduction, %DR is defined as the ratio of reduction in the frictional pressure drop using drag-reducing surfactant to the frictional pressure drop without using additive at the same operating conditions:

$$\%DR = \frac{(\Delta P_f - \Delta P_{f\text{drag}})}{\Delta P_f} \times 100 \quad (3)$$

where ΔP_f is the pressure drop with no drag-reducing additive and $\Delta P_{f\text{drag}}$ is the pressure drop using drag-reducing additive.

%*QI* is defined as the ratio of the increment in the flow quantity using drag-reducing surfactant to the flow quantity without using additive at the same operating conditions:

$$\%QI = \frac{(Q_{\text{drag}} - Q)}{Q} \times 100 \quad (4)$$

where Q is the flow quantity with no drag-reducing additive and Q_{drag} is the flow quantity using drag-reducing additive.

Turbulent flow in pipelines occurs when the Reynolds number exceeds 2000. As a non-Newtonian fluid, the Reynolds number of the crude oil would be defined as [39]:

$$Re = \frac{\rho d^n v^{2-n}}{8^{n-1} \cdot k} \cdot \left(\frac{4n}{3n+1}\right)^n \quad (5)$$

where ρ is the density of crude oil; d is the pipeline diameter; v is the flow velocity of crude oil; n and k denote flow behaviour and the consistency index of the crude oil solution, respectively.

The behaviour of the surfactant in crude oil pipelines with a Reynolds number of 4400 at various temperatures was measured. Figures 9 and 10 illustrate the variation of the pressure drop reduction in the closed flow loop. It is seen that the pressure drop reduction exhibited with temperature decreased, and thus, the drag reduction rate strongly depended on the experimental temperature range. This is probably because of the higher solubility of the surfactant and the easier formation of hydrogen bonds at these flow conditions. As mentioned earlier, the performance of the surfactant additive in decreasing the skin friction factor is more intense at and below the WAT of crude oil. %*DR* is 20%–25% in the range of 45–40 °C, reaches 30%–40% when the temperature falls to 40–35 °C and still remains above 15% near the pour point. Furthermore, the experimental results indicate that the flow rate in the pipeline can be enhanced when the biobased surfactant obtained by enzymatic syntheses was used under the same pressure drop conditions, and %*QI* can reach 25%. In other words, for transporting the same amount of crude oil, the pump can be replaced by a smaller one. However, the %*DR* of contrast additive is 15%–20% in the whole temperature range in experiments, and the %*QI* is less than 15%. This further reveals that the biobased surfactant obtained by enzymatic syntheses has superior performance in pressure drop decreasing and energy saving in oil transportation.

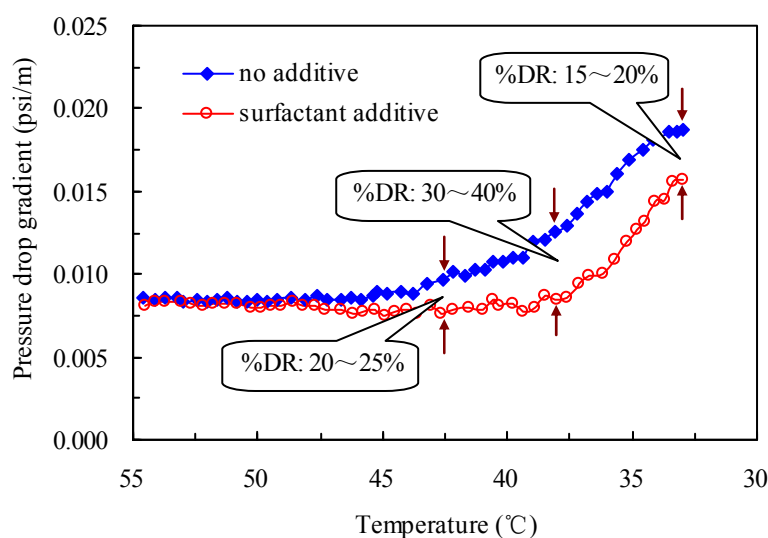


Figure 9. Variation of the pressure drop reduction before and after the drag-reducing surfactant addition (adding 100 mg/L of biobased surfactant).

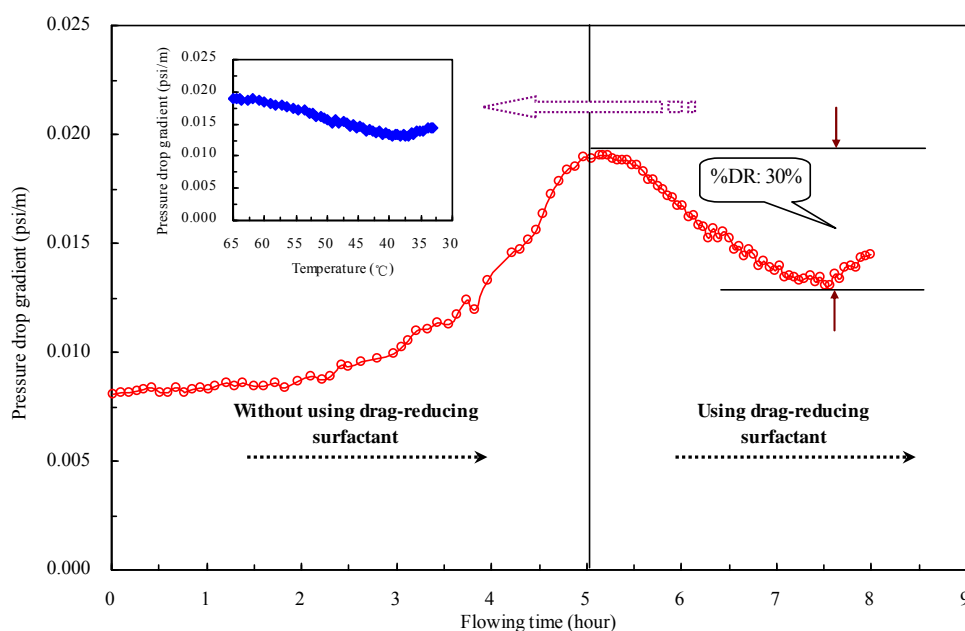


Figure 10. Variation of the pressure drop reduction before and after the drag-reducing surfactant addition (adding 100 mg/L of biobased surfactant).

It is worth noting that the reduction in the pressure drop can still be obtained by adding drag-reducing surfactant to the flow after wax has deposited in the pipeline and the accessible cross-sectional area for oil flow has been reduced. As shown in Figure 10, though compared to the flow behaviour in a loop without any deposition, the pressure drop reduction is slowed down and delayed. A maximum drag reduction of about 30% for waxy crude oil flow was still exhibited in experiments with the surfactant additive of 100 mg/L. This indicates that the drag-reducing surfactant could dissolve paraffin due to better arrangement of molecules through the flow and, thereby, greatly decreasing the turbulent frictional factor. It can be concluded that the biobased surfactant may act partly by modifying the pipe wall surface, rather than just the wax crystals. That is to say, the underlying mechanisms of the drag reduction surfactant are rod-shaped micelles with shear degradation resistance performance formed. Then, the excessive energy of the turbulent flow-generated shear stresses of the pipe wall surface can be absorbed by rod-shaped micelles formed by the biobased surfactant, which controls the excessive generation and growth of the turbulent flow.

To quantify the contribution to the decreased pressure drop in oil pipelines, the experimental data are divided into two groups using WAT (40 °C) as a critical point. There will not be appearances and precipitates of wax crystals above WAT, and the decreased pressure drop in the flow loop can only be attributed to viscosity reduction and turbulent drag reduction. However, as seen in Figure 6, the viscosity reduction rate is about 20%–25% above WAT when drag-reducing surfactant was used, according to the formula of pressure drop [40–42]:

$$\Delta P = 0.2411 \frac{Q^{1.75} \rho^{0.75} \mu^{0.25} L}{D^{4.75}} \quad (6)$$

where ΔP is the pressure drop; Q is the flow rate; ρ is the density of crude oil; μ is crude oil viscosity; L is the length of pipeline; and D is the inner diameter of the pipeline.

It is evident that the pressure drop will reduce by about 7.0% above WAT. An average %DR of 25% is exhibited in the temperature range in Figure 9, so it can be concluded that 70% of the contribution, at least to the decreased pressure drop by turbulent drag reduction, could be obtained. According to Equation (6), viscosity reduction to the contribution of pressure drop is still less than 30% in the range of 40–30 °C, which is below the WAT. Although wax deposition behaviour will occur in this

temperature range, wax deposition is a kinetic process, so the rest of the construction must be coming from wax deposition inhibition and turbulent drag reduction, as Figure 9 presented above. Thus, this reveals that the drag reduction caused by threadlike micelles interacting with the turbulent flow field is a key performance of the surfactant additive obtained by enzymatic syntheses.

2.7. Field Application Effect of the Drag-Reducing Surfactant

Large-scale oil production in Daqing Oilfield has been faced with severe wax precipitation due to the cold weather and poor physical properties of the crudes [43]. A 6.3 km-long and 0.219 m-diameter pipeline in Daqing Oilfield transports waxy crude oil with water content less than 0.3%. The throughput is about 7300 bbls/day. The wax content of the crude oil is 23.7%; the pour point is 30.2 °C; and the initial heating temperature is 68 °C. In the operation of the pipeline in cold weather, the wax deposition layer grows along the pipeline wall rapidly, especially at the end of the pipeline, even though remediation methods, such as pigging, are performed, as shown in Figure 11. Pump pressure rises from 58 psi–102 psi for a short time. As mentioned in the above experimental results, a noticeable drag reduction was achieved by adding 100 mg/L of surfactant additive at the beginning of the pipeline. The pump pressure was reduced more than 30%, and the friction pressure losses remained at a low level. Moreover, the initial heating temperature fell to 63 °C. Normal transportation of the crude oil is assured, and the efficient production of the oilfield is promoted. After the drag-reducing surfactant is used, the eddies are inhibited; the skin friction factor is reduced; and the energy supplied for pumping is decreased. The field application result also indicated that higher drag reduction rates can be obtained in rougher pipelines. This indicates that the fluid-mechanical efficiency is improved by means of the active agent. The field application further validated that the biobased surfactant obtained by enzymatic syntheses can inhibit wax deposition, reduce the friction or the pressure drop of crude oil and increase the transportation efficiency. This means that the energy consumption per unit volume of crude oil throughput has decreased. Furthermore, the successful field application has supported the functions of surface-active flow improvers due to their ability to inhibit wax settling and depositing.



Figure 11. Illustration of pipeline sections with wax deposition in the field.

3. Experimental Section

3.1. Materials

The heavy crude and light waxy crude, produced by enhanced oil recovery (EOR) methods of steam flooding and polymer flooding, respectively, were all sampled from the Daqing Oilfield, Daqing, China. The produced water in the field (4850 mg/L) was collected and employed in preparation of heavy crude emulsions. Seed oil and biodiesel were used as source materials. The chemical reagent, glycerol (Xilong Chemicals, Guangzhou, China), was used without any treatment. A commercial immobilized lipase of Chirazyme L-2 (Roche Diagnostics (Shanghai) Ltd., Shanghai, China) was used as the catalyst. The experimental materials also include special fillers and additives.

3.2. Enzymatic Preparation of Biobased Surfactant

Fatty acid and glycerol at an appropriate component ratio as the substrate for reaction and Chirazyme L-2 catalyse the formation of ester bonds between fatty acid and glycerol. Then, the enzymatic preparation of biobased surfactant was carried out in a stirred-tank reactor at 70 °C. In order to control water content in the system and further increase the activity of the product, a small amount of special fillers and additives as the reaction medium were also added. The water generated during esterification was removed from the reaction medium by azeotropic distillation and was regenerated by membrane vapour permeation. The molecular structure of the main component in the biobased surfactant obtained by enzymatic syntheses is shown in Figure 12.

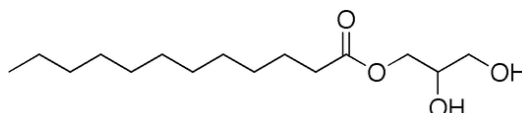


Figure 12. The molecular structure of the main component in the biobased surfactant.

For comparison, a gemini quaternary ammonium surfactant manufactured with chemical processes was extracted, and the role of the contrast additive in wax deposition inhibition and drag reduction of crude oil pipelines was also introduced.

3.3. Characterization

In view of the reference that polyisobutylene of polymer DRAs is usually added into a given pipeline at a concentration of 60 mg/L to convey a larger amount of crude oils with a given pump, the concentration value was designed at 50–100 mg/L during the characterization of the surfactant drag reducing. In addition, it is an objective fact that the crude oils' physical properties, the wax content above 20% and the pour point near 30 °C, are poor in the Daqing Oilfield. Furthermore, the target engineering systems of using the surfactant additive are the gathering pipelines of the field in this work, and there are elbows and valves of greater resistance in these pipelines, so intensive energy cost is required consequentially in crude oil transport. Thus, the final concentration may be designed higher than that of polymer DRAs to realize a perfect efficacy.

The emulsified heavy oil droplet size distribution was analysed by a laser particle analyser (Easysizer20, OMEC Instruments Co., Ltd., Zhuhai, China). Viscosity tests of different viscous oil before and after drag-reducing surfactant addition were conducted in the range of 55–25 °C according to ASTM D4287-2000 (2010) (Standard Test Method for High-Shear Viscosity Using a Cone/Plate Viscometer) using the stress-controlled rheometer (AR2000ex, TA Instruments, Newcastle, DE, USA). The pour point depressant function of the surfactant obtained by enzymatic syntheses was evaluated by the reduction level of the pour point, using the pour point test according to ASTM D97-2011 (Standard Test Method for Pour Point of Petroleum Products). The onset of wax crystallization and the changes in the characteristic temperatures were measured by differential scanning calorimetry (DSC) with a modulated differential scanning calorimeter (DISCOVERY DSC, TA Instruments, Newcastle, DE, USA). Microscopic observation of crude oil was performed below the WAT using a polarizing microscope (DM2500P, Leica Microsystems, Wetzlar, Germany), and the effect of drag-reducing surfactant addition on wax crystals' agglomeration structure was recorded. A flow loop device was established to observe the flow regime and to characterize drag reduction, as shown in Figure 13; the tube section was 2.4 m-long and had a 50-mm internal diameter. There is a 1.2 m-long visual glass tube in it, and the flow regime during the flowing can be captured and identified with the external help of a high efficiency CCD camera (MV-EM, MicroVision Inc., Redmond, WA, USA). The drag-reducing surfactant was pumped into the constant temperature tank with a concentration of 100 mg/L via a ram pump. Then, a mixture was pumped in the loop for recycle flow via a screw pump after the emulsions were created or crudes were modified in the tank. The flow rate was measured by a mass flow meter, and

the pressure drop was tested by pressure transducers, while temperature was controlled by a constant temperature bath. The flow regime was observed by means of the visual glass tube; wax deposition inhibition and pressure drop reduction in the oil pipeline caused by the drag-reducing surfactant were identified and determined.

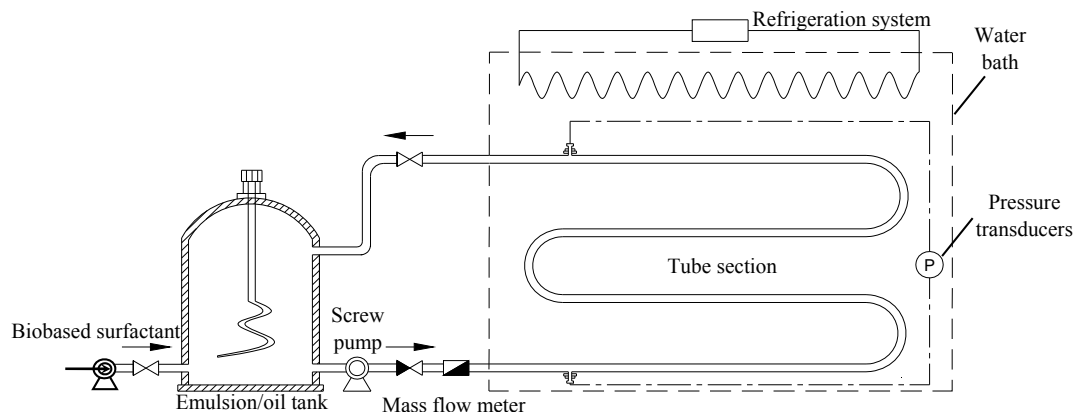


Figure 13. Schematic illustration of the flow loop device.

4. Conclusions

Scientific progress is making enzymatic bioprocessing increasingly attractive for high-value specialty surfactants. By optimizing catalysis conditions, a biobased surfactant obtained by enzymatic syntheses, which screens the fatty acid and glycerol as biobased resources and a commercial immobilized lipase of Chirazyme L-2 as the biological catalyst, was successfully used for wax deposition inhibition and drag reduction in crude oil transport. As a biocompatible and biodegradable nonionic surfactant, lipase-catalysed reactions can also be controlled and result in a narrower product distribution. The advantages of green-manufacturing approaches are highlighted during the preparation. The biobased surfactant can promote the form of a stable O/W emulsion, change the flow pattern of heavy oil two-phase flow and, therefore, significantly enhance the flowability of heavy crude oil in pipelines. The excellent activity and solubilization performance of the biobased surfactant can cause a reduction in viscosity, pour point and WAT of the waxy crudes. The wax crystals can also be modified so as to prevent their aggregating and depositing in transportation pipelines at low temperatures with the aid of the surfactant. The biobased surfactant caused a drag reduction of about 30% for waxy crude flow, and a successful practical field application of the biobased surfactant in a 6.3 km-long, 0.219 m-diameter pipeline in the Daqing Oilfield was carried out. The key role of the surfactant obtained by enzymatic syntheses is to promote emulsification, modify the wax crystals and suppress the growth of turbulent eddies. The enzyme technology is impacting a wide variety of fields, and it promises to highlight enzyme technology employed in the petrochemical industry.

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